An Investigation of the Behavior of Raw Calcareous Fly Ash in Mortar Mixtures

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ABSTRACT

The behavior of unprocessed calcareous fly ash in cement mortar mixtures is often questionable and unpredictable, that is one of the difficulties in confining these fly ashes within the limits of standards. This work aims at correlating the material's characteristics with its behavior in mortar mixtures. An effort is made to understand how the three reactive constituents lime (CaO), silica (SiO_2) and sulfates (SO_3) affect the strength and volume stability. Two raw calcareous fly ashes of different composition emanating from the Ptolemaida area, Greece, were systematically tested to define their profile as cementitious agents that could be incorporated in a cement mixture replacing part of the cement. Apart from chemical composition, mineralogical analysis of their phases was carried out by x-ray diffraction and SEM microscopy. Fineness was measured by sieving and laser particle size analysis to see the most prevalent size of grains. For soundness and water demand of the pastes the corresponding EN and ASTM standards were followed. A number of specimens were prepared for checking the pozzolanicity index.

Furthermore, mortar mixtures with plain calcareous fly ashes and in combination with cement (50/50) were made with and without superplasticizers (SPL) in order to monitor strength development. The early deformation of these mortars, stored at low relative humidity (<65%) and 20 ºC, were also measured. Evaluating all the results, some remarks are made about the performance of the existing standards. It is also obvious that the water/binder ratio is an important parameter which can be modified by using SPL and improving significantly strength and volume stability of cement fly ash mortar mixtures.

INTRODUCTION

There are only a few standards covering the use of calcareous fly ash in construction applications. In Europe, there is no standard available for the use of calcareous fly ashes in concrete, as in the case of siliceous fly ashes (EN 450). This is partially due to the particularity of this material, which contains three reactive constituents: lime (CaO), silica (SiO_2) and sulfates (SO_3). Since bad experiences in cement performance have been connected with lime and sulfates, the limits of the existing standards are very strict and most of the calcareous fly ashes are rejected as improper. However, the high volumes of the produced calcareous fly ashes press for exploitation, especially if sustainability issues will be adopted in the construction sector. Of course, there are ways of processing calcareous fly ash in order to reduce its free lime content or to increase its fineness [1], but then the market price of the fly ash is increased. On the other hand, there are many applications in construction for which low strength levels are required, and these fly ashes could be used without any cement addition. Therefore, in order to maximize the utilization of these fly ashes, performance type criteria should be established in relation to the field of application or end product.

Long-term experience with Greek fly ash [2] has shown that it possesses hydraulic and pozzolanic properties and that if it is under proper control, it can be used either blended with cement clinker [3] or as a separate constituent of the concrete mixture [4] for the benefit of both economy and technical characteristics of the fial product.

SCOPE

The aim of this experimental research was to find how the three more reactive constituents of calcareous fly ash influence the behavior of fly ash or cement-fly ash mortar mixtures, which of them is of greater significance for strength and volume stability. Of course, fineness of fly ash is another parameter that affects its reactivity. That is why two samples of near fineness values and particle size distributions were selected for comparison. The two calcareous fly ashes from the power stations of Ptolemaida area named Ptol I and Ptol II differ mainly in the content of silica and reactive silica, in the available lime amount as well as in sulfate content. The profile of Ptol I implies cementitious material with self cementing capacity while the Ptol II is more siliceous and of pozzolanic character which is expected to be enhanced. An effort was made to explain their behavior by subjecting the fly ashes and mortars to different tests. The conclusions are expected to contribute in a proper manipulation of these fly ashes.

EXPERIMENTAL

Materials

The calcareous fly ashes were selected from the power stations of Ptolemaida area in Northern Greece. The criteria were to differ in reactive silica, in available lime content as it is defined in EN 451.1 and in sulfates. One sample should contain SO_3 more than 5% and the other less than 4%. Since high content in sulfates is often accompanied by high sulfate values the sample Ptol I was of high lime and sulfate value. After continuous checking of the silica, lime, sulfate and fineness (R_{45} %) the Ptol I and Ptol II samples were stored in airtight containers of adequate volume capacity. To avoid the impair of aggregate in the mortar mixture properties, standard AFNOR sand was used for all the mixtures.

