Case Study
16

A Novel Way to Upgrade the Coarse Part of a High Calcium Fly Ash for Reuse Into Cement Systems

A Novel Way to Upgrade the Coarse Part of a High Calcium Fly Ash for Reuse Into Cement Systems

Abstract

Reject fly ash (*r*FA) represents a significant portion of the fly ashes produced from coal-fired power plants. Due to the high carbon content and large particle mean diameter, *r*FA is not utilized in the construction sector (for example as supplementary cementing material) and is currently dumped into landfills, thus representing an additional environmental burden. Recently, the feasibility of using *r*FA in a relatively small number of applications, like solidification/stabilization of other wastes, has been investigated by different researchers. However, as the overall amount of fly ash utilized in such applications is still limited, there is a need to investigate other possibilities for *r*FA utilization starting from a deeper understanding of its properties. In the work presented herein, mechanical and hydration properties of cementitious materials prepared by blending the coarse fraction of a lignite high-calcium fly ash with ordinary cement were monitored and compared with the respective ones of a good quality fly ash-cement mixture. The results of this work reveal that a relatively cheap, bilateral classification-grinding method is able to promote the pozzolanic behaviour of the *r*FAs, so that the overall performances of *r*FA containing cements are drastically improved. The evaluation of these results supports the belief that appropriate utilization of non-standardized materials may lead to new environmental-friendly products of superior quality.

1. Introduction

During the last decades fly ashes produced in power plants have been commonly used in the construction sector as additives either to ordinary cement or to ready-mixed, high-performance and lately self-consolidating concrete (Brameshuber and Uebachs, 2003; Oh et al, 2002; Xie et al, 2002). The utilization of such by-products, in addition to supporting sustainable development principles, contributes directly to the protection of the environment by reducing the amount of wastes to be landfilled thus also preventing impact related to leachate generation and migration (Cheerarot and Jaturapitakkul, 2004; Sajwan et al, 2003). Reductions of the amount of residues to be landfilled along with partial substitution of common raw materials used in cement making are the major beneficial effects of the recycling process (Filipponi et al, 2003; Bijen, 1996). Normally, cement industries utilize good-quality, or at least suitable-quality, fly ashes for manufacturing cement and concrete. Fly ash suitability is determined from its compliance with specified criteria, such as unburned carbon, reactive silica and alumina, and sulfur trioxide and FA fineness. Fly ashes can comply with the current European standard EN 450-1 or with National Specifications, the latter ones published in order to also classify the fly ashes that do not comply with the EU standard. The possibility however, that electricity producing companies will adjust their productivity plans according to the quality of the derived by-product is unrealistic. In view of the above considerations, each producing country has determined not only the quality but also the variability range of the inorganic components of the local coal.

In general, fly ash utilization rate is mainly governed by: (i) the annual ash production levels in each country, (ii) the FA demand of local cement and concrete industry and finally (iii) the qualitative variation of the product with regard to the specifications in force. With the above criteria in mind, it is understandable that Germany and the Netherlands present impressive fly ash utilization rates (that is almost equal to 100%) whilst in other countries, including Greece, the corresponding rates remain low (approximately 10-12%). In Greece efforts have been made during the last years to promote ash utilization. The most significant of those is a draft proposal with specifications regarding the use of high-calcium fly ash (which is the local paramount solid by-product) in non-reinforced concrete. Even though the clearest distinction between suitable and reject fly ashes is derived from the conformity or not with specifications that are in force in each country, it seems that after a size classification, ashes initially classified as reject could provide fractions that may meet the suitability criteria. In any case, it is very important that the reuse of fly ash would increase every year. A practical way to achieve this goal would be the application of a relatively inexpensive method that would enable the recovery, upgrade and reuse of *r*FA.

December 2007

Coarse ashes, representing the most relevant subcategory of *r*FA, are composed of particles having a small specific surface area and containing high levels of residual organic carbon. Apart from being less reactive, such ashes are also characterised by problematic setting behaviour into the cement paste environment (Ghosh and Sarkar, 1993). Despite being an arduous task, a respectable number of scientists have dealt with low-quality ashes in an attempt to improve their unique assets. In previous investigations (Kiattikomol et al, 2001), five different fly ashes were fractionated on a dimensional basis in order to investigate the effect exerted by each different class on the chemical and physical properties of the cement mixtures. The results revealed that the observed improvement in the strength development of concrete containing ground coarse fly ash (GCFA) was mainly due to the pozzolanic behaviour exhibited by the GCFA itself; moreover, the degree of the pozzolanic reaction increased with GCFA fineness (i.e., grinding degree). In another attempt Jaturapitakkul et al (2004) managed to improve the efficiency of coarse ashes by inserting them into mortar systems after reducing the average particle size to 3.8 μm. It was found out that concrete with about 25% of GCFA attained excellent strength values, comparable to that attained by silica fume-concrete. A large effort was also undertaken by CANMET on the mechanical and durability properties of high-volume fly ash (HVFA) cement by using a coarse fly ash that did not meet the fineness requirements stated in ASTM C618 (Bouzoubaa et al, 2001). Their results showed that HVFA cement making technology offers an effective way of utilizing coarse fly ashes that do not meet the criteria stated in the relevant American standard. Other researchers studied the effect of specific additives on the properties of cement mixtures containing the coarser fraction of high calcium fly ash, in order to highlight whether such a fraction could exhibit a pozzolanic behavior. Yan and Yang (2000) for instance mixed low-quality fly ashes and waste fluorogypsum to develop a new binder with satisfactory strength and high-volume stability. The mixtures were prepared with fly ash-fluorogypsum-cement ratios (w/w) of approximately 45:40:15.

