

Influence of quicklime addition on the mechanical properties and hydration degree of blended cements containing different fly ashes

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Abstract

Even though the use of pozzolanic and latent hydraulic materials (such as fly ash, slag and natural pozzolans) in the construction sector is nowadays a common practice, certain deficits associated with these materials have initiated research that aims to reduce the negative effects that they introduce into cementitious systems. With respect to fly ash, its relatively slow pozzolanic reactivity hinders its greater utilization; hence cost efficient methods of activation are on demand. In this work, cement systems containing the two typical types of Hellenic fly ashes (of high and moderate calcium content) were chemically activated by adding industrially produced quicklime. A first step in assessing the efficiency of the above procedure was based in monitoring the compressive strength development, lime depletion values and data derived from a selective dissolution procedure (based on a mixture of picric acid–methanol). Moreover, evolution of the fly ash reaction and the morphology of the formed hydration products were examined by means of scanning electron microscopy. Evidence included in this investigation reveal that quicklime presence accelerated the reaction rate of high-calcium fly ash, whereas in the case of lower-calcium fly ash, quicklime had a positive impact only during the very early stages of hydration and thereafter acted inhibitory with respect to its reactivity development.

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1. Introduction

The continual increase in energy demand that marks the last decades has caused a higher consumption of coal and lignite sources, despite the introduction of natural gas in the energy market. This has led to an increase of the global fly ash production. In the literature body regarding fly ash, it has been fairly well shown that its incorporation in mortar and concrete is not only associated with eco-

nomical and environmental benefits, but also with certain technological improvements for the final product [1–3]. There is an increasing awareness within the construction industry nowadays for using material resources prudently, in terms of technical performance, environmental impact and cost effectiveness. With respect to this trend, there is an ongoing effort for the extensive utilization of fly ash and other supplementary cementing materials (SCMs) into a variety of products that could be used in several construction applications.

Although fly ash is the main by-product being incorporated into building materials, its utilization rate remains low in many countries. In Greece for example, a recent report [4] revealed that from the approximately 11.5 million tons that are generated annually (most of which are of high calcium content) a low 10–12% is absorbed in several sectors, principally the cement industry. The main

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reason for that, apart from the absence of an integrated quality control scheme, is the slow pozzolanic activity of this material, a fact that inhibits its wider use especially when market demands are exigent. In the light of the above considerations, it is a primal need for the researchers and the industry to come up with feasible and cost-effective methods to enhance the reactivity of fly ashes in cementitious systems. As long as this requirement is fulfilled, mechanical and durability improvements can be ensured for the final product.

In the literature there is extensive information concerning the activation of fly ashes. Prolonged grinding [5], curing at elevated temperatures [6], alkali [7] and chemical activation [8] are some of the methods that have been used to achieve enhanced fly ash action. The efficiency however, of some of these methods is debatable since a number of them are too energy demanding, while others fail a simple cost-benefit analysis. In the present paper, industrially produced quicklime was used to activate two types of fly ash (of high and low calcium). The interaction of fly ashes and lime (hydrated or in powder form) has attracted the attention of many researchers. All of them seem to agree that the quality and quantity of lime (and the subsequently generated calcium hydroxide) that is present in the matrix of a fly ash–cement system is critical for the future performance of these systems. From the mid-eighties, Huang [8] investigated the fly ash–Ca(OH)₂–H₂O 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 though on the fact that this acceleration effect would be minimal unless curing takes place at higher than room temperatures. Ma et al. [9] hydrothermally treated both types of fly ash in the presence of CH. 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 CH did not appear to accelerate the formation of any of the cementing phases.

Even though lime has been often added into the fly ash–cement blend, either hydrated [8,9] or in the form of putty [10], providing very promising results, only Shi [11] has used it in the form of quicklime to activate the action of natural pozzolans. 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. In the work presented herein, quicklime was inserted in fly ash–cement binary systems replacing equal amounts of fly ash. Strength development and degree of fly ash reaction was monitored during the curing period applied and compared with the corresponding non-activated systems. Moreover, evolution and alterations in the microstructure of each activated blend were recorded in order to provide additional explanations for the effect of quicklime in the aforementioned systems.

2. Experimental procedures

2.1. Raw materials

Two different fly ashes, one with a high calcium content (class C according to ASTM classification), designated here as T_D , and one with lower calcium content (T_M), all received in a dry state, were used in the present study representing the two types of fly ashes derived in Hellenic power stations. Both types of materials have a typical (and relatively constant) chemical and mineralogical composition, thus no other specimens with significantly altered composition could be obtained in order to comment into the effect of the variations in the chemical properties of fly ash. Normal setting cement (CEM I 42.5 according to European Standard EN 197-1) was used during the construction of the paste specimens. Commercial quicklime of high purity (CL90 type according to EN 459-1) was used as the chemical activator. In order to investigate on the pozzolanic effect of fly ashes, both pozzolans were ground (in a lab ball mill) – prior to use – to similar fineness and particle size distribution, in an attempt to deactivate the physical effect of fly ashes (by means of the filler effect). The chemical composition and the main physical characteristics of the cement and fly ashes are given in Table 1, whilst their similar PSD image is shown in Fig. 1. As testified by data given in Table 1, T_D is a low quality fly ash judging by its relatively low reactive silica content (less than 25% which is the minimum requirement stated in

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

| | Cement | T_D | T_M |
|--------------------------------------|-------------------|-------|-------|
| CaO | 65.54 | 34.13 | 13.80 |
| CaO _f | 0.74 | 8.93 | 0.95 |
| CaO _{re} ^a | n.a. ^c | 26.33 | 9.42 |
| SiO ₂ | 21.51 | 29.73 | 51.36 |
| SiO _{2re} ^a | n.a. | 24.07 | 31.36 |
| Al ₂ O ₃ | 4.88 | 13.90 | 16.73 |
| Fe ₂ O ₃ | 3.79 | 6.49 | 8.75 |
| MgO | 2.23 | 3.56 | 2.26 |
| SO ₃ | 1.36 | 5.13 | 1.49 |
| R ₂ O | 0.48 | 1.80 | 2.29 |
| LOI | 2.31 | 4.03 | 4.86 |
| γ_s^d | n.a. | 80.96 | 61.05 |
| IR (%) ^a | 0.18 | 9.51 | 25.16 |
| Glass content S^b (%) | n.a. | 90.49 | 74.84 |
| Blaine fineness (cm ² /g) | 4.120 | 5.600 | 5.550 |
| Specific gravity | 3.13 | 2.72 | 2.59 |

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

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

^c n.a.: not available.