The mixture with cement CEM I 42.5 was used as control. Apart from the mortar mixtures prepared for the pozzolanicity index with cement and with lime, other eight mortar mixtures were prepared. Two with plain Ptol I, Ptol II and two with cement/fly ash

= 50/50 combinations. The four mortar mixtures were repeated by adding superplasticizers of lignosulfonic base in order to reduce the water requirement.

TESTS AND RESULTS

The chemical analysis of the fly ashes is given in Table 1. The methodologies prescribed in EN 196-2 were used for SiO_2 reactive, LOI, SO_3, while the available lime content was determined according to EN 451.1. The free CaO (non-hydrated) was determined by subtracting the amount of $Ca(OH)_2$ from the available lime. The amount of $Ca(OH)_2$ was determined by DTA-TG method. Alkalis and chlorides were measured according to EN 196-21. The mineralogical phases recognized in diagrams of dry fly ashes by x-ray diffractometry are also shown in Table 1.

Table 1. Chemical and mineralogical composition of the calcareous fly ashes

Oxides	Ptol I	Ptol II	Mineralogical phases in Ptol I and II detected by X-ray diffraction
SiO_2	33.50	41.15	- SiO_2, quartz
Al_2O_3	13.90	16.00	- CaO, lime
Fe_2O_3	5.60	6.75	- $Ca(OH)_2$, portlandite
CaO	27.0	17.88	- $CaSO_4$, anhydrite
MgO	2.90	4.05	- $(Na,Ca)AlSi_3O_6$, feldspar
SO_3	5.10	3.95	- $CaCO_3$, calcite
L.O.I.	5.80	4.05	- $Ca_2Al(Al,Si)_2O_8$, gehlenite
CaO_{avail}	8.52	3.15	- $MgO.Al_2O_3.SiO_3$
CaO_{free}	4.85	1.60	- $3CaO.Al_2O_3$, calcium aluminate
Insoluble residue (IR)	24.65	37.0	
K_2O	1.15	1.08	
Na_2O	0.68	0.52	
$SiO_{2\ reactive}$	24.80	30.50	

The physical characteristics of the two calcareous fly ash samples are shown in Table 2. The fineness $R_{45μm}$ was measured by using Alpine apparatus, since EN 451 methodology follows a wet process not suitable for calcareous fly ashes. The setting time values were determined according to EN 196-3. The soundness of the fly ash pastes was checked by the Le Chatelier method (EN 196-3) and also by the autoclave method (ASTM C151). The water demand for the normal consistency of the fly ash pastes has been also recorded. The strength development of cement/fly ash 80/20 mortar mixtures (pozzolanicity index) was determined according to EN 450 and ASTM C311-02, while the 28-d strength of fly ashes with lime was tested following the ASTM C593-95 methodology.

Indicative picture of SEM microscopy of calcareous fly ash is indicated in Fig 1, while the particle size analysis of the two fly ash samples is given in Fig 2.

Apart from the tests of describing the profile of the two fly ashes, additional mortar mixtures with standard AFNOR sand were made by using plain fly ashes and their combination with cement (cement/fly ash, 50/50). The consistency of all mortars was measured by flow table expansion and was stable 14.2 – 14.8 cm. A control mortar mixture of the same consistency with net cement CEM I 42.5 was also manufactured. This consistency was achieved for the two fly ashes Ptol I and Ptol II with and without addition of superplasticizer (SPL). The proportions of the mortars are shown in Table 3, while the strength results are depicted in Table 4. In Fig 3 and 4 the rate of strength development of the mortars is plotted.

