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Incorporation of CCPs in Cement and Concrete: the Hellenic Case

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ABSTRACT

Coal Combustion Products (CCPs) are produced in million tons every year and a large quantity of them either due to the fact of non-conformity with the existing standards or due to their overproduction, are dumped causing serious problems to the environment. In this work, the main CCPs, as are Fly ashes and FGD Gypsum are investigated, for a potential use in cement and concrete. The study is focused to Class C (or High Calcium Fly Ashes) due to the fact that these ashes are not covered by any European specification and therefore the extension of their uses meets serious problems eventhough the technical, environmental and economical benefits from their application in the construction sector have been verified in laboratory as well in industrial scale. Special topics discussed in this paper are also: i) The CO_2 emissions reduction gain from the incorporation of CCPs in cement and concrete and ii) the available managerial tools aiming to increase their application rate.

INTRODUCTION. STATISTICAL DATA

Fly ash (FA), bottom ash (BA) and Flue Gas Desulphurization (FGD), are obtained from the combustion process of lignite in power plants according to scheme showed in fig 1

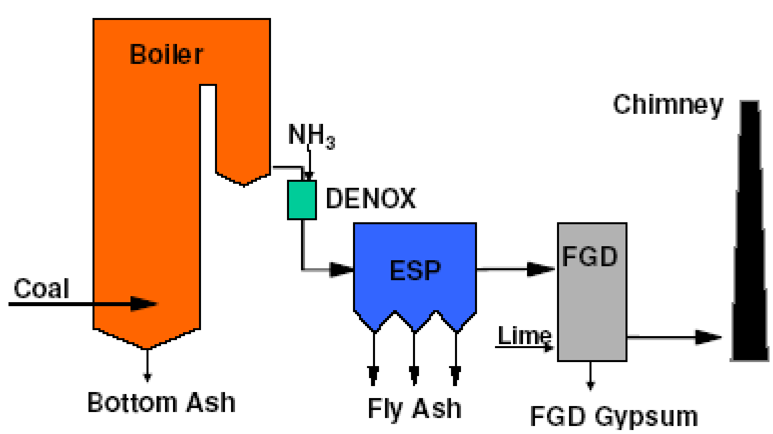

Fig.1. Combustion Process and CCPs Generation in a Lignite Fired Power Plant.

As these materials can be utilized in many applications, especially in the construction sector are called Coal Combustion Products (CCP.)

With regards to the information derived from ECOBA's current statistical data [ECOBA][W. v. Berg, H-J Feuerborn,2006], it can be observed that the total amount of CCPs produced in European (EU 15) power plants was 65 million tons while in the larger EU of 25 member states, the total production is estimated to be about 95 million tons. Exact figures from the new member states are not available, yet. Focusing on fly ash, its production in EU15 has been raised, for the year 2005, to 44.23 million tons (about 2/3 of the total CCPs). This production consists of 20.6 million tons of FA derived from hard coal (LCFA) which confront to the specifications stated in the European standard EN450-1 [EN 450-1,2005] (as they possess reactive CaO, free CaO and SO_3 contents less than 10%, 2,5% and 3% respectively) and 23,6 million tons derived from lignites (HCFA) which do not confront to EN 450-1 as the majority have either reactive CaO more than 10% (and free CaO more than 2,5%) or a SO3 content higher than 3%.

Consequently, there is a significant difference in the utilization rates in the construction sector, among the two types of fly ash, which in general approaches 48% (21.15 million tons); thus the construction sector utilizes the majority of LCFA (78%, that is, 16.75 million tons) whereas in the case of HCFA the respective numbers are 18.2% and 4.4 million tons [Tsimas S , Moutsatsou A., Antiohos S.,2006]. In a final approach (taking into consideration the major fields of application for European fly ashes in the construction sector) the image summarized in Table 1 can be obtained;

Table 1. Quantities of LCFA and HCFA Absorbed in the Main Application Fields of the Construction Sector

Field of application	LCFA(X106 t)	(%)	HCFA(X106 t)	(%)
Concrete	6.00	36.4	-	-
Blended cements	1.67	10.0	0.93	21.2
Cement raw materials	4.73	28.3	0.80	18.1

The current situation in Greece is as follows: Produced quantity; 11,5 million tons of HCFA (i.e. almost half of the European), exploited quantity 1,1million tons (in blended cements); thus the utilization rate in Greece is 10% while the relevant in Europe is 18,2%. On the same time about 800.000t of FGD Gypsum have been produced.