^d γ_s : active ratio (ratio of active: total silica).

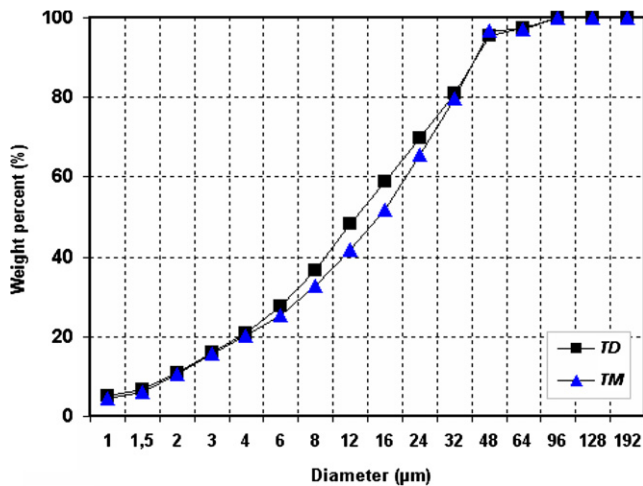


Fig. 1. Particle size distribution of ground fly ashes.

the European standard EN 450-1 for fly ashes used in concrete [12]) and T_M a siliceous rich ash with considerable percentage of reactive silica and moderate lime content.

2.2. Quicklime addition

When quicklime was added, equal weight 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. In general, small dosages of chemical activator were provided considering the relatively high cost of quicklime and the fact that the systems are already abound in CaO due to the presence of high- and moderate lime fly ashes. Additionally, since a significant part of the total CaO content in high-lime fly ash is free (approximately 26%) and thus can be transformed into $\text{Ca}(\text{OH})_2$ when hydrated, it was gathered that for comparison purposes higher amounts of CaO should be added to the system containing the lower-lime T_M fly ash. Therefore, in the case of high-calcium ash T_D , 3% and 6% fly ash replacement by quicklime was adopted, whilst in the case of T_M ash, higher replacements (i.e. 5% and 15% by weight of fly ash) were applied. The new blends were prepared by mixing the raw materials in a rotating blender until homogeneity of the new mix was achieved. The activated blends were named after the ash contained in them and the proportion of quicklime added. For example, T_D -Q6 corresponds to the specimen prepared when 6% of quicklime replaced equal weight of T_D fly ash. A specimen with no fly ash at all (reference) was prepared for comparison pur-

poses. The detailed proportioning summary of the specimens tested is given in Table 2.

2.3. Testing

2.3.1. Compressive strength development and k -value concept

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. Cement replacement was kept constant at 20% to avoid significant alterations in the hydration degree of the examined blends (due to increasing fly ash addition) (1,2) Keeping the w/b ratio constant, a cement mortar without any fly ash or quicklime was prepared as the reference specimen. Additionally, two mortars incorporating the initial fly ashes, without any activator added, were manufactured for comparison purposes. The dry materials were sufficiently mixed before they were cast into 40 mm × 40 mm × 160 mm prisms. One day after casting, the samples were stripped from their molds and the specimens were placed in lime-saturated water at 20 °C until testing. A Toni Technik 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 after mixing the specimens were removed from water and tested according to European Standard EN 196-1. For each age, two specimens of every mixture were tested and the mean value of these measurements is reported. Strength results were used to calculate the efficiency factors (k -values) in each case.

2.3.2. Lime depletion rate

Pozzolanic reaction evolution (and thus the effectiveness of quicklime addition) was monitored in paste specimens. The dry materials were sufficiently mixed, water was added (water/binder ratio kept constant at 0.5) and then the pastes were cast in plastic cylindrical vials. These were intensively shaken to remove the air content and they were kept closed in room temperature. After 24 h, the pastes were demoulded and cured under water at 22 °C. At 2, 7, 28 and 90 days after mixing, hydration was stopped with the addition of organic solvents and overnight drying (to remove the evaporable water) in a vacuum pump. Fragments from the core of each dried sample were taken and were further pulverized to assure that they all run through the 125-µm sieve.

Table 2
Mix proportions of specimens tested (as % by weight of cementitious materials content)

| | Ref | T_D | T_D -Q3 | T_D -Q6 | T_M | T_M -Q5 | T_M -Q15 |
|----------------------|-----|-------|-----------|-----------|-------|-----------|------------|
| Cement | 0 | 80.0 | 80.0 | 80.0 | 80.0 | 80.0 | 80.0 |
| Fly ash type | – | T_D | T_D | T_D | T_M | T_M | T_M |
| Fly ash content (%) | – | 20.0 | 19.4 | 18.8 | 20.0 | 19.0 | 17.0 |
| Quicklime dosage (%) | – | – | 0.6 | 1.2 | – | 1.0 | 3.0 |

Thermogravimetric analysis was adopted to monitor the progress of the pozzolanic reaction in each blend. This can be accomplished by determining the amount of unbound CH (expressed as the sum of the abrupt weight loss occurring in the temperature region of 400–550 °C and the freeportlandite transformed into calcium carbonate) 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 nitrogen atmosphere (50 ml/min) at a heating rate of 10 °C/min from ambient temperature to 1000 °C. CH measurements were also used to compute the percentage of fixed lime in the constructed pastes, according to the following equation proposed by Paya et al. [13]:

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

where CH_c is the CH content of the reference (no fly ash) paste for a given curing time, CH_p is the CH content of the fly ash–cement (FC) paste at the same age and $C\%$ is the proportion of cement in the examined paste (obviously in this case where a 20% cement was substituted, $C\%$ is 0.8).