Table 2. Physical characteristics of the calcareous fly ashes

Fly ash samples		Ptol I	Ptol II	CEM I42,5
Density (kg/dm^3)		2.47	2.48	3.11
Fineness R_{45}(%) by Alpine		32.2	30.8	3.5
Water demand for normal consistency pastes (%)		30.5	42.8	27.7
Setting time of pastes (min)	Initial	180	210	110
	Final	240	295	145
Fly ash pastes Le Chatelier soundness (mm)	48h in water	12	15	1.5
	After boiling	4.5	2.5	0.85
Cement/fly ash pastes Le Chatelier soundness (mm)	48h in water	2.5	1.0	-
	After boiling	0.5	1.2	-
Fly ash pastes autoclave soundness (%)		0.20	0.15	0.25
Cement/fly ash pastes autoclave soundness (%)		0.10	0.07	-
Pozzolanicity index EN 196-1 (MPa)	7-d	32	25	36
	28-d	43	40	49
Pozzolanicity index with lime ASTM C593-95 (MPa)	28-d	5.2	3.8	-

Table 3. Proportions of fly ash mortars of standard consistency

Constituents* Code No.	CEM I42,5 (g)	Ptol I (g)	Ptol II (g)	water/binder	Spl (%) by mass of binder
Control CEM I42.5	450	-	-	0.50	-
IA	225	225	-	0.54	-
IB	-	450	-	0.589	-
IA + SPL	225	225	-	0.50	0.67
IB + SPL	-	450	-	0.50	2.01
IIA	225	-	225	0.567	-
IIB	-	-	450	0.667	-
IIA +SPL	225	-	225	0.50	2.2
IIB + SPL	-	-	450	0.50	2.8

*For all the mixtures AFNOR standard sand (1350g) was used and the flow table expansion was between 14.2 cm and 14.8 cm

Table 4. Strength development of mortar mixtures with calcareous fly ashes (standard consistency)

Code No.	Compressive strength (MPa)				Flexural_strength (MPa)			
	3-da	7-d	28-d	90-d	3-d	7-d	28-d	90-d
Control CEM I42.5	31.5	40.5	51.3	59	7.1	7.6	8.7	9.1
IA	8.1	15.5	32.0	37.8	1.95	3.7	7.8	9.7
IB	1.9	2.5	12.5	22.5	0.25	0.53	3.9	4.9
IA + SPL	11.0	20.5	34.2	42.0	3.2	4.7	8.5	9.8
IB + SPL	1.0	2.8	13.8	25.2	0.35	0.75	3.5	5.38
IIA	7.37	14.5	24.3	29.5	3.6	5.7	7.4	7.5
IIB	1.4	2.6	8.4	17.3	0.8	1.25	1.30	1.77
IIA +SPL	5.5	22.7	28.3	48.7	1.5	5.8	8.4	9.6
IIB + SPL	1.5	2.95	9.8	19.0	0.76	1.31	2.78	2.05

