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High Volume of Calcareous Fly Ash for the Production of a Hydraulic Binder for Road Pavements

C. Charalampidou[1], M. Chaniotakis[2], I. Papayianni[1], S. Tsimas[3]

[1] *Laboratory of Building Materials, Civil Engineers Department, Aristotle University of Thessaloniki*
[2]*Titan Cement S.A.,*
[3]*Laboratory of Inorganic and Analytical Chemistry, Chemical Engineers Department, National Technical University of Athens*

Abstract

The construction of road pavement with concrete seems very advantageous from technical point of view especially for heavy load transportations. However, the use of concrete pavement often results in higher initial cost in comparison to asphalt one though the service life of concrete road is generally longer.

The development of a commercial low cost hydraulic binder of adequate strength capacity will contribute to the reduction of the initial cost of concrete pavement.

In the paper, an effort in this direction is described. Fly ashes of different compositions in terms of free lime and sulfate content are blended at laboratory with clinker and other mineral admixtures so as in the mixed systems the fly ash to be at least 50% and the clinker 20%. Limestone filler and natural local pozzolana were used as additions. A series of mixes produced at a laboratory mill were tested to find the optimum blending for required mortar 28-d strength of 40MPa. Apart from strength development the volume stability was also measured. Remarks concerning the grindability of the fly ash are made as well as comments about the relationship of fly ash composition and strength results. Although, the capacity of existing laboratory mill was limited and did not correspond to the real blended potential of the constituents, it seems that by achieving a fineness R45 value of 2-10% a 28-d strength level of 40 ± 2 MPa was obtained in mixes where 60% of clinker was replaced by calcareous fly ash. These strength values were obtained even though the water demand was greater compared to that of the control mixture. For mixed systems in which 70% clinker was replaced, this strength level was achieved at 90 days. In mixtures where 80% of clinker was replaced by calcareous fly ash a strength level of 30 ± 2 MPa was developed at 90 days. Net fly ashes mixes of R45 2-5% showed a 28-d strength of 10-20 MPa. Based on this research, the production of a high volume fly ash hydraulic binder seems feasible and a new field of exploitation of calcareous fly ash is opened.

Keywords: high volume fly ash hydraulic binder, calcareous fly ash, cement, clinker, pozzolana, limestone

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Introduction

The production of high volume fly ash concrete for pavements is a common fact in USA and North Europe. However, the relatively higher initial cost in comparison to asphaltic pavement inhibited the wide use of it. Therefore, the production of a low-cost, mixed type, effective hydraulic binder opens new perspectives for concrete road pavements. Fly ashes from Hellenic Energy plants are mainly high calcium and only 10% of 12Mt annual production is used in cement

production [1]. Furthermore exploitation of these by-products will develop if the following fly ash's properties such as high free lime content, high sulfate content, chemical / fineness variety and the need for supplementary grinding, are capably managed. The introduction of high volume fly ash in blended cement for the production of an economical quality controlled hydraulic binder for pavements is the scope of the following primary study. Blended cements incorporating high volume fly ash are considered comparable to high-volumes of fly ash that are added in concrete batch plants [2].
Previous research work [3] about blending clinker and fly ash has shown even from 90's that the fly ash contributes to strength development in higher percentages than those often added in the case of siliceous fly ashes.

Experimental

Scope

The scope of the laboratory experiments of co-grinding (Portland clinker with fly ash with other addition) was to produce hydraulic binders of adequate strength. The goal was to achieve 28-d strength values of 40±2 MPa by co-grinding mainly fly ash and clinker. Also small amounts of limestone and pozzolana were used.
Four different fly ashes from 2 different electrical stations were tested. Firstly blind samples were produced of 100% clinker (clinker+gypsum) and 100% fly ash. Secondly clinker was partially replaced mainly by fly ash and further by limestone and pozzolana. The fly ash was at least 50 % at all mixtures and the clinker was reduced till 20%.

Constituents

The main idea was to produce a cost effective high volume fly ash binder. The constituents that were used are listed in Table 1. Clinker was produced by TITAN industry by burning high sulfate pet coke on July 2011. The origin of gypsum was Crete's quarry called Altsi. Pozzolana and very pure limestone filler came from North Greece quarries not far away from Thessaloniki's plant. Four types of fly ash were provided by two different energy production plants, Agios Dimitrios and Aminteo at Florina. Clinker, gypsum, pozzolana and limestone were dehydrated (except from clinker), crushed very fine and homogenized prior to their use. Triethanolamine was used at all mixtures as grinding agent.