Having the aforementioned in mind, it becomes evident that in European countries where lignite or subbituminous coal is used, the rejected (unused) fraction of fly ashes (rFA) comprises a significant part (approximately 80%) of their total production. The suitability of the reject fraction for use in the construction sector is determined from its compliance with certain criteria, such as the content of unburned carbon, percentages of reactive silica and alumina, sulfur trioxide levels and fineness.

The attempt to increase the utilization rate of HCFA is obvious. Under a tight control of the entire design-production-application process; the use of selected fractions of HCFA can be proved more beneficial than LCFA. This observation must be attributed to the fact that, referring to mechanical properties, the contribution of HCFA to the hardening of the cementitious phases is greater. Also referring to durability, the positive role of FA in cement and concrete has been extensively discussed in the past showing that fly ash can be used in concrete either as a separately batched material or as an extra ingredient in several types of blended cements [Mehta, P.K,1998] [Papayianni I.,1986].

FLY ASH AS SUSTAINABLE CONSTRUCTION MATERIAL.

Besides the benefits associated to the synergistic action of FA with cement which leads to the improvement of the properties of concrete in certain applications, the incorporation of fly ash in the construction material shows definitive advantages in the environment and contributes to different parameters of sustainability. The scheme in Fig 2 summarizes the gain to the environment from each utilized ton of fly ash.

More specifically the use of fly ash as a Supplementary Cementing Material (SCM) leads to a substantial energy saving by reducing the amount of Portland cement, which is an energy intensive product [E. Worrell, N. Martin, L. Price,2000] [Bentur, A.,2002][Bijen, J., 1996]. It contributes also to the reduction of CO_2 emissions produced during cement manufacture[Bentur, A.,2002][Bijen, J., 1996]. Apart from assisting sustainable development, utilizing such a by-product contributes to the protection of the environment since, when not recycled, fly ash is land filled or disposed to inappropriate sites [Bijen, J., 1996] [Cheerarot, R. and Jaturapitakkul, C., 2004]. Reductions of the amount of residues to be land filled along with partial substitution of common raw materials used in cement making are the major beneficial effects of the recycling process.

Additionally to Fly ash, FGD gypsum has very similar properties to natural gypsum and can successfully replace it as setting controller in cement manufacture . [A. Papageorgiou, G. Tzouvalas and S. Tsimas,2005]

Analysing the CO_2 emissions reduction gain we remark that this period the contribution of fly ash incorporation in blended cements and the relevant substitution of clinker leads to a significant reduction of CO_2 emissions and therefore is of major importance especially for the cement industry. Additionally, except for blended cements, the use of both bottom and fly ash as raw mix constituents for partial replacement of limestone, contribute to a small (max 4%, table 2) but remarkable CO_2 reduction during the burning process in the cement industry [S. Tsimas, G. Vardaka, M. Zervaki,2008].

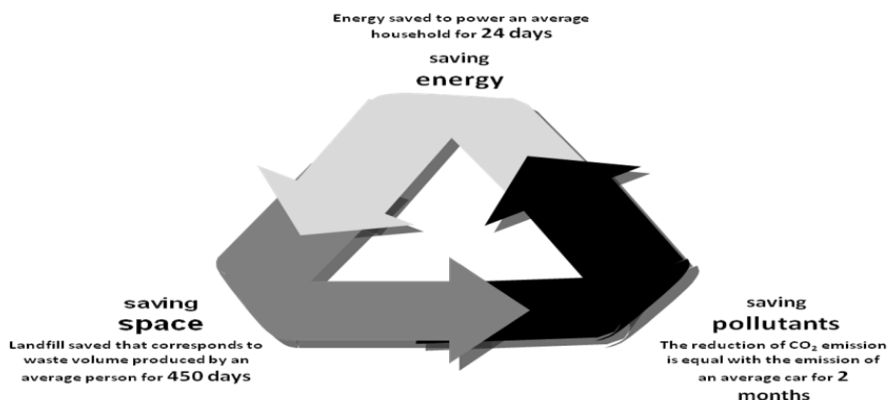

Fig.2. Environmental Gain for Each Ton of Fly Ash Utilized.

Referring to the first case, is estimated that during cement production about 0, 97 tones CO_2 are produced per each ton of clinker. The majority of this quantity (0,55t) refers to the decomposition of $CaCO_3$. According to EN197-1 [EN 197-1,2000], clinker participates in different percentages in cement depending on the cement type. For the case of fly ash substitution, apart from the specifications in the above standard, the exact percentage of fly ash depends also on its composition and especially on the percentage of some constituents (as are e.g. sulfates, SO_3) which limit their participation. Since for Greece, types CEM II and CEM IV are more commercial, it can be assumed that the mean fly ash utilization is in the order of 20-25%, so the emission reduction gain is limited to the percentages shown in the last column of table 2.

