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Statistical analysis as a key for the selection of suitable fractions of lignite fly ashes towards their further exploitation

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Abstract

The application rate of European lignite Ashes in the construction sector is still very low compared with relevant hard coal ashes. This fact must be mainly attributed to their intrinsic characteristics and specifically to the fluctuations in sulfates as well free calcium oxide contents. These characteristics exclude generally lignite ashes from the relevant European Standard (EN 450-1) even though numerous literature findings clearly demonstrate that selected qualities of them provide very good durability properties and consequently can be used in special concrete applications. In order to establish general criteria for the selection of the suitable quantities of fly ashes of Ptolemais region, a statistical analysis of the fluctuations of these parameters for the four power stations and for a temporal period of 10-20 years has been made. The very useful results, which will help Public Power Corporation to proceed to the preselection project in a definite power station, are discussed in the frame of this paper.

Keywords: HCFA, CaOf, SO_3, Statistical analysis, Preselection

1. Introduction

Hellenic ashes, especially those from Ptolemais area derived from lignites, are classified according ASTM into class C due to their high percentage of CaO (15-35%). Consequently Hellenic ashes are excluded from EN 450-1 which covers the use of Low Calcium Fly Ashes (LCFA) with reactive CaO < 10% in concrete. [1 }. To that reason must be attributed the low utilization rate of High Calcium Fly Ashes (HCFA) in Europe which is about 18% while the relevant covering both LCFA and HCFA in general approaches 48%. The utilization rate of HCFA in Greece is now much lower, not exceeding 10% [2, 3]

That difference in the utilization rate is in direct contrast with numerous literature findings (4, 5, 6) which clearly demonstrate **that selected fractions** of HCFA provide better early age strengths as well as better durability properties than LCFA. From these studies it was also concluded that, depending on the field of application fly ashes can be used either as they derive from the power station (untreated) or after special treatment aiming to minimize the particularities of HCFA (treated) [7, 8]

The discrimination in treated and untreated fly ashes is also foreseen In Hellenic Norms for Fly Ashes in Concrete (FEK 551) [9] which is in force since 2008. The following categories exist for a trial period of 10 years and for non reinforced concrete applications.

i) ET1 which is untreated fly ash with με R45<45% και SO3<7%. In ET1 are included fly ashes as received or after a homogenization of preselected material and used mainly for sub base in road construction. In this class the strength requirements are low.

ii) ET2 which is treated fly ash with με R45<30% , SO3<5% and CaOf <3%. In this class are included fly ashes which may partially replace concrete in non reinforced applications. The production of ET2 involves organized preselection system as well a milling plant with internal spraying system for the partial hydrolization of fly ashes in order to reduce their high values of CaOf.

The limits mentioned are based on the experience gained during the construction of Platanovryssi dam with HCFA as well to the existing globally Norms. [10, 11, 12]. As the majority of Hellenic ashes as they are produced do not cover the requirements for both classes, their application in the construction sector involves to face their intrinsic disadvantages, as are:

i) The variations in the chemical and mineralogical composition, as they are by-products of a process aiming to the generation of energy and not to the quality of ash. ii) The necessity for supplementary grinding for better reveal of their pozzolanic and hydraulic properties. iii) The elevated proportion of their CaOf as its hydration cause soundness problems as well as significant temperature increase. iv) The periodically elevated proportions of SO3 content with negative consequences similar to cement. It must be noticed that the problem of the periodically high percentages of LOI does not exist in Greece as the totality of our ashes have LOI less than the limit of 5%.

The confrontation of the intrinsic disadvantages of the Fly ashes led to the successful realization of projects in pilot Plant scale as are their use in road construction, in road pavements in high volume HCFA constructions as well in concrete products (blocks etc) Without any dispute the most impressive example of the use of HCFA for the construction of a high paste RCC dam is Platanovryssi Dam, on the Nestos river in north-eastern Greece. There, treated fly ash (similar to class ET2) was mixed with type I cement at a rate of Cement/Flyash = 20/80 and this mixture was applied for the construction of the main body of dam with RCC method. Until now (after 15 years), excellent results concerning strengths and other relevant properties have been obtained. [13, 14]..