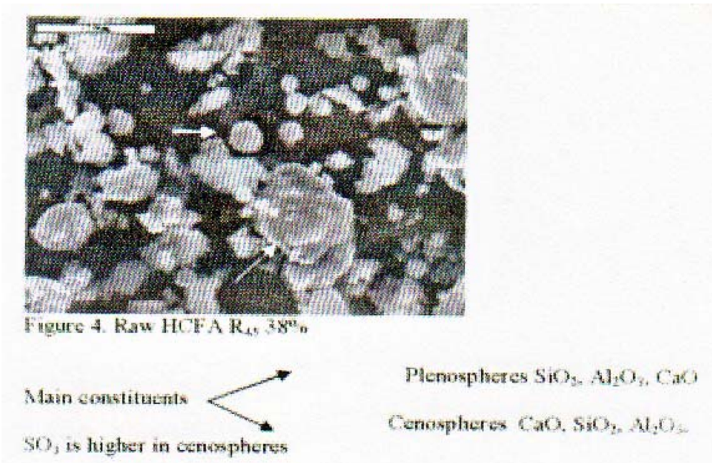

Fig.1 SEM picture of raw calcareous fly ash

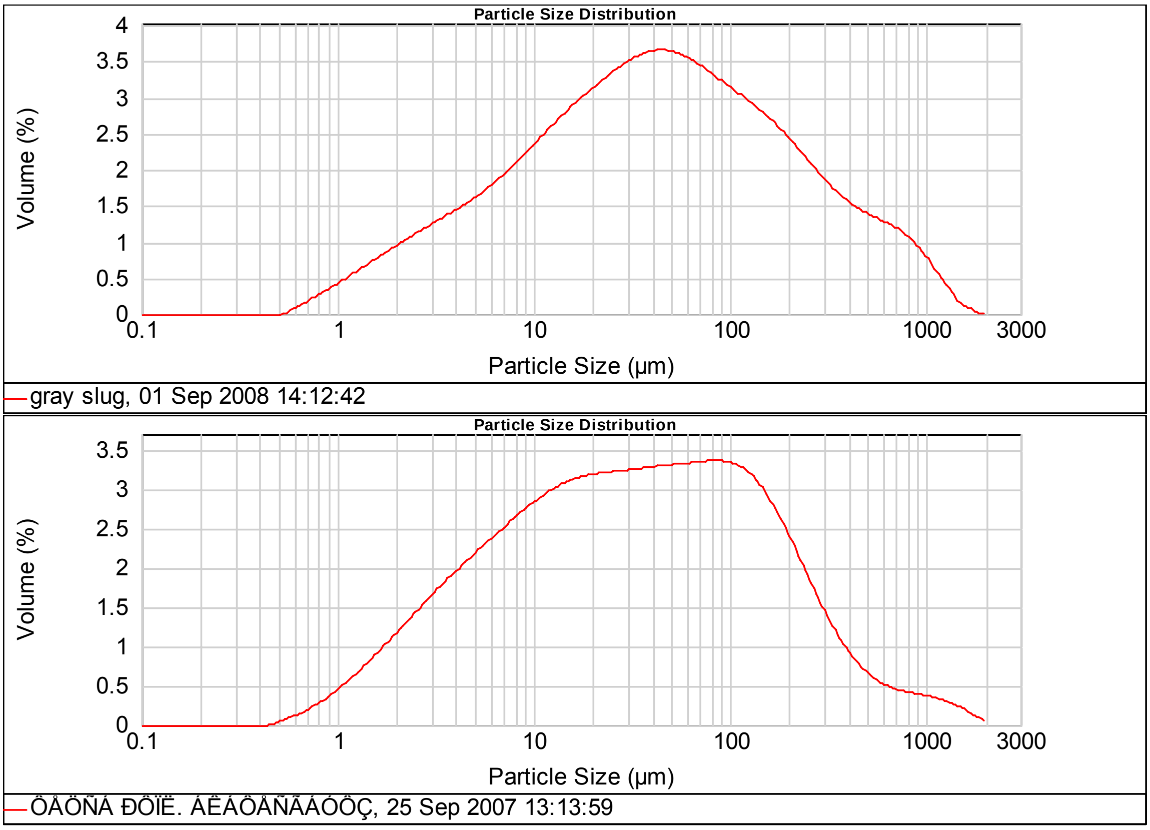

Fig.2 Particle size analyses of calcareous fly ashes

Furthermore, the early shrinkage deformations of the mortar mixtures without SPL(s) were monitored during their curing at 20 ºC and <65% relative humidity in order to see if higher water/cementitious ratios influence the shrinkage.