The hydraulic binders were produced at a small scale laboratory ball mill. The physicochemical analysis of the constituents used is presented in Table 1:

Table 1: Physicochemical properties of main constituents for manufacturing the hydraulic binder

	Loss on ignition %	Insoluble Residue %	SO_3 %	Fineness +R45μm %	Free Lime %
Clinker	0,01	0,01	1,47		
Gypsum	21,26	0,46	44,52		
Limestone	44,47				
Pozzolana (Reactive silica 30,78%)	6,04	81,58			
Fly Ash AD1	2,94	19,14	6,81	36,5	13,0
Fly Ash F	1,15	30,36	4,14	42,3	2,4
Fly Ash AD2	1,29	32,74	4,95	45,0	6,5
Fly Ash AD3	5,3	20,89	6,49	30,4	10,0

Fly ashes from Agios Dimitrios were selected to have variable sulfate content. As you can see in Table 1, it seems that fly ash's free lime values follow the increase of the sulfate content and vice versa [1] [4]. For example fly ash F has the lower free lime content of 2,4% and the lower sulfate content of 4,14%. Respectively fly ash AD1 has the higher free lime of 13% and the higher sulfate content of 6,81%.

Hydraulic binder Compositions

In Table 2 all the different fly ash cement compositions are presented. First the binary compositions were tested containing fly ash and clinker. Then 10 and 20% of limestone was introduced in the binary fly ash – clinker mixture. Finally quaternary mixtures were produced which were expected to render concretes of higher durability comparing to those of binary mixtures [5].

Table 2: Hydraulic binders composition

	Clinker %	Fly Ash %	Limestone %	Pozzolana %
Control Cement CEM I32,5N	100	0	0	0
Fly Ash Cement	0	100	0	0
	20	80	0	0
	30	70	0	0
	40	60	0	0
Fly Ash Cement with limestone	30	60	10	0
	20	60	20	0
Fly Ash Cement with limestone and pozzolana	25	50	20	5
	20	50	20	10

The compressive strength target of all the mixtures produced was 40±2 MPa after 28-d moist curing. In order to achieve the desirable target, different combinations of grinding time and batch quantity were evaluated for each mixture. After many trials for reaching the prescribed blaine value, prismatic test specimens were produced accordant to EN 196-1, conditioned for 28 days and tested for compressive strength. If the developing value was not between 38 to 42 MPa, this certain composition was reproduced but aiming at a different blaine value.

Control Mixture CEM I 32,5N

The control mixture CEM I32,5N was produced by clinker and gypsum only in order to compare the physicochemical differentiation by adding fly ash. Three control mixtures of different blaine were tested as presented in Table 3. The same composition was used for all three mixtures.

First the control mixture C_B was produced and tested. The compressive strength value was 45,7 MPa higher than the target, so the grinding time was reduced to 25 minutes. Also the quantity was reduced from 7 Kg to 5 Kg to avoid ungrindable material because of the low grinding time. The produced control mixture C_A had 38,2 MPa at 28-d exactly in the desired target area. Finally the higher blaine control mixture C_C achieved 51,9MPa strength with 29,5% water demand. The 1,5% water demand increase following the 1200 blaine rise from 2400 cm^2/g (C_A mixture) to 3566 cm^2/g (C_B mixture) is not considered important valuating the high 13,7MPa increase of 28-d strength.

The initial setting time is almost the same for the two mixtures C_A and C_B, 190 and 200 min respectively which was expected because they had the same sulfate content. Mixture C_C has lower initial setting time - 170min- which is in contradiction to the slightly higher sulfate content of 2,49%.

The 7 to 28-d strength ratio shows that the strength step is the same for all mixtures.

Table 3: Physicochemical and Mechanical properties of control mixtures CEMI32,5N

	Control Mixtures	C_A	C_B	C_C
	Quantity Kg	5	10	10
	Grinding time min	25	45	75
Physical properties (EN 196-6)	Blaine cm²/g	2400	3000	3566
	Fineness +R45μm %	14,7	5,7	1,5
Chemical properties (EN196-2)	Loss on ignition %	1,0	1,1	1,2
	Insoluble Residue %	0,08	0,10	0,08
	SO_3 %	2,21	2,35	2,49
	Free Lime %	1,2	1,4	1,4
Mortar Testing (EN 196-3)	% Water	28,0	29,0	29,5
	Initial setting time min	190	200	170
	Soundness mm	0,0	1,0	1,0
Compressive strength (EN196-1) Expressed as MPa	At 1 day		17,2	21,9
	At 2 days	20,7	24,5	30,9
	At 7 days	29,7	36,5	42,8
	At 28 days	38,2	45,7	51,9
	At 90 days	47,3	52,5	54,7
7days/ 28days compressive strength ratio %		82,5	79,9	82,5

As you can see in Fig.1 at mixture C_A, the strength development follows the same pattern and with almost the same strength steps at all ages. At mixture C_B and C_C the step strength of 2 to 7 days increases to 12MPa from 9MPa. The 2-d strength is climbing from 20,7MPa (C_A) to 24,5MPa (C_B) and finally at 30,9MPa (C_C). The 28 to 90 days step strength is decreasing from 9,1 MPa at C_A mixture to 2,8 MPa at C_C mixture. It seems that at the higher blaine mixture a "plateau" is reached for the clinker strength potential. At higher blaine values, it's obvious that strength potential is appearing at younger ages.