Two significant tools have been studied and developed in Greece leading to the confrontation of the intrinsic disadvantages of Hellenic HCFA.: The Pre-selection system of fly ashes aiming to face the inhomogeneity problem as well that of elevated proportions of SO3 content and ii) the milling plant with the simultaneous spraying system aiming to face the problems of the necessity for supplementary grinding as well that of the elevated proportion of their CaOf.

Concerning the addition of Hellenic FAs in mixed hydraulic binders, the above factors are limited to the need of additional grinding and the problem of SO3 and CaOf varieties. Several peaks of those elements lead to unsoundness, thus prohibiting the incorporation of FA and clinker mixture into EN197 and EN196 specifications.

Given the big in-homogeneity problem, a proper pre-selection system is needed in order to meet with the requirement of the Hellenic Technical Specification concerning the two types of FA, ET1 and ET2. A direct target of this system is to locate and remove any FAs that demonstrate high values of either CaO_f or SO3. Given the experience of the dam construction, pre-selection is based in three actions:

i) Installation of a constant FA sampling system after the ignition and before its its storage in FA silos, ii) determination with modern and rapid analytical techniques, even in situ, of CaOf and SO3 having or not accepted values and iii) storage and mixture of the appropriate quality ashes.

With pre-selection the storage of the appropriate quality ashes is achieved. If this process reveals that an ash silo of one unit from a Power Plant is filled with “good” quality ash, then ii can be transferred to another ash silo or it can be co-fed for another application with an worse quality ash.

For a systematic industrial exploitation of FAs and in order to avoid possible quality mishaps during the selection of either ET1 or ET2, in the frame of this study, a statistical research was conducted aiming at finding the criteria that would eliminate the danger of throwing away quantities of FAs. Alternatively, through the statistical research, appropriate quality ashes can be easily found. This statistical study refers to SO3 and CaOf values variation gathering as increased values of theme affects negatively to their synergistic effect with cement.

Additional targets of this study are to determine whether seasonal variations are noticed and also to categorize the Power Plants of Northern Greece according to their response to the criteria required. This is necessary since it is not possible to install a pre-selection system in every Power Plant. [3,15].

The statistical study [16, 17] was based on: i) the gathering of available historical data from different Power Plants, ii) a systematic daily check for one month (November 2010) of the quality of untreated FA from Ag. Dimitrios Power Plant and iii) the selection of five samples from Power Plants of the Ptolemais area with a variety in the critical parameters values (SO_3 and CaOf) in order to perform the required physical and mechanical tests in a pyloric scale.

The limit values of the criteria for all the FA samples were set for SO3 as 5% and 7% concentration (as required by the FEK), thus setting the areas: <5%, 5-7%, >7%, and for CaOf as 9% (REACH limit) and 12,5% the limit for the successful hydration of the existing milling plant.

2. Results and discussion

2.1 Historical Data

By organizing all existing data by year and by month, a set of tables and figures was formed, which led to the creation of a series of small tables of the following form, which present the amount of compliance of each thermal power plant's fly ashes to the afore mentioned criteria in a yearly basis. Table 1 presented herein concern the plant of Ag. Dimitrios.

Table 1: Amount of Fly Ash Compliance to the Evaluation Criteria

YEAR: 2007				YEAR: 2008			
12 samples	SO_3^-<5	5<SO_3^-<7	SO_3^->7	*12 samples*	SO_3^-<5	5<SO_3^-<7	SO_3^->7
CaO_f<9	50,0%	8,3%	0,0%	[CaO_f]<9	16,7%	50,0%	0,0%
9<CaO_f<12,5	8,3%	33,3%	0,0%	9<[CaO_f]<12,5	16,7%	16,7%	0,0%
CaO_f>12,5	0,0%	0,0%	0,0%	[CaO_f]>12,5	0,0%	0,0%	0,0%
YEAR: 2009				YEAR: 2010			
12 samples	SO_3^-<5	5<SO_3^-<7	SO_3^->7	*12 samples*	SO_3^-<5	5<SO_3^-<7	SO_3^->7
[CaO_f]<9	50,0%	0,0%	0,0%	[CaO_f]<9	66,7%	0,0%	0,0%
9<[CaO_f]<12,5	50,0%	0,0%	0,0%	9<[CaO_f]<12,5	33,3%	0,0%	0,0%
[CaO_f]>12,5	0,0%	0,0%	0,0%	[CaO_f]>12,5	0,0%	0,0%	0,0%

