Standardization aspects concerning High Calcium Fly Ashes

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ABSTRACT

High Calcium Fly Ashes are reactive materials that often do not meet the limits of the standards. Therefore, most of the quantity produced annually in the world, due to lignite burning, remains unexploited and charges the environment. Efforts of standardizing these materials as supplementary cementitious materials in Europe failed because there are some bad experiences with the material in the past and many doubts about the performance in concrete mixtures. The only way of utilization of these fly ashes is to be used in the blended cement industry. Actually, a low percentage of the materials is absorbed at a permanent basis from the cement industry and huge amounts are rejected or used for reclamation of mining areas. However, investigation on these materials has shown which are the weak points and how they could be overcome by using advances in materials technology. Moreover, they could be classified in categories relative to application fields where the addition in concrete mixtures is advantageous. Following this concept, National Specifications for the use of calcareous fly ash in concrete were established and are in force in Greece, where only such fly ashes are produced at the power stations of the Public Power Corporation. Therefore, categorization of calcareous fly ashes was made according to their free lime content, sulphate content and fineness, which are considered the most influential characteristics on the performance of fly ashes. Then, criteria for their pozzolanicity and volume stability were suggested, following the pattern of the EN 450 Standard for low-calcium fly ashes, but modified in order to be more realistic for calcareous fly ashes. A complete methodology of testing these fly ashes is accompanying the National Specification document, since it was found that some modifications on the relevant methodologies were necessary. The authors, who played a leading role in the more than five year old national effort, believe that this regulative frame provides flexibility in the utilization of calcareous fly ashes and promotes their marketing.

INTRODUCTION

Although many efforts are made for developing alternative sources of energy it seems that in Europe, the basic contribution to energy balance during the next
decades will come from burning coal or lignite. That means that fly ashes will continue to charge our planet [1].

According to ECOBA statistics, the amount of High Calcium Fly Ashes (HCFA) in Europe is more than 50% of the total fly ash produced by burning hard coal and lignite [2].

The utilization of fly ash in 2006 [3] was about 20.1 representing the 50% of the total fly ash output. However, this percentage is much differentiated among the countries. For example, in Europe of the 15 members, the utilization of siliceous fly ashes reaches the 80% while this of HCFA is less than 20%.

According to the American Coal Ash association about 72 million of fly ash is produced and about 31 million tones are utilized mainly in concrete and landfill applications. There are not information about HCFA production and utilization. It seems that HCFA utilization is far less than its production. The main fields of application are the construction sector. HCFA(s) are added to concrete, replace clinker in blended type cements, used as raw material for cement manufacture, or they are used for land filling, soil stabilization or general in road base construction. The main producers in Europe are Germany, Poland and Greece. The last produces 11.5million tones annually, about the 17% of the total production of the Europe of 25 members.

THE EXISTING REGULATIVE FRAME

The most widely known standards for the use of HCFA(s) mineral admixtures are the ASTM C618-75 in which they were classified as category C and the relevant ASTM C311-90 for sampling and testing, as well as the ASTM C595 for its use in blended cement. Canadian standards CAN3-A23-5-M82 also cover the use of HCFA.

In Europe there is the EN450-1.2 for the Use of Siliceous Fly Ashes in Concrete (recently revised) while the HCFA(s) are still marginal materials and concrete with them is unconventional concrete that needs approval. However, their use in blended type cements is covered by EN197 Standards. The other Standards that refer or allow the use of HCFA(s) are the EN13282 about Hydraulic road binders and EN14227 about hydraulic bound mixtures (recently revised). In the last two the HCFA(s) meeting the EN197 requirements can be used for the production of the hydraulic road binders.

Up to now at European level HCFA(s) use in Concrete is not covered by a regulation. The only way to use it as acceptable mineral admixture is to follow EN197 limits shown in Table 1, which has been established, based on cement industry experience from the production of blended type cement. Characteristic is the definition of calcareous fly ash (W) according to EN197 in which the main parameters that influence the quality of these fly ash are related to the quality of
the produced cement and refers to specific by mass replacement of clinker by HCFA.

Table 1. Requirements for HCFA according to EN 197-1

<table>
<thead>
<tr>
<th>Requirements</th>
<th>HCFA</th>
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<tbody>
<tr>
<td>Free calcium % by mass</td>
<td>$W_1$</td>
<td>$W_2$</td>
</tr>
<tr>
<td>Reactive silica % by mass SiO$_2$ (determined according to EN196-2) by using HCl and KOH</td>
<td>$\geq 25$</td>
<td>-</td>
</tr>
<tr>
<td>Expansion (mm) in pastes (Cement 70 / HCFA 30)</td>
<td>-</td>
<td>$\leq 10$mm</td>
</tr>
<tr>
<td>Loss of ignition % by mass</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>28-d Compressive Strength (MPa) mortar prism</td>
<td>-</td>
<td>$\geq 10$</td>
</tr>
</tbody>
</table>

Since in many countries or areas HCFA(s) are the only produced fly ash this situation of the lack of standards for the use of HCFA in concrete industry is opposite to the economy in construction and to the environmental protection policy. Therefore, the States proceeded in constituting national specification. From 1991 in Catalonia Spain in valid the UNE83420—Concrete Additions—Fly Ashes specifications for Fly Ashes with CaO content in excess of 10%.