2.3.3. Measurement of the reacted fly ash fraction

Determining the degree of reaction of fly ash in cementitious systems is a hard task, not only due to the absence of any complete reaction scheme for fly ash in the literature (involving stoichiometry for the reactants and the products), but also due to the vast diversity of the material itself which consequently results in different reaction behaviours with curing time. In the present work, the determination of the degree of reaction of the fly ashes used was based on a selective dissolution procedure using a picric acid and methanol solution. This procedure has been employed recently by other researchers [14,15] and seems to provide more reliable results than any dissolution technique applied in the past [16]. The basic principle of this method is that within a blended fly ash–cement system, the reaction products of fly ash (such as pozzolanic C–S–H, calcium hydroxide, ettringite, etc.) are acid-soluble. Therefore, by dissolving the hydration and reaction products of fly ash and cement, as well as the unreacted cement constituents, the amount of fly ash that has not (yet) reacted remains undissolved and thus it is measurable.

For measuring the reacted fraction of fly ash in the initial and quicklime-activated samples, the insoluble residues of the cement and ground fly ashes were determined after a 1-h treatment with picric acid–methanol and water solution. Briefly, 1 g of each specimen was added to a beaker containing a well-stirred solution of 9 g picric acid and 60 ml of methanol. After a 15-min stirring (with the aid of a magnetic stirrer), approximately 40 ml of deionised water was added and stirring continued for another 45-min. Then it was filtered through a medium pore size filter paper and the filter was then washed with methanol (until

the yellow colour diminished) and about 250 ml of deionised water. The residue was then transferred into a platinum crucible and ignited in an electric furnace at 950 °C for 60 min. Corrections were made carrying out blank tests with no sample. The same procedure was performed for the paste samples whose hydration was terminated at selected ages. Then the reacted fraction ($R\%$) of each fly ash in the different hydrating systems was calculated with the use of Eq. (2) [17]:

$$R\% = 1 - \frac{S_s - P_c S_c}{P_f S_f} \quad (2)$$

Where S_s is the residue per gram of the paste specimen, S_c and S_f are the residue per gram of plain cement paste and residue per gram of ground fly ash, P_c and P_f are the weight percentage of cement and fly ash of each specimen tested respectively.

2.3.4. Electron microscopy examination

A XL 30 Philips ESEM equipped with an energy dispersive X-Ray analyzer (EDAX) was used both for obtaining a view of the microstructure of the activated systems and for conducting an elemental analysis of the formed hydration products in each case. Representative dried paste fragments were used during electron microscopy tests.

3. Results and discussion

3.1. Compressive strength

The compressive strength results of all manufactured mortars are given in Table 3. It may be seen that a small replacement (3%) of T_D ash by quicklime resulted in a strength increase at all ages and most importantly during the early ages, a stage where the quicklime-containing specimen exceeded the strength value of the reference specimen. The already good performance of T_D ash at early ages – as a result of its high specific surface and reactive CaO content – was further improved due to the presence of extra lime in the matrix. When quicklime addition increased to 6% (by weight of fly ash), the strength of the activated mortar was higher than that of the reference specimen at all ages, but slightly less than that of the mortar containing 3% quicklime. From the above results, it may be argued that

Table 3
Compressive strength results of the quicklime-activated fly ash mortars

| | Compressive strength (MPa) | | | |
|------------|----------------------------|------|------|------|
| | Age (days) | | | |
| | 2 | 7 | 28 | 90 |
| Ref | 24.2 | 35.6 | 47.7 | 58.1 |
| T_D | 23.0 | 34.5 | 47.7 | 58.4 |
| T_D -Q3 | 23.6 | 35.4 | 49.6 | 61.5 |
| T_D -Q6 | 23.4 | 35.3 | 48.8 | 60.8 |
| T_M | 21.1 | 31.4 | 45.9 | 57.8 |
| T_M -Q5 | 22.2 | 31.3 | 45.4 | 56.8 |
| T_M -Q15 | 20.2 | 30.8 | 44.8 | 56.2 |

3% quicklime seems to be the optimum addition (both for short and longer curing periods) in the case of high-calcium fly ash. However, since only two replacement ratios (3% and 6%) were examined, for ultimately confirming the above observation a wider range of replacement levels should be adopted. It is possible that a small offer of lime further reacted with reactive silica dissolved from the ash to form additional pozzolanic C–S–H. Observations formulated by Lokken et al. [18] and Brown [19], that in the presence of $\text{Ca}(\text{OH})_2$ 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. 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, more specifically its contribution towards the formation of flocs inside the matrix due to quicklime hydration. Pandian et al. [20] noted that these flocs reduce the effective voids, and hence the interconnectivity of the pores, leading to a denser microstructure.

The effect of quicklime on the strength development of lower-lime ash (T_M) mortars is also shown in Table 3. Contrary to what was observed before, quicklime presence (even at small percentage), did not accelerate the strength of the investigated samples. Instead it caused a decrease of the compressive strength of all examined blends at almost all ages. Only when T_M was replaced by 5% quicklime, an activating effect was observed which lasted, however, only during the first week of hydration. With increasing quicklime content, the strength of the new blends remained lower not only when compared to that of the reference mortar, but also with respect to the initial T_M mortar. 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 remaining of hydrated lime. This accounts for both fly ashes tested, but it is definitely more pronounced in the case of high-siliceous active T_M .