The main objective of this investigation is to ascertain the effectiveness of a new way of processing the coarse part of a high-calcium fly ash. The authors were initially motivated by the fact that there is still no clear picture of whether or not the coarser fraction of a fly ash could be engaged into pozzolanic reactions. Recently Antiohos and Tsimas (2002) have proved that the coarser fractions of fly ashes contain much more amorphous silica than the fine ones. Since amorphous silica is actually the main carrier of pozzolanic reactions, it is believed that if the coarse part of the fly ash could be first segregated (with the aid of an air classification process) and then ground in order to take advantage of the "filler" effect, this could lead to the production of a new type of ash of improved pozzolanicity and presumably better performance in blended systems. If the above scheme proves to be efficient, it will represent a promising option for the use of commonly discarded materials, providing a valid alternative to landfilling.

2. Experimental Program

2.1 Materials

The materials used in this investigation were a normal setting cement type I 42.5 and a high-calcium fly ash from Ptolemais area (designated as T_F). The chemical composition and main physical properties of the initial materials are given in Table 1. For estimating the oxide composition of the fly ash, the procedures described in the European Standard EN 450-1 (Fly ash for concrete – Part 1) were used. The latter were also used for determining the insoluble residue of the fly ash. The “Active ratio” shown in Table 1 is considered as the ratio of active silica to the total silica in the fly ash. For calculating the content of the LOI-free fly ash constituents soluble in hydrochloric acid and potassium hydroxide (Glass content of fly ash, coded as *S* in Table 1) the procedure described in the RILEM recommendations (TC FAB-67 Use of Fly Ash in Building) was adopted. A procedure also described in the abovementioned recommendations was used for the determination of the free CaO content of the fly ash. Briefly, one gram of the original ash was mixed with ethyl acetoacetate and isobutanol and then heated for 1 hour. The mixture was then filtered through a filter crucible and the filtrate was titrated with 0.1 N hydrochloric acid. Finally, the specific gravity of the fly ash was determined using a standard Le Chatelier flask according to ASTM C-188.

2.2 Description of the refinement process

Bulk fly ash was fractionated using a lab classifier (alpine apparatus) with a sieve measuring 45μm followed by a cyclone, the latter aimed at collecting the underflow stream.

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

	Cement	T_F	T_{FP}	T_{FM}
CaO	65.01	29.79	21.02	33.02
CaO_f	0.63	4.05	2.36	4.45
CaO_{re}[a]	*n.a.*[c]	25.13	16.35	27.43
SiO_2	20.28	36.92	42.79	33.50
SiO_{2re}[a]	*n.a*	29.13	32.46	26.49
Al_2O_3	4.75	13.50	14.92	11.80
Fe_2O_3	3.76	7.06	5.82	5.70
MgO	1.61	2.69	3.32	3.43
SO_3	2.55	5.10	3.09	8.79
Na_2O	0.17	0.92	0.74	0.71
K_2O	0.35	0.50	0.56	0.61
LOI	2.31	4.36	4.66	4.01
Y_s[d]	*n.a*	78.90	75.86	79.07
IR (%)*	0.18	14.52	15.69	10.40
Glass content. S[b] (%)	*n.a.*	85.48	84.31	89.60
Blaine Fineness (cm^2/g)	3.760	5.450	5.420	5.250
Specific Gravity	3.13	2.80	2.92	2.78

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

[b] *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] *Y_s: active ratio (ratio of active: total silica)*

Using the above refinement process, two new fly ashes were produced: a coarse one (approximately 58% by weight of the bulk ash remained on the sieve, designated as T_{FP}) and a fine one (with particle size less than 45μm, coded here as T_{FM}). Chemical composition and physical characteristics of the fractionated ashes were estimated with the use of the same procedures that were followed in the case of the bulk ash (described in detail in 2.1.) and are also provided in Table 1. To neutralize the effect of fineness on their reactivity, all fly ashes (i.e., the bulk and the two fractions) were ground (different retention times were applied in each case) in a lab ball mill to reach similar particle size distributions, as shown by Blaine fineness measurement (according to ASTM C-204) and by the data shown in Fig. 1 (determined by means of laser granulometry).

Case Study 16

2.3 Preparation of specimens and testing

In order to have a first indication of the pozzolanic behavior of T_F, T_{FM} and T_{FP} fly ash, the Fratini test was carried out on different suspensions containing the cement-fly ash mixtures (fly ash to cement ratios equal to 1:5 and to 1:2.5). The test involves accelerated curing of the suspensions for 8 days at 40°C and RH=100%. At the end of the curing period, the suspension is filtered through a filter crucible and analysed for Ca content (titration performed with HCl 0.1 N) and alkalinity (titration with standard EDTA solution). Comparisons are made using the solubility curve of $Ca(OH)_2$. Each mixture was tested twice and the mean values are reported. Compressive strength development was monitored on mortar specimens prepared following a procedure described in earlier works (cementitious materials-to-sand ratio of 1:3 and W/C_M of 0.5) (Antiohos et al, 2004; Papadakis et al, 2002). In the present study 20% and 40% replacement of cement by fly ash were adopted and compression tests were conducted at 2, 7, 28, 90 and 365 days after mixing. A mortar with no fly ash was also prepared (control) for comparison. Strength results were used to calculate the efficiency factors (*k*-values) in each case. To simulate paste into mortar, paste specimens were also prepared and cast in plastic vials after being intensively shaken to remove any air content. At the same time intervals adopted for the compressive strength measurements (with the exception of 1 year old samples), the samples were broken into pieces, treated with organic solvents (acetone and diethylether) so as to stop any further hydration, and dried by means of a vacuum pump. The dried fragments were further pulverized to less than 125 µm and kept sealed until testing. Testing involved thermogravimetric analysis for monitoring the evolution of the pozzolanic reaction. TG measurements were performed into a platinum crucible (volume equal to 70 µl) by means of a Mettler STARe 851/LF/1600 TG operated in nitrogen atmosphere (50 ml min^{-1}) at a heating rate of 10°C min^{-1} from ambient temperature to 1000°C. The phase composition of powder XRD characterization of the fractionated ashes and the detection of possible alterations in the nature of hydration products was carried out by means of a Siemens D 5000 X-ray diffractometer (CuK_∂ radiation, 40KV, 30mA) operated at 0.02°/sec in a 2θ scale. Identification of the diffractogram was carried out using a Diffrac-AT Database (PDF-release year 2000).