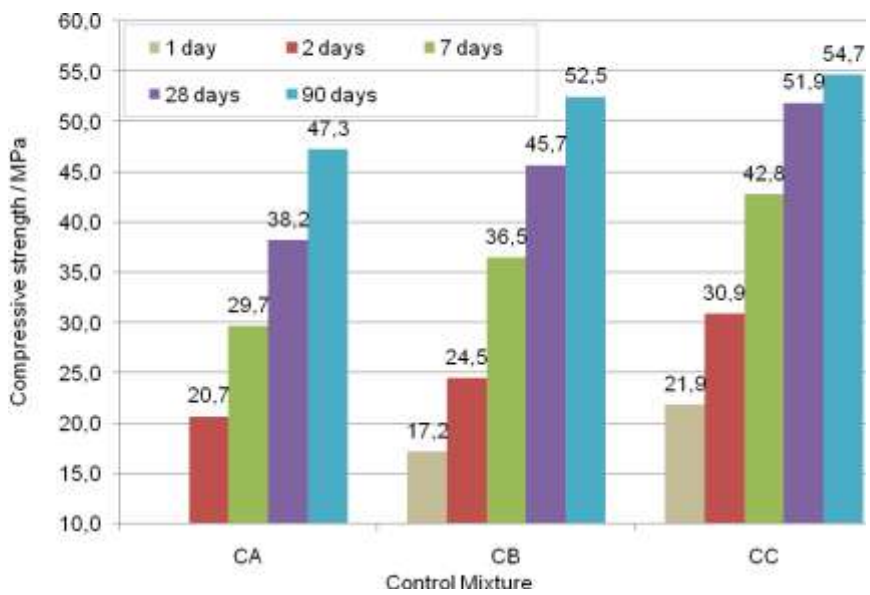

Fig.1: Strength development of control mixtures CEMI32,5N

High fly ash - clinker mixtures

60% fly ash mixture

Due to the high sulfate content of fly ash, gypsum was not added to the clinker-fly ash mixtures. All the results concerning the 60% fly ash-40% clinker mixtures are shown in Table 4. Two different mixtures are presented for each F and AD1 fly ashes and also one mixture for AD2 fly ash and one for AD3 fly ash. The second $AD1_B$ mixture was produced for the verification of $AD1_A$ soundness results.

The AD fly ashes were ground with difficulty because they had adhering problems. It was noticed that the higher was the free lime content the bigger were the grinding problems. A very good parameter to evaluate the material agglomeration is the fineness +R45μm. Fly Ash $AD1_A$ and $AD1_B$ mixture with the higher free lime had soft agglomerates in the bulk which were easy to break by hand. This is obvious from the high fineness of near 10%. F fly ash with free lime of 2,4% showed much better grinding behaviour with high blaine values and low fineness<2,0 %. As you can see comparing the fineness data in Table 4, mixture AD3 had 16,2% fineness and 6300 blaine after 40 min grinding time. It was so sticky that it was difficult to empty the mill. This was caused primary from the low initial fly ash fineness of 30,4 % and secondly from the high mixture free lime of 6,1%. Only AD2 fly ash of AD fly ashes with the higher initial fineness of 45,0% and the lower 6,5% free lime was managable and gave strength and soundness results between limits.

Table 4: Physicochemical and Mechanical properties of 60% Fly Ash – 40% Clinker Mixtures

	Fly Ash $_{Batch\ No}$	F_A	F_B	$AD1_A$	$AD1_B$	AD2	AD3
	Quantity Kg	10	5	10	10	5	7
	Grinding time min	75	90	100	60	30	40
Physical properties (EN 196-6)	Blaine cm²/g	4400	5063	4460	4453	4770	6300
	Fineness +R45μm %	1,4	2,0	8,4	9,5	5,0	16,2
Chemical properties (EN196-2)	Loss on ignition %	0,9	0,9	1,6	1,7	1,2	3,2
	Insoluble residue %	18,43	19,16	11,66	12,04	19,21	13,55
	SO_3 %	2,96	2,89	4,54	4,74	3,64	4,55
	Free lime %	2,6	2,5	7,8	8,4	3,9	6,1
Mortar testing (EN 196-3)	% water	31,0	29,5	(32,0)	(31,5)	32,0	(37,0)
	Initial setting time min	190	270	(150)	(165)	230	(180)
	Soundness mm	1,0	0,0	(15,0)	(24,0*)	3,0	(4,0)
Compressive strength (EN196-1) expressed as MPa	At 1 day	10,9		8,6		6,8	8,8
	At 2 days	17,5	15,9	17,0	9,7	15,9	17,7
	At 7 days	24,4	24,3	31,8	23,2	25,6	29,9
	At 28 days	38,5	39,0	48,5	40,7	38,9	44,6
	At 90 days	51,2	46,0	55,9	52,5	47,7	50,6
7days/ 28days compressive strength ratio %		63,4	62,3	(65,6)	(57,0)	65,8	(67,0)

* Le Chatelier rings were above boiling water.