3.2. *k*-value concept

It has been well established [2,4,10] that in the case of mortars and concrete that incorporate supplementary cementing materials, the *k*-value derives from the following expression for the measured compressive strength (f_c):

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

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 a a parameter depending mainly on curing conditions (thus its numerical value for the tested samples changes with curing time). Using the mean measured values of the compressive

strength of the control specimen, the parameter a was estimated as 1.37, 1.08, 0.77 and 0.50 for 2, 7, 28 and 90 days respectively. Based on the above expression and strength values shown in Table 3, indicative *k*-values for the bulk and activated ash mortars were calculated and provided in Table 4. Data in Table 4 reveal once again the inability of the bulk ashes to act drastically from the start of the curing process and the effectiveness of quicklime addition in high-lime fly ash. The latter exhibits higher *k*-values than the reference mortar since it reaches unity very quickly and it easily exceeds it with curing time. The negligible or even negative effect of quicklime in the case of T_M , is also highlighted. Only when a small replacement of T_M ash by quicklime (5%) was applied and for the very early period of hydration (up to 7 days), the *k*-values of the new blend were higher compared to the non-activated 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 (T_M –Q15).

3.3. Fixed lime evolution

The fixed lime values of the T_D ash series are shown in Fig. 2 as a function of curing time. Samples containing T_D ash, present an erratic behavior (as indicated by the negative fixed lime values) characterized by a simultaneous production and depletion of calcium hydroxide. This phenomenon can be explained by the co-existence of three different sources of lime in the matrices, that is, from hydrated cement grains, free lime liberated from the ash particles and quicklime added for activation purposes. Data included in Fig. 2 show that a small quicklime addition (3%) significantly 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 respective binary system, more calcium hydroxide has reacted after the first week of hydration. As the hydration progresses, it becomes obvious that despite the fact that the blend with quicklime contains less fly ash – compared to the non-activated mix – the addition of 3% quicklime accelerates the consumption of $\text{Ca}(\text{OH})_2$. This is obviously the

Table 4
Efficiency factors for cement-fly ash and cement-fly ash-quicklime mortars

| | <i>k</i> -value | | | |
|------------|-----------------|------|------|------|
| | Age (days) | | | |
| | 2 | 7 | 28 | 90 |
| T_D | 0.93 | 0.92 | 1.00 | 1.01 |
| T_D –Q3 | 1.04 | 1.01 | 1.12 | 1.21 |
| T_M | 0.81 | 0.72 | 0.88 | 0.97 |
| T_M –Q5 | 0.88 | 0.74 | 0.85 | 0.91 |
| T_M –Q15 | 0.75 | 0.68 | 0.81 | 0.87 |

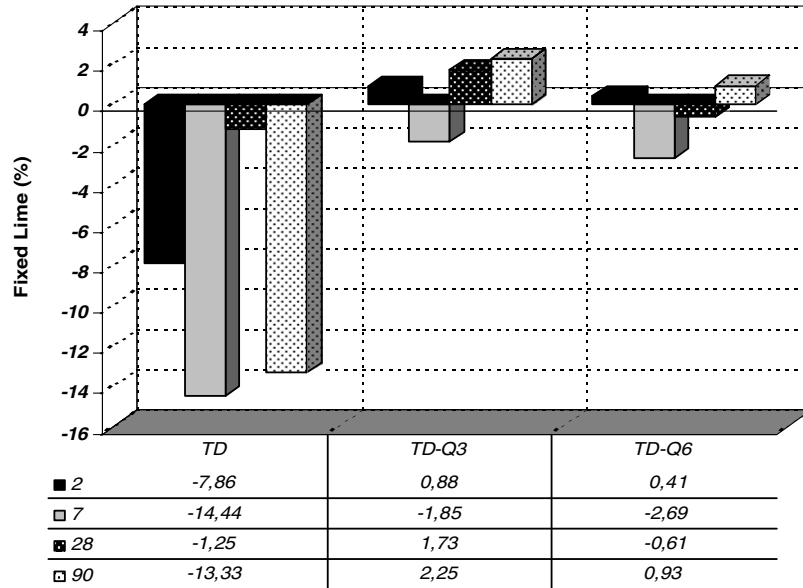


Fig. 2. Fixed lime values of T_D ash series with curing time.

outcome of the activation of the glass constituents of the ash, due to the formation of a higher alkalinity environment [21]. Albeit fixed lime slightly decreases with increasing quicklime content (i.e. 6%), T_D -Q6 blend binds greater quantities of calcium hydroxide after the first month of curing, completely consuming the extra 3% of quicklime supplied. This could be an indication that this is the optimum range of quicklime dosage for ensuring superior performance at advanced ages.

The situation differs substantially when quicklime was added in the system containing lower-calcium T_M ash, as

shown in Fig. 3. In this case, the beneficial effect of quicklime is detected only during the early stages of hydration and for a small replacement of the tested ash. This is validated by the fixed lime values of the T_M -Q5 specimen, which are greater than the ones observed for the binary system with no quicklime addition during the first month of hydration. After 3 months curing, the same activated system is incapable to incorporate additional CH into hydration products; thus unreacted $Ca(OH)_2$ remains available in the matrix. This becomes clearer when more quicklime (15%) is added. Negative fixed lime values observed