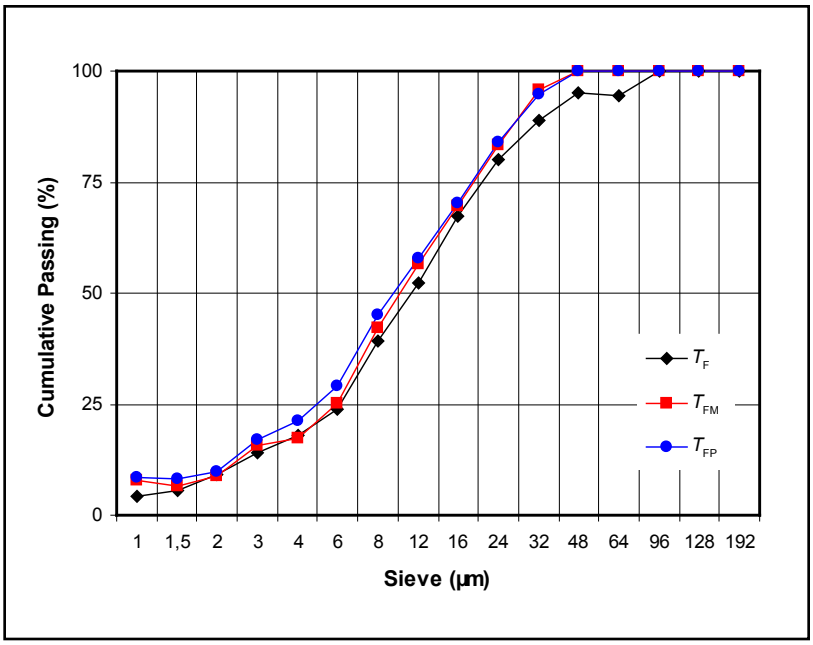

Figure 1 Particle size distribution of T_F, T_{FM} and T_{FP} samples

3. Results and Discussion

3.1 Properties of fractionated ash samples

Although the effect of classification processes on the chemical composition of fly ash has been questioned by numerous researchers (Erdoglu and Turker, 1998; Berry et al, 1989) a close look at the data of Table 1 reveals that the individual fractions differ substantially with regards to the percentage of some of their principal constituents. This is of primary importance since differences in the chemical composition are expected to influence the pozzolanic potential of each fraction. The coarser fraction (T_{FP}) for instance is notably enriched in total and active silica, but its free CaO and SO_3 contents are closer to the requirements (not greater than 2.5% and 3% respectively) stated in the European standard EN 450-1, if compared to

Case Study
16

the bulk ash. On the contrary, the T_{FM} fraction contains much more CaO (as this is concentrated in the smaller size particles), but also unusually high percentages of free CaO and SO_3. With respect to the last two parameters, the use of ground coarse fly ash may be advantageous since both free CaO and SO_3 may be harmful to mortar and concrete durability. The loss-on-ignition (LOI) values of the fractioned samples did not change appreciably compared to that of the initial fly ash. In other works (Berry et al; 1989), the finer ash (obtained by classification) is reported to show higher LOI values than the original bulk fly ash. This is very encouraging since higher LOI is usually (but not always correctly) associated with high unburned carbon that causes undesired swelling effects in the paste. No significant differences were detected regarding the glass phase content of T_F and its fractions, while a notable increase in the specific gravity value of T_{FP} was attributed to prolonged grinding that caused the breaking of cenospheres and plerospheres (Mora et al, 2003). Finally, from the mineralogical point of view (Fig. 2) it can be qualitatively observed that in the T_{FP} fraction more silica compounds like quartz, mullite and cristoballite were detected and lime was hardly traced, whilst intense reflections for the presence of CaO were detected in the respective finer fraction. The pattern of T_{FM} diffractogram reveals higher contents of anhydrite and C3A compounds, in accordance with the abundant presence of CaO.

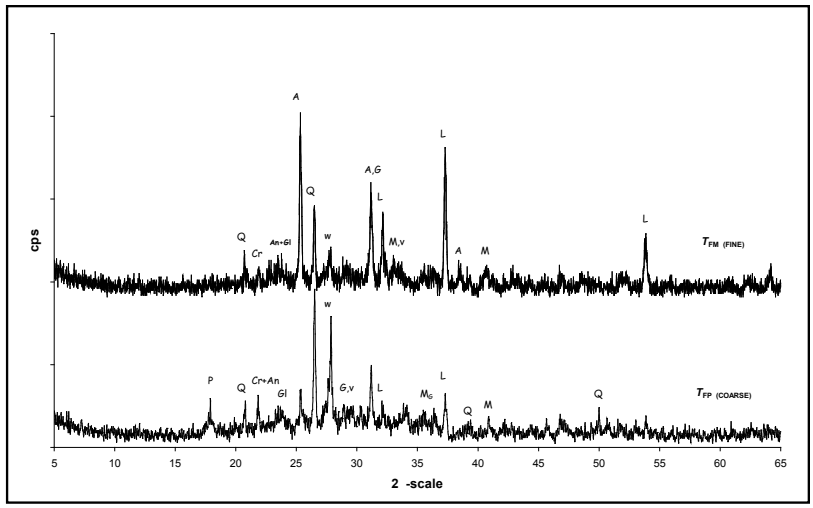

Figure 2 XRD patterns of fractionated T_{FP} and T_{FM} fly ash samples (Q: Quartz, L: Lime, Cr: Cristobalite, A: Anhydrite, M: Mullite, MG: Magnetite, W: Wollastonite, V: Vaterite, CA: C3A, An: Anorthite, Gl: Gehlenite, G: Gismondine, P: Portlandite)