Comparing the grinding time of all mixtures, F Fly ash mixtures needed more time in order to achieve the same strength level. For example AD2 fly ash mixture needed just 30 min grinding time to reach 28-d strength of 38,9 MPa. In the contrary F fly ash needed over one hour grinding to reach 38,5 MPa.

The 7-d early strength of the acceptable mixtures of F_A,F_B and AD2 fly ashes were lower than the one of the control mixture C_A. It is obvious also from the decrease of the 7-d to 28-d ratio from over 80% to 63-65%.

All mixtures had higher water demands for standard consistence compared to control mixture C_A. The C_A mixture had 28,0 % water demand when all fly ash mixtures except AD3 mixture, varied between 29,5 to 32,0%. The F_B Fly ash mixture had the lower water demand of 29,5%. The 37% water demand of AD3 mixture was justified by the 6300 blaine value.

The high free lime of AD fly ashes caused expansion which was measured by soundness mortar test. In the case of AD1 fly ash, the raw material with 13% free lime gave soundness outside permisible limits of 10mm. The $AD1_A$ gave 15mm soundness result and the $AD1_B$ 24mm soundness although the Le Chatelier rings were not immersed in boiling water but were placed above boiling water. The AD2 and AD3 mixtures gave soundness results between limits.

It is worth noting that the high free lime content of the fly ash results in high 28-d strength values. In Table 4, the 28-d strength values for AD1 mixtures are high 48,5 and 40,7 MPa. In the case of AD3 mixture the 44,6 MPa 28-d strength due to high blaine value which occurred from the low net fineness of fly ash. The F and AD2 mixtures presented strength of the desirable target.

The Control mixture had 2,2% of sulfate content and initial setting time of 190min. The sulfate content of the F mixtures was 2,96-2,89 lower than the AD_2 mixture 3,64 but higher than the control mixture C_A. It seems that the lower F sulfate content acts as set retarding agent more than AD2 sulfate content because it keeps at the same level as AD2 mixture the initial setting time.

<u>70% fly ash mixture</u>

In Table 5 the best performing mixtures are presented. All the 70% fly ash mixtures did not manage to reach the desirable 28-d strength of 40±2 MPa although $AD2_B$ mixture was close to target strength with a value of 37,5 MPa . On the contrary the 90-d strength values was 40 MPa for the F_B mixture and even higher for the $AD2_B$ mixture with a value of 44,7 MPa.

The F_A fly ash mixture was produced using 90 minutes grinding time. The specified blaine target could not be reached and so a new production of F_B fly ash mixture with half quantity was made. Even thought the blaine was high enough, the 28-d strength was 31,3MPa.

The $AD2_A$ mixture was produced at a 30 minutes grinding cycle and even though had lower blaine by 1000 points, it reached the same as previous 28-d strength. A new batch aiming at a higher blaine but with a slightly different production procedure led to the $AD2_B$ mixture. The mixture had a small amount of soft agglomerates which make difficult to evaluate the mortar tests results. In the case of compressive strength where the specimens are produced with a constant water/dry mixture ratio and conditioned under water, it is quite safe to assume that especially the 28-d and 90-d results are reliable. As a result the 28-d strength was 37,5MPa.

The $AD2_A$ fly ash mixture had higher water demand at 33,0% compared to F mixtures which were between 30 and 31,5 %.

Table 5: Physicochemical and Mechanical properties of 70% Fly Ash Mixture

	Fly Ash Batch No	F_A	F_B	$AD2_A$	$AD2_B$
	Quantity Kg	10	5	5	7
	Grinding time min	90	75	30	101
Physical properties (EN 196-6)	Blaine cm²/g	4629	6038	5089	5794
	Fineness +R45μm %	3,3	2,0	4,8	6,9
Chemical properties (EN196-2)	Loss on ignition %	1,1	1,0	1,3	1,4
	Insoluble residue %	22,0	21,04	23,85	19,47
	SO_3 %	3,24	3,11	4,03	3,66
	Free lime %	1,5	2,6	5,2	
Mortar testing (EN 196-3)	% water	31,5	30,0	33,0	(34,0)
	Initial setting time min	320	200	185	(120)
	Soundness mm	2,0	0,0	6,0	(7,0)
Compressive strength (EN196-1) expressed as MPa	At 1 day	3,3		4,2	14,5
	At 2 days	8,5	11,5	9,4	19,0
	At 7 days	15,1	20,1	20,4	26,0
	At 28 days	26,8	31,3	31,5	37,5
	At 90 days	37,3	40,0	37,4	44,7
7days/ 28days compressive strength ratio %		56,3	64,2	64,8	69,3

It can be mentioned that the initial setting time levels of F fly ash mixtures are higher than the $AD2_A$ fly ash mixture even thought the sulfate content is 1% higher. It seems again as in 60% fly ash mixtures that the lower F sulfate content acts as set retarding agent more than AD2 fly ash sulfate content because it keeps at a higher level (320-200 min) the initial setting time than the AD2 mixture (185min).