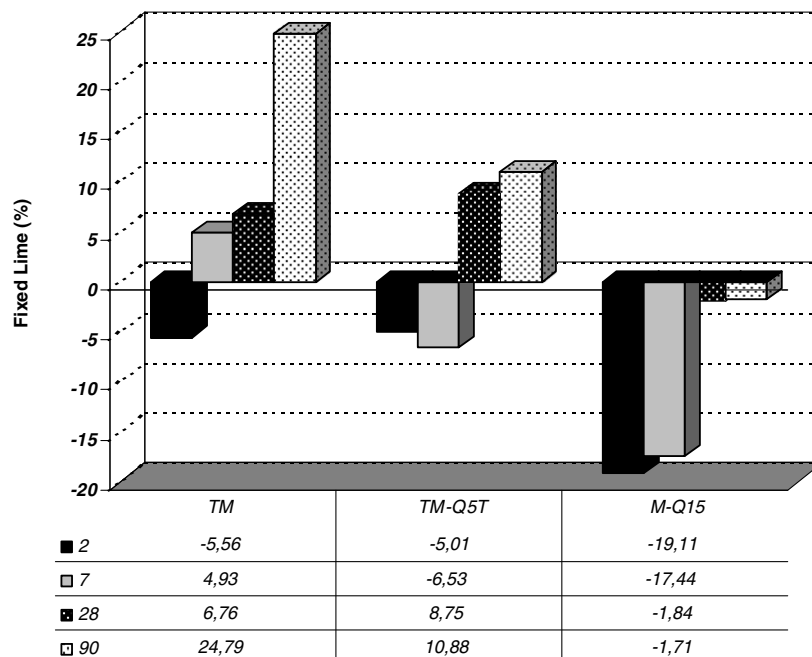


Fig. 3. Fixed lime values of T_M ash series with curing time.

throughout the curing period are indicative of the excess of hydrated lime that remains contingent in the pore solution due to less proportion of ash present. CH is known not to possess any cementitious properties; hence the significant presence of unreacted CH in the system will most certainly not enhance the strength of the hardened paste. This is in agreement with compressive strength results of the tested blends reported in Section 3.1.

3.4. Reacted fly ash fraction

The results of the reacted fraction of fly ash in each examined system are summarised in Table 5 in relation with hydration age. It may be noticed that as early as 7 days after mixing, both types of fly ash have undergone reaction. This could be the result of the initial attack of alkali ions that are present in the pore solution [22]. From the beginning of the nineties, Berry et al. [23], among others, have demonstrated that fly ash particles are quite early involved in chemical reactions forming ettringite. As hydration continues, more high-calcium fly ash has reacted compared to the lower-lime ash, possibly due to its stronger glassy character (as manifested by its notably lower insoluble residue given in Table 1). The situation remains the same until the end of the testing period (90 days), where a significant difference of approximately 11% between the reaction rates of the two types tested can be observed.

The addition of 3% and 6% quicklime severely raised the fraction of T_D fly ash that reacted, especially at early ages. During this period, when a notable increase of fixed lime percentage was observed (and given the fact that this is not consumed in the production of AF_t phases), it is gathered that more fly ash active centres have been liberated to form additional C–S–H. As curing continues, the fly ash reaction rate in the quicklime-activated samples is almost two times of that at 7 days, but the difference with the non-activated samples is only a little compared to the one measured at the beginning of hydration. This increase corresponds to the respective increase of the fixed lime values of the same systems, indicating that pozzolanic reaction becomes increasingly active with time. According to the reacted fly ash fraction data, 3% quicklime addition seems to be the optimum replacement percentage for high-calcium fly ash. Similarly, a small quicklime addition enhanced the fraction of low-lime fly ash that reacted dur-

ing the first week, but then again after the first month of curing, reaction rate diminished compared to the plain T_M -cement paste.

The close relationship of the reacted fly ash fraction with the mechanical performance of the corresponding activated mortars is best demonstrated in Fig. 4, where the percentage of fly ash that has reacted in each age tested is plotted against the efficiency factors of the mortars that they utilized them. The almost linear connection among the two factors examined reveals the strong effect of the pozzolanic reaction progress (as this is described via the reacted fraction of fly ash) on the future strength performance of blended cements (as this is represented by the efficiency factor of the mortars prepared with the same cements).

3.5. SEM test

The gradual formation of the microstructure was monitored in an attempt to provide additional explanation for the effect of added quicklime. Special attention was given in the systems that the activator had a severe impact that is T_D -cement pastes. Pastes containing lower-calcium fly ash were also monitored for comparison purposes. Fig. 5a is a typical image of the microstructure of the T_D paste, with no quicklime addition, after the first week of hydration. Unreacted fly ash particles retaining their smooth and spherical shape are easily distinguishable, while some others have already been covered by calcium hydroxide. Numerous voids visible indicate the presence of large pores in the matrix. Upon 3% quicklime addition (Fig. 5b), most fly ash particles – previously intact – have been either etched or almost entirely covered with hydration products. Precipitation of calcium hydroxide and small rodlets of ettringite (mainly on the center of the photo) can be ascribed to the instant hydration of lime supplied and the relatively high sulphur content of T_D ash. Formation of calcium aluminate compounds was also detected in the same sample at the same age (see Figs. 5c and 5d). The formation of such products, which may be

Table 5
Fly ash reacted fraction in fly ash-quicklime-cement pastes

| | Fly ash reacted fraction (%) | | | |
|-----------|------------------------------|-------|-------|-------|
| | Age (days) | | | |
| | 2 | 7 | 28 | 90 |
| T_D | 22.25 | 32.70 | 46.20 | 61.09 |
| T_D -Q3 | 25.12 | 38.15 | 51.25 | 63.44 |
| T_D -Q6 | 24.45 | 33.50 | 48.12 | 61.15 |
| T_M | 16.72 | 35.50 | 41.56 | 50.02 |
| T_M -Q5 | 20.38 | 37.08 | 42.01 | 48.50 |

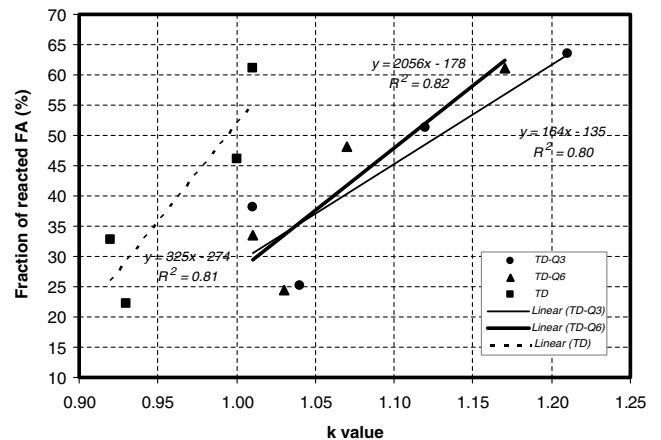


Fig. 4. Correlation between reacted fraction of high-calcium fly ash and k -values.