3.2 Pozzolanicity test results

Results of the Fratini test are presented in Fig. 3 both for the 20% and 40% fly ash addition. It is known that a measured point below the solubility curve of $Ca(OH)_2$ is an indication that the examined suspension is undersaturated in $Ca(OH)_2$ due to the fact that $Ca(OH)_2$ produced during cement hydration has been consumed by pozzolanic reactions. Obviously, when a measured point is above the saturation curve, it is concluded that the generation of $Ca(OH)_2$ from cement hydration is greater than the equivalent amount of $Ca(OH)_2$ that reacts with the material inside the suspension. If so, the examined material can hardly be described as pozzolanic. From the data shown in Fig. 3 it can be seen that almost all mixtures tested presented pozzolanic behavior especially at high levels of cement substitution (i.e., 40%

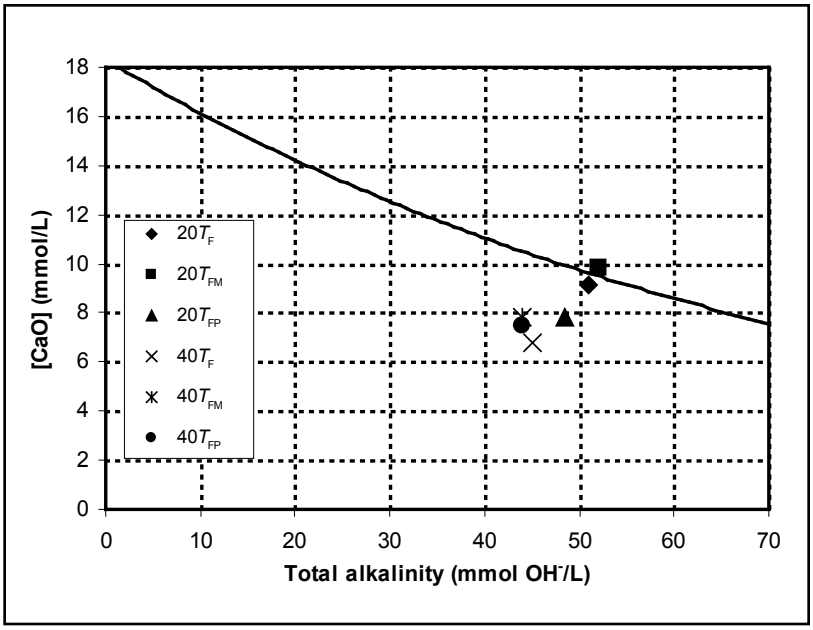

Figure 3 Fratini test results for fly ash – cement mixtures (FA content equal to 20% and 40% respectively)

FA content). The only measured point that was found to be over the saturation curve corresponds to the mixture containing 20% of the fine T_{FM} ash. This is probably due to the very low active silica content of this sample. On the other hand both mixtures incorporating the ground coarse fraction T_{FP} exhibit superior pozzolanic action even when compared to the cement prepared with the bulk ash. This is the result of its very high active silica content which is the main binder of available $Ca(OH)_2$ and the factor that governs the pozzolanic performance of the ashes tested. Despite the encouraging results presented here, they should only be used as a first indication for the future performance of the corresponding pastes and mortars since the Fratini test was performed under controlled-accelerated conditions and it cannot predict the actual behavior of the same samples under normal hydration conditions.

3.3. Mechanical Properties

Compressive strength development of the control and fly ash mortars is presented in Table 2. During the first week of hydration, specimens containing the bulk T_F develop strength slower than the control since at this stage ash acts mostly as an inert material. The rate of strength development increased significantly for the two samples containing the T_{FP} fraction, which outperformed the reference specimen as early as two days after mixing. In contrast, T_{FM} inclusion retarded notably the strength gain of mortars. Considering that the particle size distribution of the two processed samples is practically the same, the best performance observed for the samples containing the T_{FP} was ascribed to the different chemical composition, and specifically to the higher contents of active silica and alumina which are the main carriers of the pozzolanic reactions.

Table 2 Compressive strength development of reference and fly ash mortar samples

	Compressive strength (MPa)				
	Age (days)				
	2	7	28	90	365
Control	24.7	39.2	50.6	59.7	68.0
20T_F	19.4	38.0	49.4	59.7	68.4
20T_{FM}	14.0	28.0	46.6	58.0	67.2
20T_{FP}	25.8	38.3	51.7	62.7	71.6
40T_F	12.8	26.8	42.8	57.3	64.8
40T_{FM}	10.6	16.9	39.2	55.6	68.0
40T_{FP}	22.1	33.3	49.0	60.3	70.3

As hydration evolves, T_{FP} mortars continue to show better performance than the other ash-containing samples, reaching emphatic values of 62.7 and 71.6 MPa after three and twelve months of curing respectively. The difference observed in the strength development grows larger with curing time, and becomes high after the first month, since during this stage the role of active silica is known to be predominant (Antiohos et al;2004).