From these small tables, in turn, a set of figures presenting the amount of each plant's fly ash compliance to both the criteria over time was made. Figures 1 & 2 which are presented as an example also concern the power plant of Ag. Dimitrios.

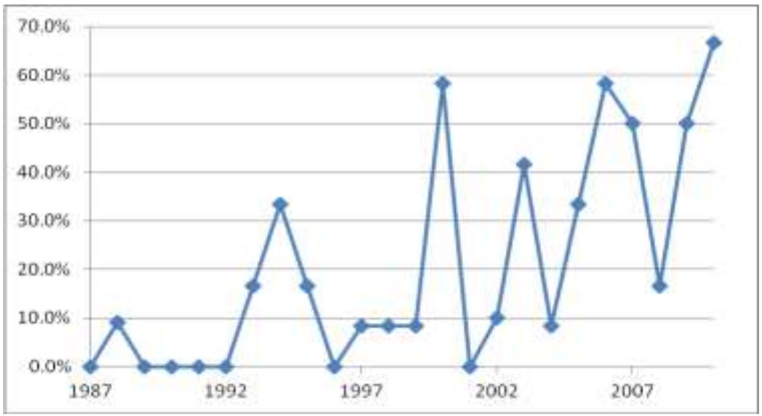

Figure 1. Percentage of fly ash from ag. Dimitrios thermal plant meeting the criteria SO_3^-< 5% and CaOf <9% over time

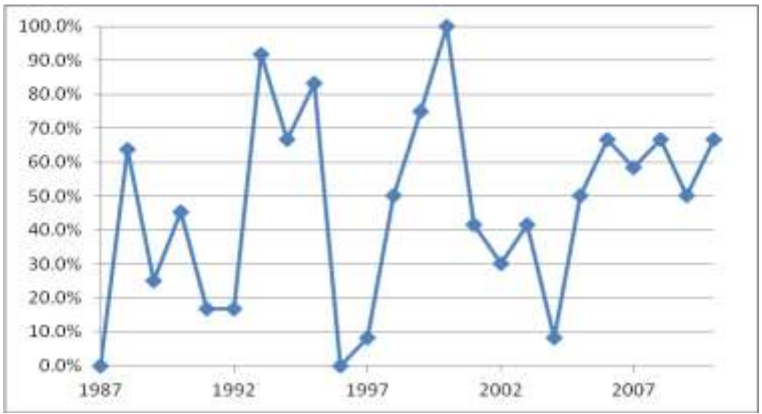

Figure 2. Percentage of fly ash from ag. Dimitrios thermal plant meeting the criteria SO_3< 7% and CaOf <9% over time

2.2 Systematic daily monitoring (November 2010)

A systematic daily monitor of the fluctuation of the values of the most important parameters was organized during November 2010, in order to detect any possible daily peaks which were "normalized" in a monthly sample. At the following figures, only the parameters which were also evaluated before are being presented (Figure 3: SO_3^{2-}, Figure 4: CaOf), while in addition, the amount of compliance of the daily samples to the evaluation criteria were recorded (Table 2). Finally, table 3 presents the fluctuations in fineness values.