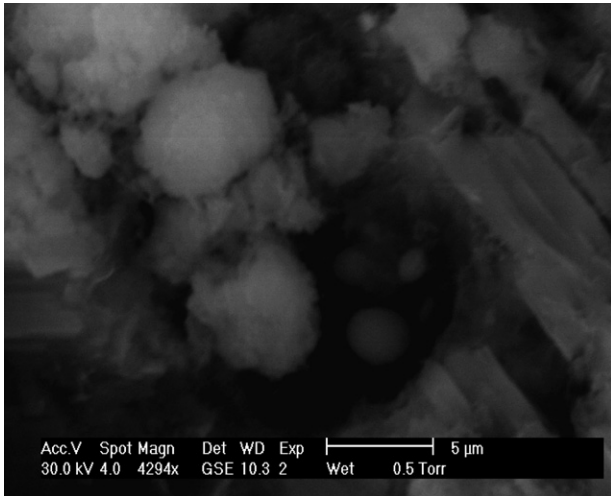
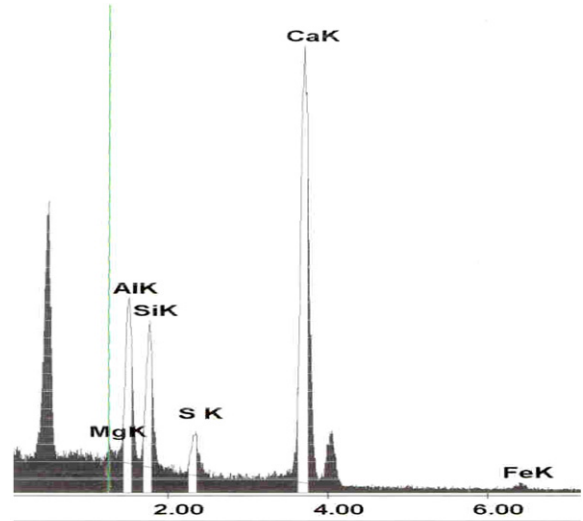


Fig. 5a. Unreacted fly ash particles in T_D – 7 days.



| MgO | Al ₂ O ₃ | SiO ₂ | SO ₃ | CaO | Fe ₂ O ₃ |
|------|--------------------------------|------------------|-----------------|-------|--------------------------------|
| 1.61 | 16.27 | 15.21 | 4.76 | 59.58 | 2.56 |

Fig. 5d. EDX analysis on the black point of Fig. 5c.

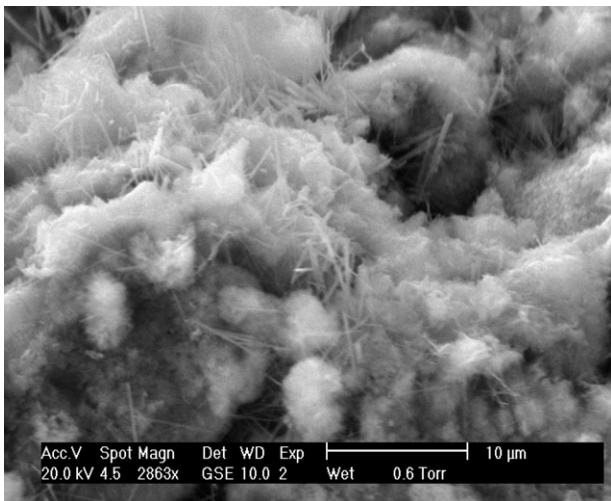


Fig. 5b. Precipitation of needle-like hydration products in T_D -Q3 paste after 7 days.

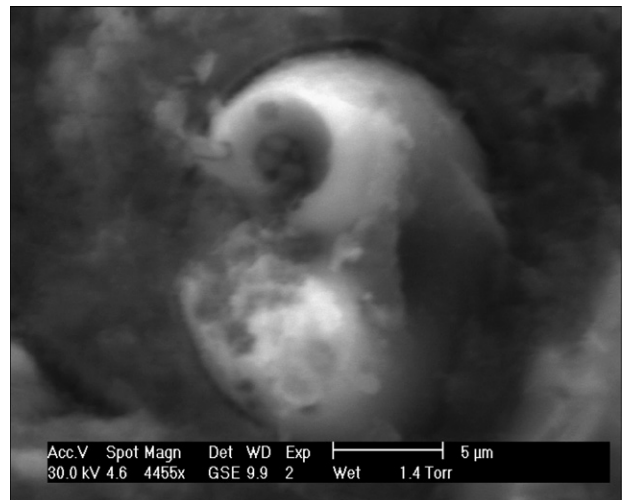


Fig. 5e. Heavily reacted fly ash particle in T_D -Q3 paste after 90 days curing

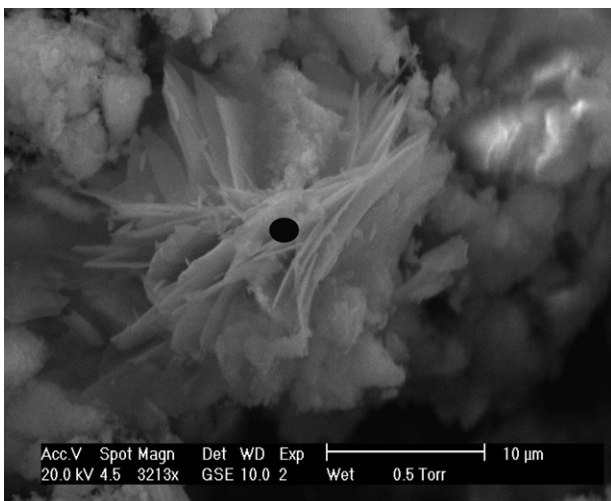


Fig. 5c. Calcium aluminate hydrate formed in T_D -Q3 paste after 7 days curing.