The soundness results were between limits but a little higher from the 60% mixtures which was expected because of the higher mixture free lime..

<u>80% fly ash mixture</u>
At the 80% fly ash mixtures it seems that the strength potential of the AD2 fly ash mixture is better than the F fly ash mixtures comparing the 28-d strength.

The excess 150 min grinding time of the F_B mixture produced hard agglomerates which is obvious from the 10,5% +R45μm. Even thought the strength raised from 17,8 MPa to 23,6 MPa, it could not reach the value of 27,5 MPa of the AD2 mixture. The ratio 7-d to 28-d strength is pretty much at the same level for all mixtures (61,8-62,3%), but a little lower than the 70% mixtures (64,2-69,3).

When 90-d strength is compared, it is obvious that the F_B mixture had reached 33,9 MPa overcoming the 90-d strength of AD2 mixture.

The initial setting time result because of the agglomerated material it cannot be evaluated. For the rest results it seems again as in previous fly ash mixtures that the lower F_A sulfate content (3,58%) acts as set retarding agent more than AD2 sulfate content (4,38%) because it the AD2 mixture has lower (235 min) initial time than the F_A mixture (330 min).

There was no expansion according to the soundness test.

Table 6: Physicochemical and Mechanical properties of 80% Fly Ash Mixtures

	Fly Ash $_{\text{Batch No}}$	F_A	F_B	AD2
	Quantity Kg	10	5	5
	Grinding time min	60	150	40
Physical properties (EN 196-6)	Blaine cm²/g	4700	5960	5643
	Fineness +R45μm %	2,7	10,5	3,2
Chemical properties (EN196-2)	Loss on ignition %	0,8	1,3	1,7
	Insoluble residue %	23,56	24,51	26,45
	SO_3 %	3,58	3,32	4,38
	Free lime %	2,9	2,7	5,5
Mortar testing (EN 196-3)	% water	31,5	(32,0)	35,4
	Initial setting time min	330	(155)	235
	Soundness mm	0,0	1,0	1,0
Compressive strength (EN196-1) expressed as MPa	At 1 day		5,0	3,2
	At 2 days	4,1	7,8	5,6
	At 7 days	11,0	14,7	16,8
	At 28 days	17,8	23,6	27,5
	At 90 days	24,4	33,9	31,6
7days/ 28days compressive strength ratio %		61,8	62,3	61,6

In Fig. 2 and Fig.3 all the binary mixtures are presented in comparison to the control mixture C_A. In Fig. 2 all the AD2 fly ash mixtures and in Fig.3 all the F fly ash mixtures.

It is obvious that 80% substitution of clinker has a detrimental effect on strength development. The 70% mixture with fly ash AD2 has pretty much the same performance as C_A but with lower early strengths. The 60% substitution of clinker is performing very well at late ages but with a slight decrease of early strengths. In the case of F fly ash (Fig.3) only the 60% substitution had equivalent to the control mixture late age strength development.

Strength development of high volume fly ash/clinker mixtures compared to control mixture C_A

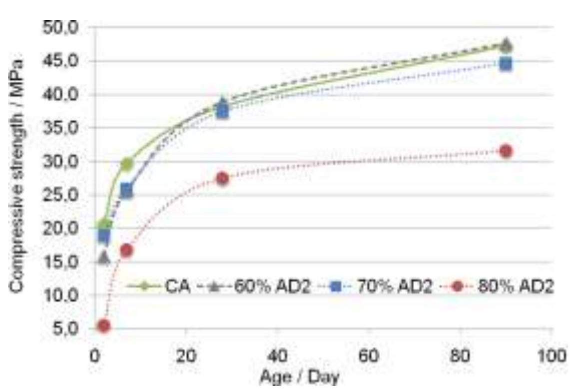

Fig. 2: AD2 fly ash

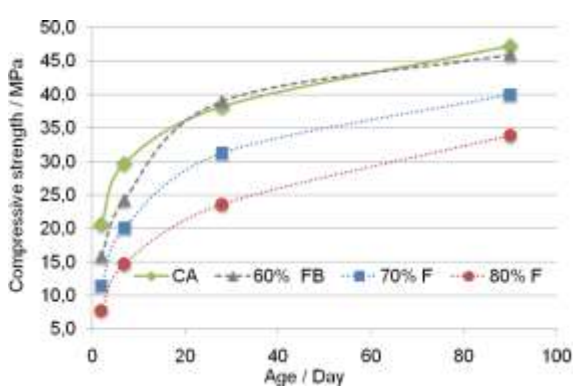

Fig. 3: F fly ash

Net fly ash mixtures

For the following mixtures the procedure of Calcareous fly ashes of EN 197-1, paragraph 5.2.4.3 was implemented but without keeping fineness at the prescribed range (10<F<30). The grinding time was set at 60 min for all fly ashes in order to check the strength potential at the same grinding time.