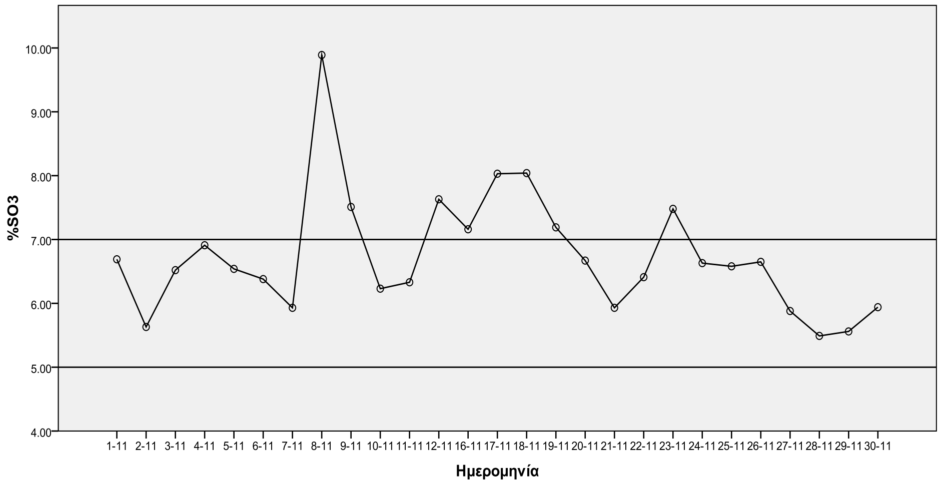

Figure 3: SO_3 Fluctuation of daily samples from ag. Dimitrios Thermal Power Plant (November/2010)

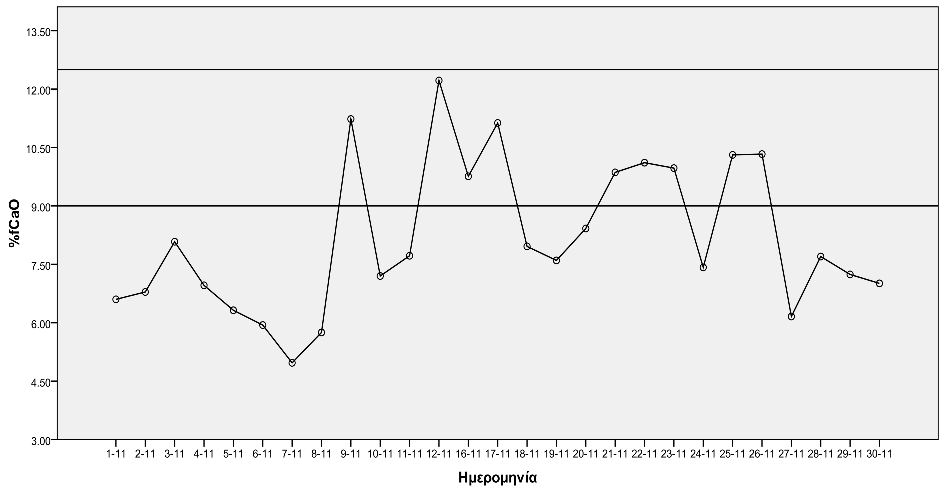

Figure 4: CaOf fluctuation of daily samples from ag. Dimitrios Thermal Power Plant (November/2010)

Table 2. Amount of compliance of daily fly ash samples from ag. Dimitrios thermal plant to the evaluation criteria

	November 2010		
27 samples	SO_3^-<5	5<SO_3^-<7	SO_3^->7
CaO_f<9	0,0%	55,6%	11,1%
9<CaO_f<12,5	0,0%	14,8%	18,5%
CaO_f>12,5	0,0%	0,0%	0,0%

Figure 3 shows that SO3 are fluctuating intensively between 7 & 10/11, while during the next days those fluctuations are being smoothed. The mean value is 6,73% and about 30% of the samples (8/27) present a value higher than 7% and therefore, if they are treated separately, the respective fly ash quantities would have to be rejected. All the rest of the samples are found in the area between 5 and 7%. As far as CaOf and the limit of 9% are concerned (figure 4) two distinct time periods can be seen. One that corresponds to the first eight days with lower values and another that includes the rest of the month with values close to 9%

(excluding again the last 4 days which again present low values). The mean value for CaOf is 8,17% which leads to the conclusion that if all the fly ash production of the month is mixed, the requirement for CaOf <9% is met. Table 2 presents the amount of fly ash that in daily basis met both criteria. It can be observed that while none of the sample from this period can be used as an ash of the EIT2 class, 56% of the samples meet the requirements for qualification as EIT1 according to FEK 551. In the case that exists the possibility of mixing the monthly ash production, it is obvious that 30% of the ash that would have been rejected because of the SO3 criterion, could be reused, given the fact that the monthly average is 6,73<7%.