easily formed in fly ash mixtures with lime, is known to hold a critical role in diminishing the porosity of the system leading to a denser microstructure (Fig. 5e).

As the hydration evolves (90 days), the erosion of ash particles progresses dramatically as shown in Fig. 5d. In that case the glassy surface of the spherical ash particle has been severely broken down, possibly due to the extended curing and higher alkalinity inside the matrix caused by the CaO addition. EDX analysis in the surrounding area of the particle indicated the presence of amorphous C-S-H with a mean C/S ratio of 1.5. The significant presence of silica in the product can be considered as an indication that silica liberated from the eroded ash sphere has been dissolved in the matrix, binding available CH towards the formation of secondary C-S-H. Severe

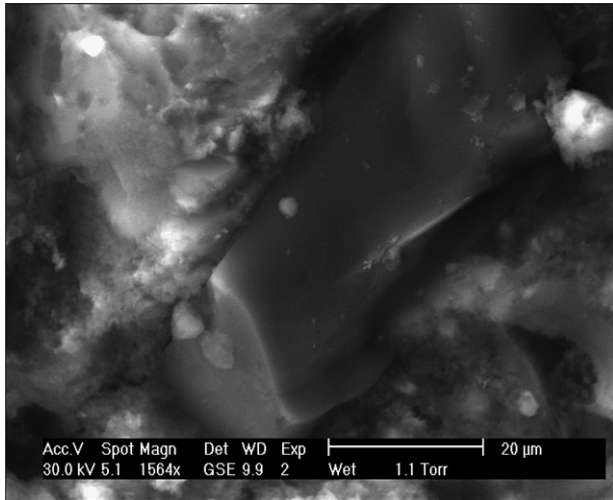


Fig. 5f. Crystal of gehlenite hydrate intercepting massive C–S–H production in T_D -Q3 paste at 90 days.

sphere corrosion manifested here coincides with the results presented earlier on the reaction rate of fly ash at the end of curing (approximately 64% of the ash has reacted). In Fig. 5f; a large crystal of gehlenite hydrate (CAS₂H₄) intercepts the production of C–S–H as shown by the respective EDX analysis (Fig. 5g) conducted on the body of the crystal. Since neither ettringite nor monosulphate hydrates were detected at this stage, it seems that remaining CH has been finely incorporated into such highly crystalline hydration products, which are partly responsible for the compaction of the paste. This is expected to further reduce the porosity of the system and subsequently strengthen the blend.

With respect to the low-lime fly ash–cement pastes, small addition of quicklime did not bring forward significant differences in the microstructure of the binary system incorporating low-lime T_M ash. On the contrary and despite the fact that the reaction degree of T_M ash was enhanced at the early stage of hydration, SEM test revealed

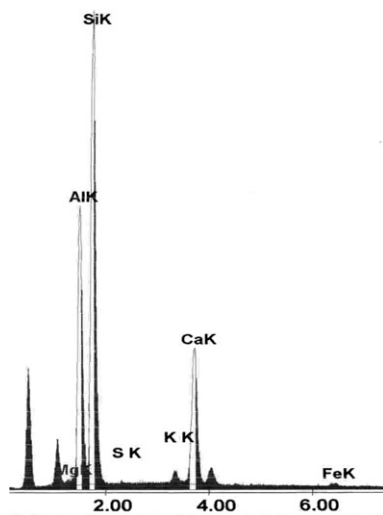


Fig. 5g. EDX analysis on the body of the crystal shown in Fig. 5f.

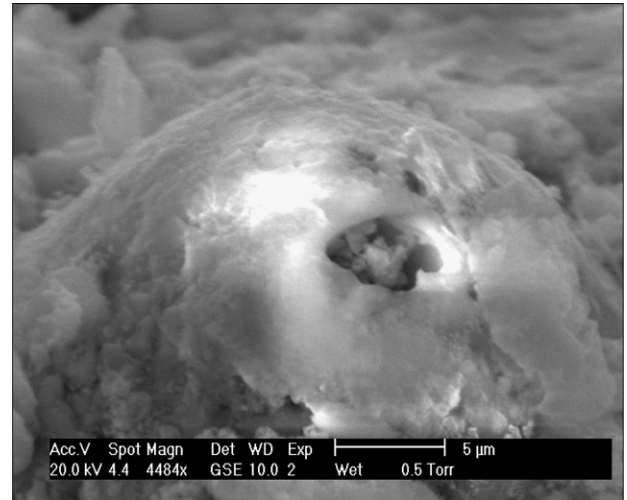


Fig. 6. Fly ash particle surrounded by massive CH production in T_M -Q15 – 90 days.

a large number of intact fly ash particles. Even at the end of the curing period (90 days), fly ash particles are extensively surrounded by CH as depicted in Fig. 6. It is possible that in the case with low-lime ash, the excess of CH created by added quicklime acts inhibitory for the action of fly ash. From the early 80s Grutzeck [24] noticed that extensive surrounding of fly ash particles by calcium hydroxide abundant in a cementitious matrix results in a substantial limitation of the reactivity of the particles. That possibly accounts for the negative effect of added quicklime on the action rate of low-lime ash discussed earlier.