As presented in Table 7 fly ash AD2 exhibited 28-d strength at 19,3 MPa. The adhering fly ash AD3 was ground with great difficulty and triple time than usual needed to empty the mill. The fineness was 23% but the 28-d strength was 11,5 MPa > 10MPa.

Table 7: Physicochemical and Mechanical properties of 100% Fly Ash Mixtures

	Fly Ash	F	AD2	AD3
	Quantity Kg	10	5	5
	Grinding time min	60	60	60
Physical properties (EN 196-6)	Blaine cm²/g	4987	6356	
	Fineness +R45μm %	2,5	4,7	23,5
Chemical properties (EN196-2)	Loss on ignition %	1,1	1,7	5,3
	Insoluble residue %	28,16	31,46	20,89
	SO_3 %	3,97	4,91	6,49
	Free lime %	2,4	6,5	10,0
Mortar testing (EN 196-3)	% water	29,5	28,5	29,0
	Soundness mm	2,0	1,0	2,0
Compressive strength (EN196-1) expressed as MPa	At 7 days	6,4	11,2	8,1
	At 28 days	11,2	19,3	11,5

Fly Ash - Clinker Mixtures with limestone

Fly ash F and AD2 were used to produce the three constituents' mixture. The 60% substitution of fly ash was selected as the best performing of the previous binary mixtures. The presented mixtures had 60% of fly ash, 10-20% of limestone and the rest was clinker (20-30%).

The introduction of easy to grind limestone in the mixture caused the appearance of extremely hard agglomerates in the case of F_{10} fly ash mixture (60% F fly ash – 30% clinker and 10% of limestone) and $AD2_{20}$ fly ash mixture (60% AD2 fly ash – 20% clinker and 20% of limestone). It is considered that the strength results at late ages are reliable.

For the production of F_{20} a slightly change in the grinding procedure was used and no agglomerates appeared after 102 min grinding time. In the case of $AD2_{10}$ mixture the 40 min grinding time with the regular procedure did not show the presence of agglomerates.

From all the mixtures only the F_{10} could reach the desired target. In the case of $AD2_{10}$, 28-d strength of 35,2MPa was developed which reached 44MPa at 90 days. The mixtures with 20% limestone indicated much lower strength than that of control C_A mixture.

The 7d/28d ratio fell from 63% (binary 60% F fly ash mixture) to 60,7% (60% F fly ash mixture with 10% limestone) and at 54,8% (60% F fly ash mixture with 20% limestone). In the case of AD2 fly ash, the 7d/28d ratio fell rapidly from 65,8% (binary 60% AD2 fly ash mixture) to 50,9% (60% AD2 fly ash mixture with 10% limestone) and at 45,5% (60% AD2 fly ash mixture with 20% limestone). This decrease follows the clinker decrease from 40% to 20% finally, which clinker is the one to give early strength to the mixture.

The water demand was a little bit lower than the 60% binary mixture and the initial setting time stayed at the same level.

Table 8: Physicochemical and Mechanical properties of 60% Fly Ash Mixtures
with 10-20% limestone and clinker 20-30%

	Fly Ash % limestone	F_{10}	F_{20}	$AD2_{10}$	$AD2_{20}$
	Quantity Kg	5	7	5	5
	Grinding time min	120	102	40	60
Physical properties (EN 196-6)	Blaine cm²/g	5276	5314	5796	6196
	Fineness +R45μm %	13,3	10,6	6,2	16,1
Chemical properties (EN196-2)	Loss on ignition %	5,2	9,5	5,5	9,7
	Insoluble residue %	18,15	13,78	19,45	19,66
	SO_3 %	2,72	2,87	3,41	3,35
	Free lime %	2,2	2,2	3,4	4,1
Mortar testing (EN 196-3)	% water	(31,5)	29,0	30,5	(32,0)
	Initial setting time min	(120)	235	250	(240)
	Soundness mm	(1,0)	0,0	2,0	(6,0)
Compressive strength (EN196-1) expressed as MPa	At 1 day	7,1	3,4		1,8
	At 2 days	11,9	6,8	11,5	4,3
	At 7 days	23,9	14,9	17,9	12,2
	At 28 days	39,4	27,2	35,2	26,8
	At 90 days	47,0	36,1	44,4	32,9
7days/ 28days compressive strength ratio %		60,7	54,8	50,9	45,5

In Fig. 4 and Fig.5 all the binary and three constituents' mixtures with 60% of fly ash are presented in comparison to the control mixture C_A. In Fig. 2 all the AD2 fly ash mixtures and in Fig.3 all the F fly ash mixtures.

It is obvious the introduction of 20% limestone led to lower early and consequently lower late strengths. The 60% F mixture with 10% limestone has excellent late strength development which is not the same for AD2 fly ash mixture. That may give a sign of better cooperation between F fly ash and limestone.