Table 2 Emission Reduction Data in Cement Manufacture

Fly ash in blended cements and raw mix constituent	emission reduction based on max possible substitution (EN 197-1)	emission reduction based on current substitution
CEM IIa	21%	16%
CEM IIb	37%	23%
CEM IVa	37%	26%
CEM IVb	58%	42%
Fly ash	0,5 – 4%	
Bottom ash	0,5 – 4%	

Consequently, the use of suitable fractions of fly ashes which are deriving after treatment aiming to face their disadvantages will play an important role to both the improvement of concrete properties and the CO_2 emission reduction in cement industry.
So the need to increase the utilization rate of HCFA, overcoming their particularities which inhibit or limit their use in the construction sector, is compulsory.

HCFA MANAGEMENT METHODS TOWARDS WIDENING THEIR APPLICATION FIELDS

It is evident that aiming to maximize the use of HCFA especially in the construction sector, a management system must be developed able to face their intrinsic disadvantages and to provide suitable fractions that may meet the suitability criteria for their further use. This management system is associated with the appropriate use of available tools for further treatment the main of which are: i) the milling and partial hydrolization of ash and ii) its preselection.

The disadvantages of HCFA and especially of the Hellenic HCFA have been extensively discussed in the past. Briefly 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 CaO_f as its hydration cause soundness problems as well as significant temperature increase. iv) The periodically elevated proportions of SO_3 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%.

Since the disadvantages of the need of supplementary grinding and that of high CaO_f are easily confronted, with a milling plant with a closed circuit ball mill with a partial hydrolization device (fig. 3), for the transformation of the excess of CaO_f to $Ca(OH)_2$, respectively [Kravaritis A, Tsimas S, Moutsatsou A, Tsiknakou Y, 1996][Tsimas S., Moutsatsou-Tsima A,1999][Tsimas S.,2001], efforts must be focused to the other two cases and especially to that of elevated proportions of SO_3 content. This fact is of major importance as sulphates are not subject for further reducing during the treatment in mill.

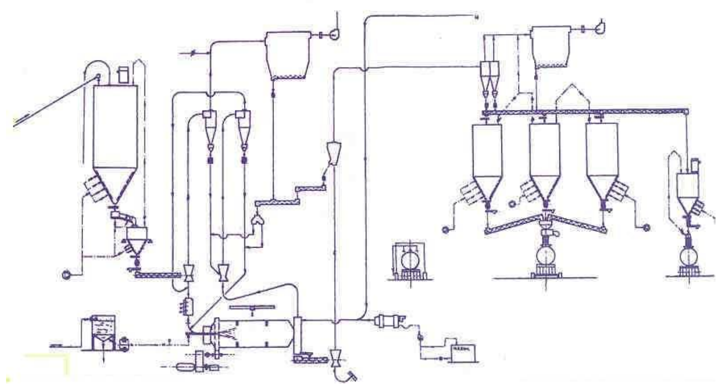

Fig. 3. The Milling Plant with the Partial Hydrolization Device.

From the previous analysis is obvious that the first step for the extension of uses of HCFA in the construction sector is the identification and separation of the suitable high quality of FA which covers the SO_3 limit, from the total quantity of fly ash of a unit of a power station. This identification and separation is the basis of the preselection method which comprises 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). ii) The carrying out of chemical analyses in the specified elements, based on rapid and modern analytical techniques. 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. [S. Tsimas, G. Vardaka, M. Zervaki,2008]

Following this preselection system with the use of the milling plant, in Greece 12 years ago was constructed a high dam (Platanovryssi dam) where selected and treated fractions of HCFA (135.000t) were the main cementicious material consisting the 81% of cementicious materials. Based on the previous analysis as well on the experience gained during the construction of Platanovryssi dam with HCFA, Greece entered in force from April 2007 the FEK 551 which contains the Hellenic norms for HCFA, mainly addressed for non reinforced concrete for a trial period of 10 years. [FEK 551,2007] The limits are indicated in table 3.

Table 3. Classes of HCFA According to FEK 551

	R45	SO_3	CaOf
EIT1	≤45%	≤7%	----
EIT2	≤30%	≤5%	≤3%

Another managerial tools well examined in Greece through relevant research programs comprises i) the exploitation of the properties of the coarse particles of FA and ii) The exploitation of high calcium high sulphate ash.