Table 3. Granulometric distribution of daily received samples (November 2010)

Sampling date	% <200μm	% <45μm	% <30μm
01/11/10	94.87	57.21	44.39
02/11/10	90.62	55.6	45.42
03/11/10	94.47	59.35	47.3
04/11/10	93.46	57.51	46.42
05/11/10	92.04	56.58	44.19
06/11/10	92.83	58.74	46.22
07/11/10	92.74	59.03	46.94
08/11/10	91.14	59.29	47.6
09/11/10	95.89	61.77	50.33
10/11/10	93.28	50.23	38.84
11/11/10	93.60	55	42.77
12/11/10	93.71	60.39	48.85
16/11/10	96.44	64.9	52.97
17/11/10	94.59	65.99	55.73
18/11/10	92.50	61.62	51.1
19/11/10	91.07	59.57	47.83
20/11/10	91.91	61.46	49.61
21/11/10	87.30	60.79	49.16
22/11/10	89.60	59.59	47.59
23/11/10	92.40	62.02	49.54
24/11/10	95.24	64.81	51.23
25/11/10	94.23	61.42	49.84
26/11/10	94.81	67.32	55.05
27/11/10	93.68	59.71	48.38
28/11/10	92.21	56.77	45.04
29/11/10	91.35	51.96	39.44
30/11/10	92.14	55.7	43.23

As far as the fineness of the ashes is concerned, small diversifications can be observed regarding the residue at the 45μm sieve. All the samples resulted in a value between 33 and 45% (55-67% passing the sieve), values that characterize the fineness of the area's fly ashes and at the same time meet the criteria set by the FEK for raw ashes. In parallel, all ashes present a residue of around 5-10% at the 200μm sieve and a amount of fines (<30 μm) around 40-50%. All of the above lead to the deduction that an additional minor but necessary grinding process is required in order to reduce the residue at 45μm at 30%max.

2.3 Conformity check of selected samples

Finally, in order to correlate data received from the statistical analysis (and a possible change of limits) with the physicomechanical properties of cements originating from grinding various clinker mixes with fly ashes having different SO3 and CaOf, it was deemed necessary to receive samples of fly ashes with different expected values of SO3 and CaOf. NTUA aimed at receiving a sample with greater amount of SO3 (around 9%) and CaOf around 10-11%. However the ashes resulting from the power plants were this period around 5-6,5% in terms of SO3. Table 4 presents data for the 5 samples as well as the degree of corresponding to the physicochemical tests, while table 5 presents the granulometric distribution of these 5 samples.

Table 4. Data and conformity check for selected samples

no	Power plant	Sampling Date	SO_3(%)	CaOf(%)	Comments
1	A. D. (II)	13/05/2011	6.89	13.44	unsuitable
2	A.F. (I)	13/05/2011	3.94	1.38	OK
3	A. D. (II)	15/07/2011	5.05	5.86	OK
4	A. D. (II)	24/11/2011	5.98	10.85	unsuitable
5	A. D. (II)	19/12/2011	5.53	9.27	OK

The suitability of a sample was based on the physicochemical test provided by the standards. Thus, samples 1 and 4 were rejected because of the high CaOf values (that led to unsoundness concerning volume stability) and not because of the SO3 values (which were the highest of the five samples but were not prohibitive for further use.