When cement replacement is increased to 40%, the strength values were normally diminished. This decrease is certainly more pronounced in the case where the bulk ash and its fine fraction were utilised, indicating that those ashes (especially the latter) may not be used for applications where immediate need for strength development is required. It becomes evident that reactive constituents contained in those ashes cannot compensate, at least during the initial period of hardening, for such an absence of clinker's strength carriers. Despite the significant cement replacement, the ground coarse T_{FP} ash performs again impressively from the first week of curing. With the progress of hydration, T_{FP} mortars develop strength faster than all the other

specimens tested (including the control one) due to the full commencement of the pozzolanic reactions. In fact, after one month of hydration, T_{FP} mortar exhibits similar strength to the non-fly ash specimen, while at the same stage, it outperforms the sample containing the original ash. The strength difference between the ground coarse ash-containing samples and the other samples is continuously growing towards the end of the curing period (1 year), thus confirming once again the observations made by the authors on the significance of active silica for long-term strength evolution.

3.4 Efficiency factors

It has been well established (Papadakis and Tsimas; 2001) that in the case of mortars and concrete that incorporate supplementary cementing materials, the k-value is derived from the following expression for the measured compressive strength (f_c):

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

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 *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 1.36, 0.98, 0.69, 0.46 and 0.24 for 2, 7, 28, 90 and 365 days, respectively. Based on the above expression and strength values shown in Table 2, the *k*-values of the bulk and fractionated ash blends were calculated and presented in Table 3. Data in Table 3 reveal once again the inability of the bulk and fine ashes to act drastically from the start of the curing process and the high reactivity of the ground coarse fraction. The latter exhibits higher k-values than the control mortar (in the case of moderate cement replacement) and in the case of severe cement replacement (i.e., 40%) it reaches unity very quickly and it exceeds it at the end of the curing process.

Table 3 Efficiency factors of fly ash samples

	***k*-values**				
	Age (days)				
	2	**7**	**28**	**90**	**365**
$20T_F$	0.66	0.92	0.92	1.00	1.01
$20T_{FM}$	0.31	0.28	0.74	0.89	0.93
$20T_{FP}$	1.07	0.94	1.07	1.19	1.21
$20T_{FP\ (theor\text{-}v)}$[a]			1.05	1.23	1.41
$40T_F$	0.62	0.60	0.75	0.92	0.89
$40T_{FM}$	0.55	0.28	0.63	0.87	0.99
$40T_{FP}$	0.92	0.81	0.95	1.02	1.03

[a] *Theoretical values derived using equation (2)*

In a recent work Papadakis et al. (2002) have reported, for the first time, analytical expressions that related active silica of artificial pozzolans with k-values of their respective cementitious systems aiming to enable a first approximation of their performance starting from the amount of amorphous silica. The authors concluded that for a cementitious system containing SCMs (supplementary cementing materials), *k*-values can be expressed as follows:

$$k = (Y_S f_{S,P}/f_{S,C})(1 - a\ W/C)$$

where: Y_S is the weight fraction of the oxide SiO2 in the SCM (given in Table 1), which contributes to the pozzolanic reactions (i.e. the ratio of active silica to the total silica in the SCM) and fS,P and fS,C are the weight fractions of silica in the SCM and cement respectively. By applying the above equation in the case of $20T_{FP}$ blended cement after the first 28 days (a stage where active silica is known to hold a critical role), almost identical *k*-values (with the experimental ones) were calculated. The latter observation denotes the consistency of the results from the theoretical model even when reject fly ashes are considered.

3.5 Pozzolanic reaction evolution

By estimating the available Ca(OH)2 that exists in a cementitious matrix at different stages of curing, the rate at which pozzolanic reactions are taking place can be obtained. For the ashes used herein, Table 1 shows that their free lime contents are practically the same. Therefore the amount of secondary portlandite generated by fly ash hydration would be the same for all ashes tested. Based on this assessment, thermogravimetry results were used to evaluate the progress of pozzolanic reactions for the cements that performed best from the mechanical point of view, that is, for a 20% ash addition. The results were then inserted in the following equation proposed by Paya et al. (2003) to calculate the percentage of fixed lime (FL), a factor directly associated with the progress rate of the pozzolanic reaction (results are demonstrated in Fig 4):

$$\textbf{Fixed Lime (\%)} = \frac{(CH_c \cdot C_{\%}) - CH_P}{CH_c \cdot C_{\%}} \times 100$$

where CH_c is the CH content of the control 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.

In all cases fixed lime values increase with curing time. Negative values observed for the fractionated ash pastes after 2 days of hydration are indicative of the excess of CH created from the instant hydration of their free lime and of the incapability of both ashes to contribute from the beginning of hardening. The inclusion of the coarse T_F ash in the cement system brings forward positive results, especially after the first week, as manifested by the impressive FL value measured at 28 days (more than 18% compared to around 6% measured at the same age for the other ash samples). Throughout the examined curing period (up to 90 days), the cement containing the ground coarse ash fraction exhibits higher fixed lime percentages than the other blended cements as a result of the higher active silica contained in the specific fraction. This is increasingly liberated from the core of the ash to participate in the reactions with available lime to form additional, secondary C-S-H gel that brings about a