The exploitation of the properties of the coarse particles of FA

A novel way to deal with the fineness problem of FA is based on the fact that the coarse fractions of fly ashes contain more amorphous silica than the fine ones. Since the latter form of 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 ash of improved pozzolanicity and presumably better performance in blended systems.[S. Antiohos, G. Tzouvalas and S. Tsimas,2007]

Appropriate application of this method may enable an increase of the possible applications for HCFA since it is associated with a severe reduction of its CaO_f and sulfur contents, up to a point that a part of reject fly ash has acceptable quality. From the above table is derived that the coarser fraction (TFP) is notably enriched in total and active silica, but its CaO_f and SO_3 contents are remarkably reduced compared with the bulk ash. On the contrary, the fine fraction of TF contains much more CaO (as this is concentrated in the smaller size particles), but also unusually high percentages of CaO_f and SO_3. With respect to the last two parameters, the use of ground coarse fly ash may be advantageous since both CaO_f and SO_3 may be harmful to mortar and concrete durability. The LOI values of the fractioned samples did not change appreciably compared to that of the initial fly ash. In other works it was the finer ash (obtained by classification) that contained higher LOI than the original. This is very encouraging since that higher LOI is usually (but not always correctly) associated with high unburned carbon that causes undesired swelling effects in the paste. An additional observation with regard to the coarse part is that it presented lower mean diameter than the bulk ash.

The exploitation of high calcium high sulphate ash,

With this last managerial tool the problem of periodically high sulphate values of HCFA can be effectively managed. In most cases, the enrichment of HCFA in lime is followed by a high percentage of sulphates which are bound to calcium or calcium aluminates. The elevated values in SO_3 content of fly ashes are associated with significant danger for the durability of concrete since an excess of sulfur ions can initiate expansion processes that may lead to the cracking of the paste. This is the reason why relevant specifications specify an upper limit (usually 5%) for the sulphates. Normally HCFA produced globally do not confront with the requirements of relating standards and thus they are being dumped, amplifying the environmental burden.

The partial replacement of natural gypsum in blended cements by high calcium high sulphate ash may contribute to the increase of uses of HCFA. High sulphate high-calcium fly ash (HSHCFA) performs both as pozzolanic material and as sulphate bearing material. In research work carried out by the authors [S. Antiohos, Stamatis Tsimas,2007] blended cements were prepared by replacing 20 and 30 % by weight of clinker with equal amount of fly ash (SO_3 =6.7%). All samples tested exhibited satisfactory initial and final setting times as a result of the rapid dissolution of sulphate ions from the ash particles. Additionally, the examined specimens presented decent compressive strength values when compared to the control specimen (with no fly ash). Strength development of the new blended cements increased notably with the application of a bilateral activation process consisting of a small offer of Na_2SO_4 and a half-day thermal treatment.

INCORPORATION OF FGD GYPSUM IN CEMENT INDUSTRY

The advantage of FGD Gypsum is based to the fact that has almost the same chemical and mineralogical composition with natural gypsum (NG) and hasn't detrimental constituents which may cause problems when used as calcium sulfate bearing materials (CSBM) as cement setting retarder. From our recent research findings [A. Papageorgiou, G. Tzouvalas and S. Tsimas,2005][Tzouvalas G., Dermatas N., Tsimas S.,2004] [Tzouvalas G., Rantis G.., Tsimas S., 2004]the partial or total displacement of NG do not deteriorate the compressive strength of concrete, ii) the durability of concrete seems to be improved with the use of FGD Gypsum as setting regulator instead of the NG. This must be attributed to the fact that the use of chemical byproducts leads to the reduction of voids in concrete. More precisely FGD Gypsum compared to NG and Anhydrite is classified in the following range from the worst to the best for each one of testified properties:

Capillary sorptivity: anhydrite < natural gypsum < FGD
Chloride penetration: natural gypsum, anhydrite < FGD
Sulfate attack: anhydrite < natural gypsum < FGD

CONCLUSIONS

The majority of the problems associated with HCFA as are Hellenic Fly Ashes and FGD Gypsum, are - to a large extent - manageable. Through scientifically justified and inexpensive tactics it is possible to increase their application rate especially in the construction sector. In particular, results from this study denote that certain fractions separated or selected from ashes not primary in compliance with relating standards, can ensure excellent performance for the final product when properly used. Moreover, extensive know-how may enable the use of some techniques in order to manage HCFA and overcome difficulties associated with their nature. These techniques mainly contain their pre selection and their grinding with simultaneous hydration. The existence of National or European norms addressed to different qualities of ashes, contribute to the increase of their utilization rate, which is the final objective of this effort.