Table 5. Granulometric distribution of selected samples

a/a	Power plant	Sampling Date	% <200μm	% <45μm	% <30μm
1a	A. D. (II)	13/05/2011	93.73	56.71	45.94
2a	A.F. (I)	13/05/2011	90.61	50.59	38.22
3a	A. D. (II)	15/07/2011	93.74	58.36	45.84
4a	A. D. (II)	24/11/2011	93.60	61.66	48.09
5a	A. D. (II)	19/12/2011	93.47	65.41	52.99

3. Conclusions

In relation to the classification and evaluation of the FAs composition from the Northern Greece area, all the data verify the fact that there are significant variations in the ashes composition deriving from the Thermal Power plants of the area that occur not only from plant to plant but several times from unit to unit of the same plant. The boilers' conditions can cause further variations between different units from the same plant while the operation status of the dedusting systems leads to differentiations in the fly ashes fineness.

The key role of the observed differentiations lies to the calcareous origin of the lignite inorganic compounds. The frequent composition variations of the inorganic compounds of the lignite mines in correlation with the unavoidable inorganic elements of the Hellenic lignite justify the inconsistency of the FAs' quality. This situation is maximized by the circumstantial co-feedings of the units by other fuels. Given those notes, the significant differentiations in the FAs' composition, in relations to time frames, must be attributed to the lignite origin mines.

In relation to the differentiations mentioned before as well to the criteria for the limits of CaOf and SO3 the results of the study lead to the formation of table 6 in which is included the possibility of each power station to produce fly ash fulfilling the appropriate according FEK combinations of both criteria.

Table 6. Aggregate criteria compliance rate for Fly Ashes of Ptolemais area Thermal Power Plants in the last decade

Thermal Power Plant	% comfomity CaOf<9% and SO_3<5%	% comformity CaOf<9% and SO_3<7%
Ag. Dimitrios	35-40	50-70
Kardia	0	0
Amyntaio	75-80	100
Ptolemais	-	25-40

The table shows that Kardia Thermal Power Station does not fulfill both criteria due to very high values of CaOf. The same almost figure exist for Ptolemaida Thermal Power Station which meets the criterion SO3<7% at a percentage of 25-40%. Given also the recent statistical data of the last five years is proposed to not use FA from these two Stations for both foreseen classes of FEK 551/2008. Since Fly Ashes of Kardia Station does not show high values of sulphates they could be used for road construction uses (as subbases) as in that use exist limits for SO3 but not for CaOf.

On the contrary the other two Thermal Power Stations and especially FA from Amyntaion can be used without any doubt when ashes with low CaOf values are needed. The recent statistical data also from Agios Dimitrios give a promising figure concerning the degree of fulfilling of both criteria and as this Power Station continues feeding from the same quarry, the possibilities of finding ashes covering both criteria are increased. As this Station is newer, has the suitable equipment for the fly ash supply.

Additionally from the samples taken daily for a temporal period of a month, have been recorded significant deviations which are “smoothed” in the monthly sample. This observation leads to the conclusion that the real quality figure must be derived from a quality control system based on samples taken daily or even every 12 hours. That means that during a month exist peaks in the values even of sulphates or of CaOf higher than existing limits meaning that the relevant quantities must be rejected in daily basis control. This rejection would be avoided only in the theoretical case of existing equipment for the mixing of monthly quantities. Since this latter case is very difficult, has been proposed from our team the preselection of fly ashes system.

With pre-selection is foreseen to face the inhomogeneity problem of fly ashes. This is achieved through the rejection of inappropriate quantities and in the same time the storage of the appropriate quality ashes is achieved. This is the basis of the preselection method which comprises the following three individual steps:

i) The installation of continuous samplers in the point of production before the storage silos and the collection of a sample every a specified temporal period (e.g. 4-8 hours). In the case that pneumatic transportation does not exist, a person is needed for the transportation of the samples to the chemical laboratory. ii) The carrying out of chemical analyses in the specified elements, based on rapid and modern analytical techniques. A chemical laborant with an XRF device are needed in that case. iii) The rejection of quantities of ashes that refer to inappropriate samples or on the contrary, the storage in silos of ashes, which cover the limits, for further treatment. The existence of a separate silo or a raw of mixing silos with a silo truck is necessary for the transportation and storage of the acceptable quality.

The evaluation of data derived from table 4 leads to the conclusion that the limits of CaOf and SO3 can be over passed to 0,5-1 percentage units max as, no quality degradation of fly ashes was observed.

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