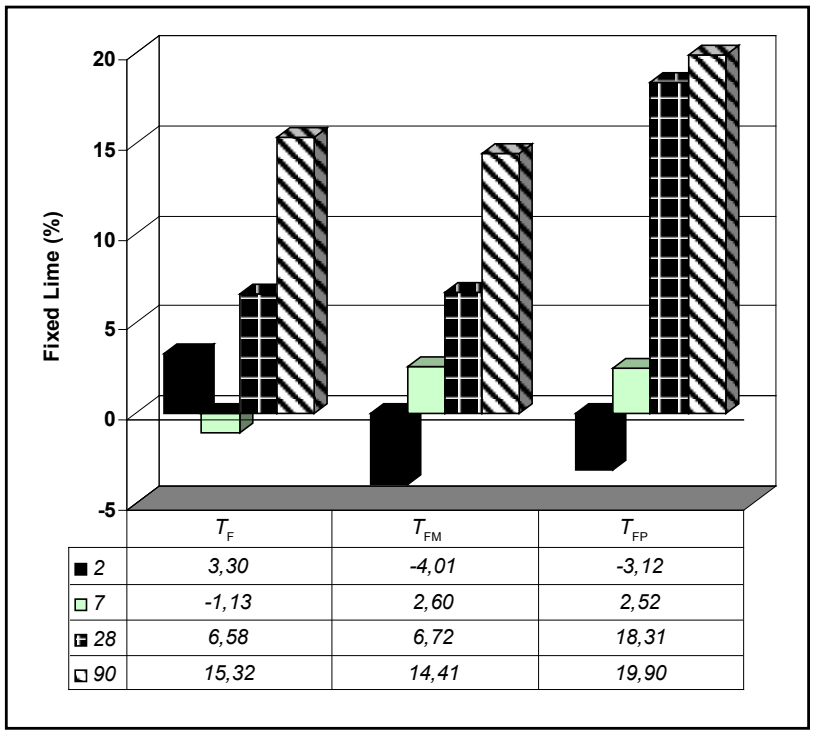

Figure 4 Fixed lime values for T_P, T_{FP} and T_{FM}–containing mixtures (FA content equal to 20%)

Case Study 16

noticeable strengthening of the paste (the corresponding mortar exhibited a very high k-value of 1.17).

3.6 Hydration products identification

XRD measurements confirmed the observations of the thermogravimetry analysis regarding the nature of newly formed products during hydration. Significant presence of portlandite and ettringite was confirmed in the XRD patterns of the fly ash pastes after 28 days of curing (Fig. 5). It can be easily seen that in every paste tested, crystalline $Ca(OH)_2$ was generated along with ettringite as a result of the strong presence of sulfur trioxide (mainly in the form of anhydrite) in the ashes used. In the recent past, Tishmack et al. (1999) have noted that ettringite formation increases with increasing anhydrite contents. This is probably the case here regarding the pronounced presence of AF_t phases in all pozzolanic specimens, especially those containing the finer fraction (T_{FM}) which contains much more anhydrite than the other samples (Table 1 and Fig. 2). The latter sample is the only one where traces of monosulfate hydrate were detected, possibly due to the dissolution of SO_3 ions from ettringite. On the samples with the coarser fraction of T_F the production of hydrated calcium aluminate hydrate phases can be clearly detected from the second week of curing, as well as some gismondine. Phases like these are both contributing towards filling the pores in the matrix and subsequently strengthening the paste. This is in accordance with compressive strength results shown in previous sections.

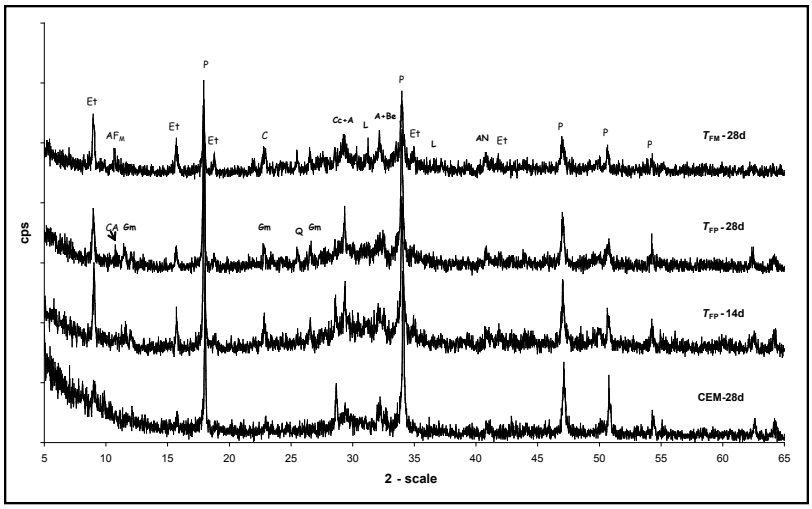

Figure 5 XRD patterns of control, T_{FM} and T_{FP} – containing cement pastes with curing time (FA content equal to 20%) (Et: Ettringite, CA: Calcium aluminium oxide hydrate, G: Gismondine, P: Portlandite, Cc: Calcite, Q: Quartz, A: Alite, Be: Belite, AN: Anhydrite, AFM: Calcium aluminum sulfate hydrate)

Inherent crystalline constituents of fly ashes, such as lime and quartz appear also in the patterns of their hydrated blended pastes, whilst presence of calcite in all systems could be attributed also to possible carbonation during handling. A decrease in the intensity of the C_2S and C_3S peaks with age corresponds to the acceleration of their hydration in the presence of finely ground fly ash, as clearly explained by Berry et al. (1989). The presence of ettringite is increased with the ash addition (i.e. 40%, Fig. 6), contrary to portlandite whose reflections are less intense as a result of the higher CH depletion after one month (coinciding with the high FL values presented earlier). In this case where an extra 20% of fly ash was added, the presence of calcium-aluminate (CA) and gismondine phases in the ground coarse fly ash sample is more pronounced, whereas such compounds are not