REFERENCES

Antiohos. S., Tzouvalas. G. and Tsimas. S., (2007), "Two stage processing to promote the use of reject fraction of fly ash into blended cement" *Proc.of the 9th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolan in Concrete", Warsaw Poland*

Antiohos. S., Tsimas.S.,(2007), "Impact of Using Reject High - Sulfur Fly Ash in the Performance of Binary Blended Cementitious Systems", *3rd International Symposium "Sustainability in Cement and Concrete", Istanbul*

Bentur.A. (2002). "Cementitious Materials-Nine Millennia and A New Century: Past, Present and Future", *Journal of Materials in Civil Engineering, 14*, pp. 1-22.

Berg. W. v., Feuerborn. H-J, (2006) ,"Lignite fly ash in Europe-Properties and Use, Proceedings of the International Seminar 'Processing and Usage of High Calcium Fly ash", *Belchatow Poland*, p. 29-38

Bijen. J. , (1996). "Benefits of slag and fly ash", *Construction and Building Materials 10,* p.309-314.

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

ECOBA “Statistics on Production and Utilization of CCPs in Europe” <http://www.ecoba.com/ecobaccpprod.html>

EN 197-1 (2000): “Cement - Part 1: Composition, specifications and conformity criteria for common cements.”

EN 450-1 (2005): “Fly ash for concrete - Part 1: Definition, specifications and conformity criteria.”

FEK 551, (18/4/2007), “Part B, National Technical Specifications, «Hellenic Fly Ashes».”

Kravaritis.A. Tsimas. S., Moutsatsou. A., Tsiknakou. Y. (1996). “Utilization of Fly Ash for Construction of Dams by RCC Method”, *Proc. Power-Gen ’96, Europe, Vol. 1,* pp 833-858

Mehta. P.K., (1998), “Role of pozzolanic and cementitious materials in sustainable development of the concrete industry”, *6th CANMET/ACI international conference on fly ash, silica fume, slag and natural pozzolans in concrete”, Malhotra V.M. (ed), I,* p. 1-20.

Papageorgiou. A., Tzouvalas G., and Tsimas. S. (February 2005), “Use of inorganic setting retarders in cement industry”, *Cement and Concrete Composites, Volume 27, Issue 2,* Pages 183-189.

Papayianni. I. , (1986), “Strength and Bond Data for Greek High-Lime Fly Ash Concrete”, *ACI-SP-91, Editor V. M. Malhotra, Volume 1, Detroit*, pp 367-386.

Tsimas. S., Moutsatsou. A. , Antiohos. S. , (2006), “The use of CCPs in cement and concrete as a key to the sustainable development”, *Retbe, Alexandria Egypt,*

Tsimas. S., Moutsatsou-Tsima. A., (1999), "Upgrade of high calcium Hellenic Fly Ashes for their use in concrete", International Conference: Creating with concrete’ *Vol: Modern concrete materials: binders, additions and admixtures, Dundee, UK,* p 159-165.

Tsimas. S., October (2001), "Beneficiation of high calcium fly ash in Greece", *Invited for presentation in the conference, Fly ash from power plants, Poland, Proceedings*, pp. 273-284.

Tsimas. S., Vardaka. G., Zervaki. M., (2008), “Composing cement raw mix by using fly and bottom high calcium ashes”, *EuroCoalAsh, Warsaw*, pp73-84

Tsimas. S., Vardaka. G., Zervaki. M., (2008), ”The preselection of high calcium fly ashes as the first step for their further evaluation”, *EuroCoalAsh, Warsaw*, pp249-256

Tzouvalas. G. , Dermatas. N., Tsimas. S., (2004), “Alternative calcium sulfate bearing materials as cement retarders. Part I: Anhydrite”, *Cement and Concrete Research, 34,* pp2113-2118.

Tzouvalas. G., Rantis. G., Tsimas. S., (2004), “Alternative calcium sulfate bearing materials as cement retarders. Part II: FGD Gypsum,” *Cement and Concrete Research, 34,* pp 2119-2125.

Worrell. E., Martin. N., Price. L., (2000), “Potentials for Energy Efficiency Improvement in the US Cement Industry”, *Energy 25,* pp. 1189-1214.