Strength development of high fly ash /clinker mixtures
with or without limestone compared to control mixture C_A

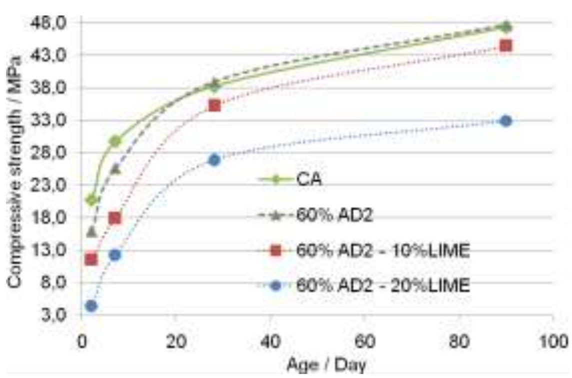

Fig. 4: AD2 fly ash

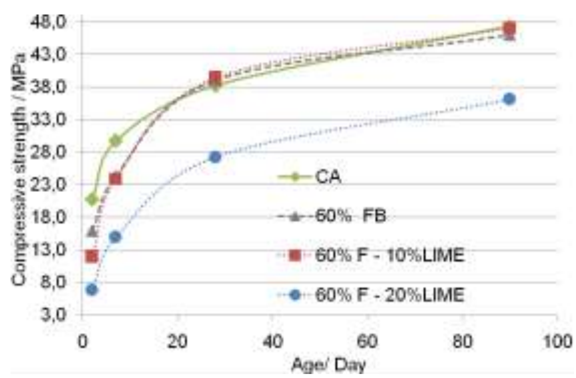

Fig. 5: F fly ash

Fly Ash - Clinker Mixtures with 20% limestone and pozzolana

At the following quaternary mixtures in Table 9, the fly ash content was 50%, the limestone 20% and 5%-10% pozzolana was introduced keeping the clinker between 25-20%. There was a agglomeration in the case of $AD2_{10}$ (50% of AD2 fly ash, 20% limestone, 10% pozzolana, 20% clinker) mixture which was not possible to make a proper mortar to safely determine the water of standard consistency, and therefore the determination of the initial setting time and soundness.

Table 9: Physicochemical and Mechanical properties of 50% Fly Ash Mixtures with 20% limestone, pozzolana 5-10%, and clinker 20-25%

	Fly Ash $_{\%pozzolan}$	$AD2_5$	$AD2_{10}$	F_{10}
	Quantity Kg	5	7	7
	Grinding time min	60	117	115
Physical properties (EN 196-6)	Blaine cm²/g	6312	7026	6685
	Fineness +R45μm %	8,9	10,4	7,0
Chemical properties (EN196-2)	Loss on ignition %	9,7	10,0	10,2
	Insoluble residue %	19,31	24,40	22,19
	SO_3 %	2,87	2,64	2,24
	Free lime %	3,6	3,6	
Mortar testing (EN 196-3)	% water	31,0	(33,5)	30,0
	Initial setting time min	215	(120)	195
	Soundness mm	1,0	(2,0)	0,0
Compressive strength (EN196-1) expressed as MPa	At 1 day	5,9	6,7	5,5
	At 2 days	9,5	9,6	8,3
	At 7 days	17,7	17,1	15,3
	At 28 days	29,4	28,9	26,2
	At 90 days	39,2	34,0	35,9
7days/ 28days compressive strength ratio %		60,2	59,2	58,4

The AD2 mixture with 5% pozzolana ($AD2_5$) developed 29,4MPa. The same strength was developed by the AD2 mixture with 10% pozzolana ($AD2_{10}$) with higher blaine (+700 cm²/g). The F mixture with 10% pozzolana (F_{10}) developed 26,2 MPa, lower than the AD2 mixtures.

The $AD2_{10}$ mixture developed 34,0 MPa strength at 90-d with high water demand (33,5%). The F fly ash mixture (F_{10}) water demand thought was kept low at 30%.

The F_{10} mixture had initial setting time 195 min with sulfate content of 2,24% exactly the same with the control mixture C_A. The $AD2_5$ mixture had initial setting time 215 min, a little higher but with higher sulfate content of 2,87%. Here also is obvious that F fly ash has “active” sulfate content

Strength development of high fly ash/clinker mixtures with or without limestone and pozzolana compared to control mixture C_A