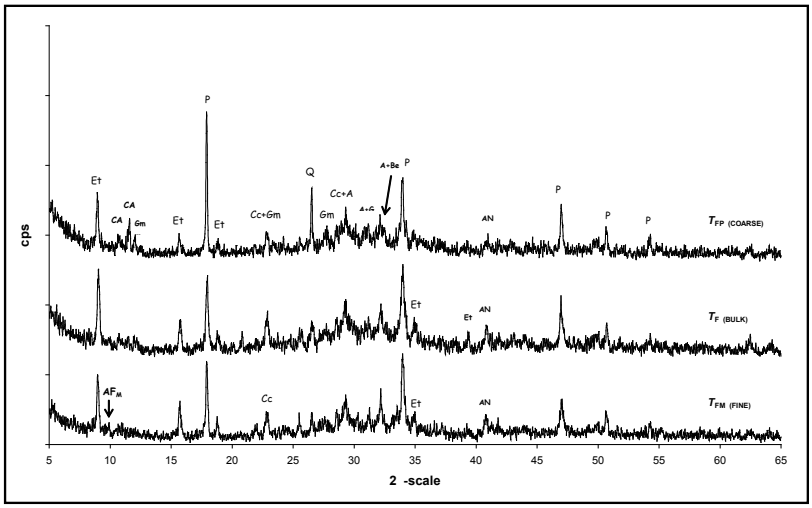

Figure 6 XRD patterns of T_{FM} T_P and T_{FP} – containing cement pastes after 28 days of hydration (FA content equal to 40%) (Et: Ettringite, CA: Calcium aluminium oxide hydrate, G: Gismondine, P: Portlandite, Cc: Calcite, Q: Quartz, G: Gypsum, A: Alite, Be: Belite, AN: Anhydrite, AFM: Calcium aluminum sulfate hydrate)

detected at all in the respective samples with the fine fraction ash. It is possible that the higher percentages of soluble silica and alumina of T_{FP} are responsible for the formation of such phases that contribute to the hardening of the paste.

4. Conclusions

In this paper, a novel way of utilizing reject coarse fly ashes was introduced. A bilateral method comprised of air-classification and further grinding of the coarse fraction of a lignite high-calcium fly ash was applied and evaluated. This effort was primarily motivated by previous experiments that revealed the enrichment of the coarse fractions of fly ashes in total and soluble (thus reactive) silica and a related increase in pozzolanic reactivity. In general the proposed method could be applied in the case of: (i) reject fly ashes aiming at recovering fractions that comply with the specifications in force, but also of (ii) good quality fly ashes that fulfill the conformity criteria, focusing at reusing specific fractions of advanced quality for certain applications.

It is noted that the authors have also worked in the same direction, that is, the upgrade and reuse of the reject part of fly ash, with fly ashes of low-lime content. The preliminary results from this attempt are very convincing also with regards to the potential use of initially rejected fractions of this valuable by-product. Moreover, given the possible retarding or accelerating (depending on their composition, chemical form and typology of the associated anion) effect of the heavy metals that may be contained in fly ash, the authors are currently investigating the presence of trace metals in the separated fractions of this work in order to clarify whether and to what extent their presence could be partly responsible for the behavior of each different fraction examined. With regards to the main findings of the present work, these are summarized as follows:

1. The air-classification process verified previous findings on the enrichment of the coarser fly ash fractions in total and active silica and of the finer ones in CaO, free lime and sulfur content. The corresponding decrease of the last two parameters, the relatively small increase of LOI and the higher pozzolanic potential (as demonstrated with the aid of the Fratini test) of the coarser fraction, might enable the incorporation of ground coarse fly ashes (GCFA) into cement and concrete. It is concluded that by applying the described technique a significant percentage (in this work approximately 58%) of fly ash could be upgraded and recycled into systems of advanced performance.

2. Inclusion of GCFA into cement mortars increased notably the rate of strength development from the beginning of the curing period, mitigating one of the biggest drawbacks associated with the utilization of fly ash. Even when large volumes of cement were substituted, T_{FP}-based systems exhibited strength superiority indicating that they may be used in the production of High-Volume FA Concrete or even High-Strength Concrete. On the other hand, the sole use of the fine fraction of the bulk ash could not present sufficient early strength; therefore its use should be excluded from structures that require adequate strength development. However, it can still be reused as an aggregate for lightweight and normal concrete or even as a road base material and flowable fill.

3. Given that the particle size distribution and specific surface of the two processed samples is practically the same, it is believed that the superiority of the coarser fraction is attributed to the differences in the chemical and mineralogical composition of the samples, mostly the excess of active silica and alumina which are the main carriers of the pozzolanic reactions.

4. Strength superiority of ground coarse fraction was testified also by means of *k*-value. A previously reported expression, correlating active silica of artificial pozzolans with *k*-values, was also validated in the present work. Using such an expression can lead to a relatively safe approximation of the future mechanical performance of the final product.

5. High FL values were measured for the coarser fraction based mortars. FL values remained notably higher than those of the other blended cements throughout the examined period. Soluble silica is

increasingly liberated to participate in the reactions with available lime to form additional, secondary C-S-H gel, causing the strengthening of the paste.

6. C-S-H gel, portlandite and calcium sulphoaluminates (mainly ettringite) were the main hydration products formed in the GCFA pastes. Peaks of gismondine were also detected after the first two weeks of hydration. Generation of these products is favored by the increasing liberation of amorphous silica that abounds in the coarse part of fly ash. Such compounds are considered partly responsible for the compaction of the paste and subsequent strength improvement.