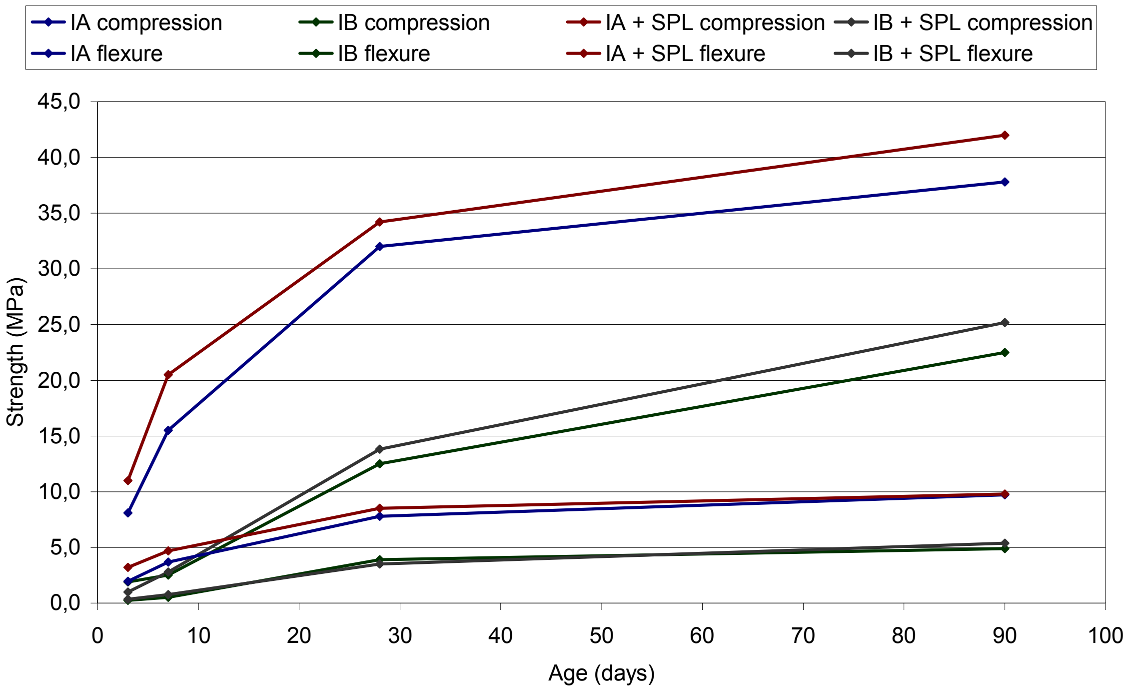

Fig.3 Strength development of calcareous fly ash Ptol I

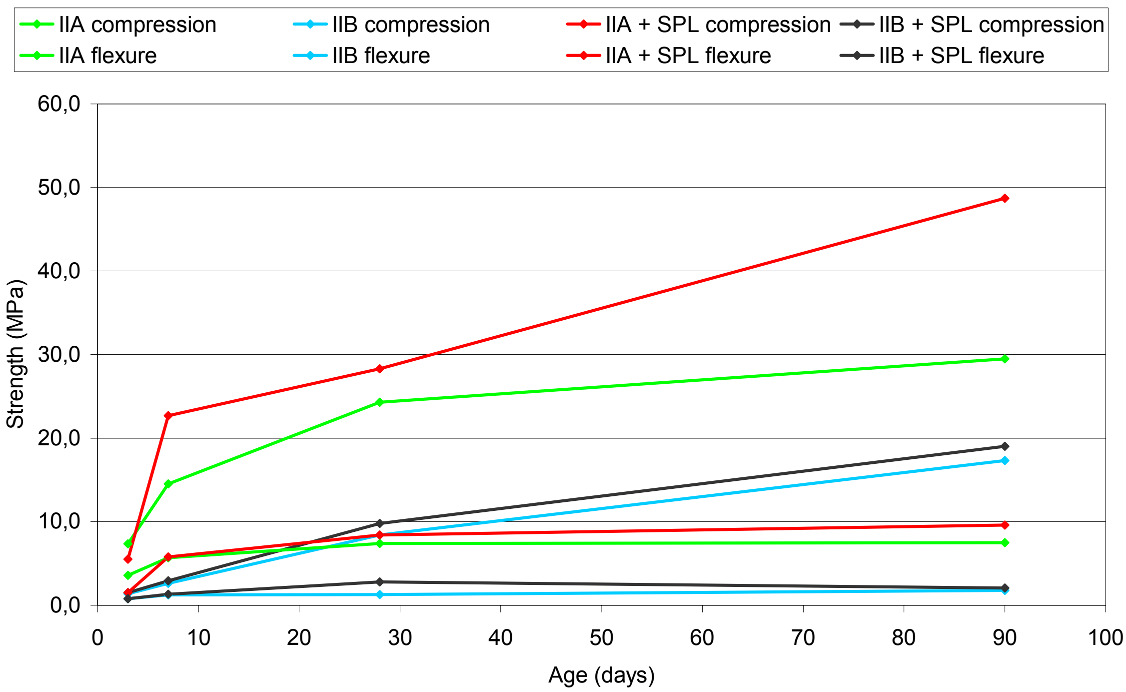

Fig.4 Strength development of calcareous fly ash Ptol II

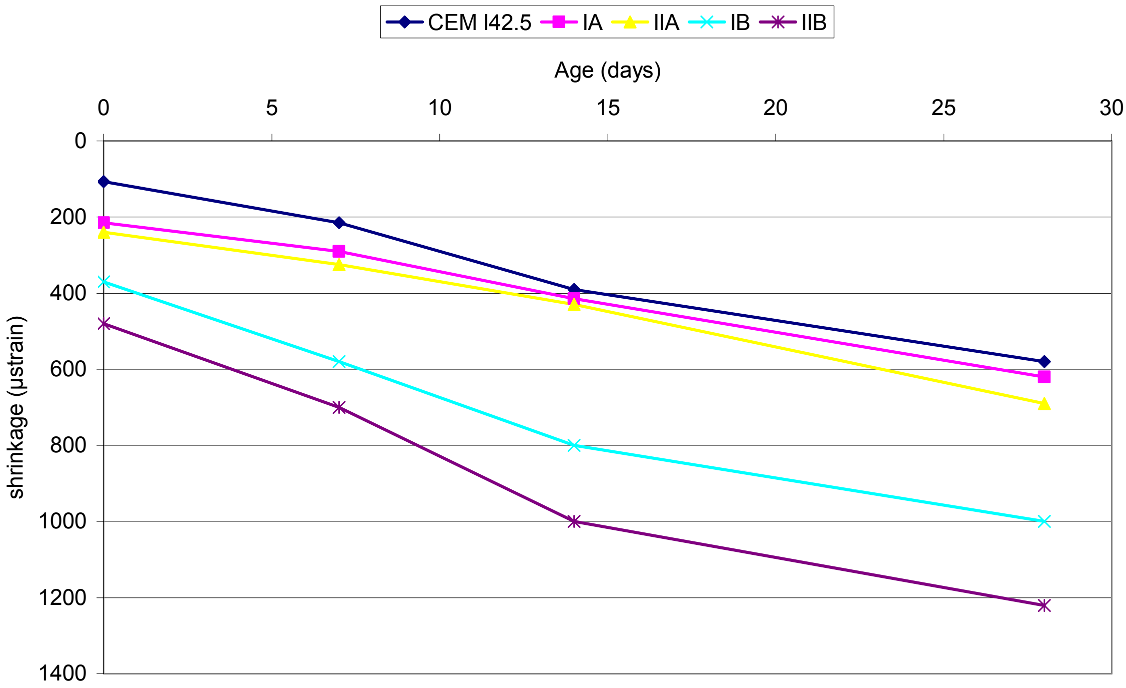

Fig.5 Early shrinkage of fly ash mortar prisms cured at 20˚C and RH < 65%

DISCUSSION OF THE RESULTS

Based on the results, it seems that fly ash Ptol I is richer in lime (total, available and free) as well as in sulfates in comparison with Ptol II which is of higher silica (total and reactive) content. The Ptol II has also higher content of alumina and magnesium oxide. The main mineral phases do not differ except for intensity of the peaks of x-ray diagrams. The fineness of the two fly ashes does not differ significantly. The finer is the Ptol II sample. The water demand for normal consistency paste is higher in the case of Ptol II. This was unexpected since the Ptol I sample has higher content of lime and sulfate. Setting time of fly ash pastes is longer than control cement paste, the longest one being that of Ptol II. As it has been shown by many researchers [5], ettringite is formed in high calcium and sulfate fly ashes, even after the first minutes from hydration. It could be said that this contributes to lower setting of Ptol I, compared to that of Ptol II sample.