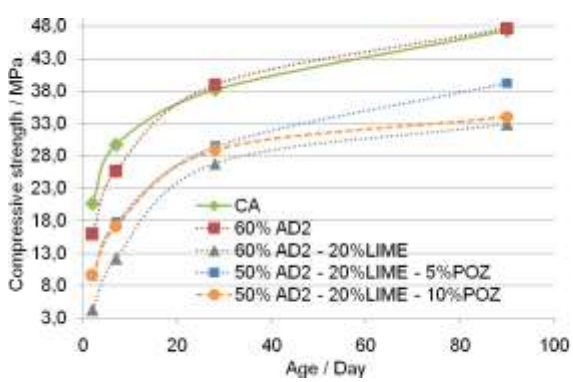

Fig.6: AD2 fly ash

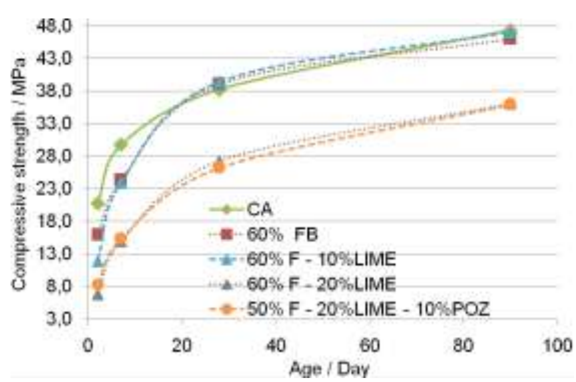

Fig.7: F fly ash

In Figure 6 and 7, all 60% and 50% fly ash mixtures are presented compared to the control mixture C_A. In Fig.6 all the AD2 fly ash mixtures and in Fig.7 all the F fly ash mixtures.

In quaternary mixtures of AD2 fly ash (Fig.6) the addition of pozzolana 5 and 10% seems to increase the 28-d and 90-d strength in comparison with those of AD2-20% limestone.

This improvement is not the same for the F fly ash in Fig.7.

Discussion

The scope of this primary study was to use different in composition Greek fly ashes and co-grind each of them with other constituents in order to produce high volume fly ash binders and evaluate their strength and expansion properties. Four different fly ashes were tested from two different electric plant stations.

Fly ash AD1 had the highest free lime (13%) and sulfate content (6,81%) which was not in consistence with the technical specification of Greek Fly Ashes [6] or the EN 13282 for Hydraulic Road Binders [7]. Although the expansion measured as soundness was out of the allowed limits, the 60 % Fly ash mixture gave high strength values. Because of the expansion problems this fly ash was excluded from further testing.

Fly ash AD3 had free lime near 10% and loss on ignition slightly over 5% (limit of technical specification of Greek Fly Ashes). Due to these properties and the low net fineness it was extremely adhering and impossible to grind. Apart of the grinding problems the late strength results for the 60% mixture were high, the soundness between limits and the water demand at 37% cause of high blaine value. Because of the grinding problems this fly ash was not tested furthermore.

Fly ash AD2 with free lime at 6% was slightly adhering in the mill, gave strength results for 60% mixture with clinker at the desired 28-d target with a sufficient decrease of early strengths and increase of water demand.

Fly ash F from a different energy plant at Amintaio Florina, had low free lime and sulfate content. The 60 % mixture with clinker had excellent results with water content lower than the one with AD2 fly ash. In addition the mixture with 10% limestone gave results within the 28-d target strength.

In the case of 70% Fly ash mixtures AD2 fly ash acted better than the F fly ash but with higher water demand. The 80% clinker substitution with fly ash led to 28-d strength below 30 MPa. AD2 fly ash had 27,5MPa (35,4% water demand) and F fly ash 23,6MPa (32,0% water demand).

All the rest mixtures that had 20% limestone with or without pozzolana the desired target of 40±2MPa at 28days was not obtained. Only the 50% mixture of AD2 flyash, 20% of limestone and 5 % of pozzolana developed 29,4MPa at 28-d and 39,2 MPa at 90-d.

Conclusions

Fly ashes from Agios Dimitrios electric plant with free lime over 10% cannot be used without expansion and grinding problems. Fly ash from Amintaio Florina exhibited a great potential because of low free lime, low sulfate content that seems to act as set retarding agent and lower water demand.

In general it seems that by achieving a fineness R45 value of 2-10% a 28-d strength level of 40 ± 2 MPa was obtained in mixes where 60% of clinker was replaced by calcareous fly ash. These strength values were obtained even though the water demand was greater compared to that of the control mixture. For mixed systems in which 70% clinker was replaced, this strength level was achieved at 90 days. In mixtures where 80% of clinker was replaced by calcareous fly ash a strength level of 30 ± 2 MPA was developed at 90 days. Net fly ashes mixes of R45 2-5% showed a 28d strength of 10-20 MPa. Based on this research, the production of a high volume fly ash hydraulic binder seems feasible and a new field of exploitation of calcareous fly ash is opened.

It is obvious that strength development is decreasing for mixtures with clinker below 30%. Although the main scope of this study was the production of a cost effective binder and for that even 20% of limestone was used, for further studies it is essential to test the total or partially substitution of limestone with pozzolana at three and four constituents' mixture, which is expected to enhance mixture's performance [8].

Furthermore a study on hydration kinetics and durability of the best performing previous mixtures has already been scheduled.

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