5. References

Antiohos, S., Papageorgiou, A., Tsimas, S., 2004. Activation of fly ash cementitious systems in the presence of quicklime. Part II – Nature of hydration products, porosity and microstructure development, Cement and Concrete Research (submitted).

Antiohos, S. and Tsimas, S., 2002. Reactive silica of fly ashes in relation to the burning condition of lignites, in: Dhir, R.K. (ed.), Proceedings of the International Conference Challenges of Concrete Construction, Dundee, Scotland, 2002, 71-80.

Antiohos, S. and Tsimas, S., 2004. Investigating the role of active silica on the hydration mechanisms of high-calcium fly ash/cement systems, Cement and Concrete Composites 27, 171-181.

Berry, E.E., Hemmings, R.T., Langley, W.S., Carette, G.G., 1989. Beneficiated fly ash: hydration, microstructure and strength development in Portland cement, In: Proceedings of the 1st International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, SP-114, Detroit, USA, 241-273.

Bijen, J., 1996. Benefits of slag and fly ash, Construction and Building Materials 10, 309-314.

Bouzoubaa, N., Zhang, M.H., Malhotra, V.M., 2001. Mechanical properties and durability of concrete made with high-volume fly ash blended cements using a coarse fly ash, Cement and Concrete Research 31, 1393-1402.

Brameshuber, W. and Uebachs, S., 2003. The Influence of Air Voids on the Properties of Self-Compacting Concretes Containing Fly Ash. In: Wallevik, O. and Nielsson, I. (Eds.), Proceedings of the 3rd International RILEM Symposium on Self-Compacting Concrete, Reykjavik, Iceland, 870-880.

Cheerarot, R. and Jaturapitakkul, C., 2004. A study of disposed fly ash from landfill to replace Portland cement, Waste Management 24, 701-709.

Erdoglu, K. and Turker, P., 1998. Effects of fly ash particle size on strength of Portland cement fly ash mortars, Cement and Concrete Research 28, 1217-1222.

Filipponi, P., Polettini, A. Pomi, R. and Sirini, P., 2003. Physical and mechanical properties of cement-based products containing incineration bottom ash, Waste Management 23, 145-156.

Ghosh, S.N. and Sarkar, L.S., 1993. Mineral Admixtures in Cement and Concrete, in: Ghosh, S.N. (ed.), Progress in Cement and Concrete, ABI Books, New Delhi, India, 118-157.

Jaturapitakkul, C., Kiattikomol, K., Sata, V. and Leekeeratikul, T., 2004. Use of ground coarse fly ash as a replacement of condensed silica fume in producing high-strength concrete, Cement and Concrete Research 34, 549-555.

Kiattikomol, K., Jaturapitakkol, C., Songpiriyakij, S. and Chutubtim, S., 2001. A study of ground coarse fly ashes with different finenesses from various sources as pozzolanic materials, Cement and Concrete Composites 23, 335-343.

Mora, E., Paya, J., Monzo, J., 2003. Influence of different sized fractions of a fly ash on workability of mortars, Cement and Concrete Research 23, 917-924.

Oh, B.H., Cha, S.W., Jang, B.S. and Jang, S.Y., 2002. Development of high-performance concrete having high resistance to chloride penetration. Nuclear Engineering and Design 212, 221-231.

Papadakis, V.G., Antiohos, S., Tsimas, S., 2002. Supplementary cementing materials in concrete - Part II: A fundamental estimation of the efficiency factor, Cement and Concrete Research 32, 1533-1538.

Papadakis, V.G. and Tsimas, S., 2001. Supplementary Cementing Materials for Sustainable Building-Sector Growth, European Commission DGXII, Marie Curie Fellowship, Final Report, Project No HPMF-CT-1999-00370, NTU of Athens, Greece, p. 74.

Paya, J., Monzo, J., Borrachero, M.V., Velasquez, S., 2003. Evaluation of the pozzolanic activity of fluid catalytic cracking catalyst residue (FC3R). Thermogravimetric analysis studies on FC3R-Portland cement pastes, Cement and Concrete Research 33, 603-609.

Sajwan, K.S., Paramasivam, S., Alva A.K., Adriano, D.C. and Hooda, P. S., 2003. Assessing the feasibility of land application of fly ash sewage sludge and their mixtures, Advances in Environmental Research 8, 77-91.

Tishmack J.K., Olek J. and Diamond S., 1999. Characterization of high-calcium fly ashes and their potential influence on ettringite formation in cementitious systems, Cement and Concrete Aggregates 21, 82-92.

Xie, Y., Liu, B., Yin, J. and Zhou, S., 2002. Optimum mix parameters of high-strength self-compacting concrete with ultrapulverized fly ash. Cement and Concrete Research 32, 477-480.

Yan, P. and Yang, W., 2000. The cementitious binder derived with fluorogypsum and low-quality of fly ash, Cement and Concrete Research 30, 275-280.

Case Study
16

Submitted By:
S. K. Antiohos, S. Tsimas
National Technical University of Athens, School of Chemical Engineering
9 Heroon Polytechniou, Zografou Campus, GR-157 73 Athens, GREECE
Tel.: +30 210 772 3095, Fax: +30 210 772 1727, e-mail: stangits@central.ntua.gr
First-author:
Stylianos K Antiohos
National Technical University of Athens, School of Chemical Engineering
9 Heroon Polytechniou, Zografou Campus, GR-157 73 Athens, GREECE
Tel.: +30 210 772 2893, Fax: +30 210 772 3188, e-mail: adiochic@central.ntua.gr
Technical University of Athens, School of Chemical Engineering
9 Heroon Polytechniou, Zografou Campus, GR-157 73 Athens, GREECE