4. Concluding remarks

The addition of industrially produced quicklime on fly ash–Portland cement pastes had a positive influence mainly on the strength development and reaction rate of high lime fly ash. It was demonstrated that replacing a small amount of a Class C fly ash with quicklime resulted in a notable acceleration of the fly ash degree of reaction throughout the curing period. It seems that apart from the physical effect of lime and the creation of CH bonds among ash particles, quicklime addition increased the solubility of SiO₂ leading to a greater release of soluble silica into the hydrating matrix. Conversely, when quicklime replaced an ash of lower lime content, activation was limited to the early stages of hydration. A close – almost linear – relationship between the reacted fraction of fly ash and the k -values of the respective activated mortars revealed the strong dependence of the mechanical performance of activated blended cements and the amount of fly ash that undergoes pozzolanic reaction. Microstructure analysis performed on the activated pastes revealed that the reaction products were similar to those formed in hydrating Portland cement. However, due to changes occurred in the reaction rates of the ash components, the amount, proportion and rate of the hydrates are expected to vary.

References

- [1] Thomas MDA, Shehata MH, Shashiprakash SG. The use of fly ash in concrete: Classification by composition. *Cem Concr Aggr* 1999;21(2): 105–10.
- [2] Papadakis VG, Antiohos S, Tsimas S. Supplementary cementing materials in concrete: Part II. A fundamental estimation of the efficiency factor. *Cem Concr Res* 2002;32(10):1533–8.
- [3] Cenni R, Janisch B, Splietho H, Hein KRG. Legislative and environmental issues on the use of ash from coal power stations and municipal sewage sludge co-firing as construction material. *Waste Manage* 2001;21(1):17–31.
- [4] Papadakis VG, Tsimas S. Supplementary cementing materials for sustainable building-sector growth, European Commission DGXII, Marie Curie Fellowship, National Technical University of Athens, Greece, Final Report (HPMF-CT-1999-00370); 2002, p. 76.
- [5] Bouzoubaa N, Zhang MH, Malhotra VM. Effect of grinding on physical and mechanical properties of high-volume fly ash blended cements. *World Cem* 1998;29(11):96–101.
- [6] Maltais Y, Marchand J. Influence of curing temperature on cement hydration and mechanical strength development of fly ash mortars. *Cem Concr Res* 1997;27(7):1009–20.
- [7] Katz A. Microstructure study of alkali-activated fly ash. *Cem Concr Res* 1998;28(2):197–208.
- [8] Huang S, Cheng J. Kinetic of reaction in the system fly ash–Ca(OH)₂–H₂O. *J Chin Ceram Soc* 1986;14(1):191–7.
- [9] Ma W, Brown PW. Hydrothermal reactions of fly ash with Ca(OH)₂ and CaSO₄·2H₂O. *Cem Concr Res* 1997;27(8):1237–48.
- [10] Mira P, Papadakis VG, Tsimas S. Effect of lime putty addition on structural and durability properties of concrete. *Cem Concr Res* 2002;32(5):683–9.
- [11] Shi C. Studies on several factors affecting hydration and properties of lime-pozzolan cements. *J Mat Civ Engrg* 2001;13(6):441–5.
- [12] European Committee for Standardization, European Standard EN 450-1, Fly ash for Concrete – Part 1: Definitions, specifications and conformity criteria, CEN, Brussels; 2002.
- [13] Paya J, Monzo J, Borrachero MV, Velasquez S. Evaluation of the pozzolanic activity of fluid catalytic cracking catalyst residue (FC3R). Thermogravimetric analysis studies on FC3R–Portland cement pastes. *Cem Concr Res* 2003;33(4):603–9.
- [14] Li S, Roy DM, Kumar A. Quantitative determination of pozzolanas in hydrated systems of cement or Ca(OH)₂ with fly ash or silica fume. *Cem Concr Res* 1985;15(6):1079–86.
- [15] Zhang YM, Sun W, Yan HD. Hydration of high-volume fly ash cement pastes. *Cem Concr Comp* 2000;22(6):445–52.
- [16] Luke K, Glasser FP. Selective dissolution of hydrated blast furnace slag cements. *Cem Concr Res* 1987;17(2):273–82.
- [17] Lam L, Wong YL, Poon CS. Degree of hydration and gel/space ratio of high-volume fly ash/cement systems. *Cem Concr Res* 2000;30(5): 747–56.
- [18] Lokken RO, Shade JW, Martin PFC. Effect of curing temperature on the properties of cementitious waste forms. In: *Proceedings of the Mater. Res. Soc. Symp. Proc.* 176; 1990, p. 23–9.
- [19] Brown PW. The system Na₂O–CaO–SiO₂–H₂O. *J Am Ceram Soc* 1986;73:3457–63.
- [20] Pandian NS, Balasubramonian S. Permeability and consolidation behaviour of fly ashes. *J Test Eval* 1999;27(5):337–42.
- [21] Fraay ALA, Bijen JM, deHaan YM. The reaction of fly ash in concrete a critical examination. *Cem Concr Res* 1989;19(2):235–46.
- [22] Feldman RF, Carette GG, Malhotra VM. Studies on mechanics of development of physical and mechanical properties of high-volume fly ash–cement pastes. *Cem Concr Comp* 1990;12(4):245–51.
- [23] Berry EE, Hemmings RT, Zhang M-H, Cornelious BJ, Golden DM. Hydration in high-volume fly ash concrete binders. *ACI Mater J* 1994;91(4):382–9.
- [24] Grutzeck MW, Roy DM, Scheetz BE. Hydration mechanisms of high-lime fly ash in Portland-cement composites. In: *Proceedings of the Mater. Res. Soc. Symp. Proc.*, MRS-N; 1981. p. 92–101.