The swelling of both fly ash samples is higher than 10 mm after 48 h in water, according to the Le Chatelier method, the highest being that of Ptol II. However, the values after boiling as well the values of dilation after autoclave curing are in the limits of requirements of relative standards. This implies that under conditions of high temperature some strength development is favored which resists the swelling tendency.

It is worth mentioning that the soundness values of the cement-fly ash combinations, do not present values above limits for both fly ashes, tested by Le Chatelier and autoclave methodology.

The pozzolanicity index is 0.91 of the control cement strength Ptol I and 0.81 respectively for Ptol II. The 7-d strength is also higher for the Ptol I and amounts the 0.86 of the corresponding cement strength. However, the rate of strength development from 7-d to 28-d is higher in the case of Ptol II sample. The strength development of fly ash mortars with lime is also higher in the case of Ptol I and above the required values using it as pozzolanic material with lime (ASTM C 593-95). Considering the results of the tests, it could be said that Ptol I fly ash with unacceptable values of free lime and sulfates developed higher strength with cement and with lime, while the rich in reactive silica Ptol II presents lower activation especially when early strength is considered. This unexpected behavior could be related with higher water/cementitious ratio of Ptol II paste and mortar for normal consistency that leads to lower strength mixtures. Of course the slight fineness of Ptol II does not explain this extra water needed. It is supposed that this is rather related to mineral phases, such calcium aluminates, which entrap water in their hydrated products [6].

Regarding the strength development of fly ash mortars and cement/fly ash mixtures, it could be said that the plain Ptol I fly ash develops the 24% and 38% of the 28-d and 90-d strength of the control cement mixture, while the Ptol II fly ash the 16.5% and 29% of the corresponding strengths of the control mortar mixture. In the case of Ptol I fly ash the water/binder ratio was 0.589, while for Ptol II fly ash this ratio amounted 0.667. Shrinkage deformations up to 28-d age are also higher for Ptol II mortar mixtures. When superplasticizers (SPL) were used for achieving the required consistency without changing the water/binder ratio, 0.5, the modified with SPL fly ash mortars exhibited considerably higher strength and reached the 43% and 29% of the 90-d strength of the control mixture for Ptol I and Ptol II, respectively. Earlier strengths were also improved.

The cement/fly ash mortar mixtures seem to have been stabilized. They exhibit lower shrinkage deformations (Fig 5) and higher level of strength ranged from 71% (Ptol I) up to 82% (Ptol II) of the 90-d strength of the control cement mortar. These strength values of 42-48.7 MPa, when 50% of cement mass is replaced by these fly ashes, are very positive for the exploitation of calcareous fly ashes. The shrinkage deformation of the cement/fly ash mortar mixtures does not differ much from the control cement mortar.

CONCLUSIONS

The prediction of the behavior of calcareous fly ashes based on their chemical composition does not represent their reactivity in mortar mixtures. The high lime and sulfate content does not necessary lead to high water demand and soundness problems. On the contrary, it contributes to early strength development in comparison with rich in silica calcareous fly ashes.

The combination of cement to a calcareous fly ash system seems to stabilize it by eliminating deformations and increasing strength. The water/binder ratio of mortar mixtures seems to be an essential parameter for strength development and early deformations. The lower the ratio, the higher the strength of mortar. Modified with SPL fly ash or cement/fly ash mortars exhibit remarkable strength level, such as 42-49 MPa at 90-days.

It seems that it is more realistic and effective to use the real combination of cement/fly ash mixture, decided for a predetermined strength level at a certain age, in order to test the suitability of calcareous fly ashes.

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