For more than 50 years knowledge and experience from HCFA(s) application in countries have been accumulated without any transfer into practice. Then, after long-term collective work, the Greek State approved (October 2007) the Hellenic Specification for the Use of High Calcium Fly Ashes in unreinforced concrete or cement products. In Germany there are also FGSV guidelines, while in Poland they have proceeded in taking national certifications for the use of concrete in road construction.

PARTICULARITIES OF HCFA(s)

It is widely acceptable that for siliceous fly ashes the most important characteristic for their effectiveness is the reactive silica content. Apart from it, in the case of HCFA, the reactive lime and sulfate are also significant parameters for its performance in concrete mixtures. Fineness is also important for both types of fly ash. The above mentioned parameters of HCFA(s) govern the self hardening capacity and the volume stability of it.

It is well known that the factors that influence the heterogeneity of HCFA(s) in chemical and mineralogical composition are:

- the lignite quarry (i.e. the quality of lignite and the amount and composition of the organic material added)
ii) the combustion conditions (i.e. the temperature and atmosphere inside the boiler) and

iii) the serving condition of electrostatic precipitators which mainly affect the fineness.

The variability in lime and sulfate of HCFA(s) is a matter of great concern, because these constituents are often accused for failures of cement fly ash systems. On the other hand, the dual character of HCFA(s) contributes more in early strength development while the pozzolanic reaction products enhance the microstructure of the matrix of cement fly ash systems. That means that higher percentages of cement could be replaced. Concrete mixtures with HCFA(s) often present higher water demand for a certain consistency to the free lime, calcium aluminate and sulfate compounds. This can be anticipated by adding proper dosage of superplasticizer. Another positive effect is the significant decrease of bleeding and segregation tendency. When dealing with HCFA(s) one has the feeling of a “tameless” material that needs a frame to be harnessed. There are different processes such as homogenization, desulfurization, mixing with other type of cementitious materials, by which the material is upgraded [4].

UTILIZATION OF HCFA IN CONSTRUCTION APPLICATIONS

Most of the research done on HCFA use in concrete was done from the mid of 60’s to 80’s. Many researchers [5] [6] proved even from past decades that HCFA(s) can replace Portland Cement in the mixer, even if they do not meet specifications and proposal revision of the standards.

Many successful projects with HCFA are mentioned in literature concerning mainly geotechnical applications, road bases or parameters hydraulic fills [7] [8] [9] [10] RCC dams [11] [12], Low Controlled Strength Concrete, flowable concrete, shotcrete e.t.c. The construction of the highest RCC dam in Platanovryssi, Greece, 1995-96 is one of the eminent applications (Table 2). Of course, the most successful construction projects with HCFA are those with maximum cost saving and optimum technical benefits, which could hardly have been achieved without the HCFA(s) addition. For example, the construction of small scale hydraulic dams by using HCFA roller compacted concrete could shorten the time of construction up to ¼ of the time required for an earth dam, resulting in significant economic and environmental benefits.
Table 2. The proportions of the HCFA roller compacted Concrete used for the Construction of the highest in Europe RCC Dum (1995-96)

<table>
<thead>
<tr>
<th></th>
<th>Freewater kg/m³</th>
<th>Portland cement kg/m³</th>
<th>Fly ash kg/m³</th>
<th>Fine agg. kg/m³</th>
<th>Coarse agg. kg/m³</th>
<th>Addit. kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCC</td>
<td>128</td>
<td>50</td>
<td>225</td>
<td>607</td>
<td>1350</td>
<td>2.2</td>
</tr>
<tr>
<td>Levelling</td>
<td>187</td>
<td>100</td>
<td>225</td>
<td>676</td>
<td>1057</td>
<td>2.0</td>
</tr>
<tr>
<td>Facing</td>
<td>173</td>
<td>140</td>
<td>175</td>
<td>753</td>
<td>957</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The utilization of HCFA in concrete should be based on two concepts:
- Flexibility in selecting and combining the material in different binding systems.
- Adaptability to environmental and functional requirement of the Construction.

THE DEVELOPMENT OF HELLENIC SPECIFICATIONS FOR HCFA USE IN CONCRETE

Based on experience from research, pilot applications and mainly from the construction of the RCC Dam in Platanovryssi with HCFA concrete a long-time effort (about 5 years) made to constitute. Specifications for the Use of Greek HCFA in unreinforced concrete and cement products. This made under the aegis of Technical Chamber of Greece with the help of the non-profit Organization EVIPAR (Industrial By-Products Research and Development Association), of Cement Industries, the Institute of Economy of Constructions and IKTESK. During previous decade a project of round robin tests on HCFA characteristics and their role in HCFA’s reactivity took place with the cooperation of Cement Industries, the Aristotle University of Thessaloniki, the National Technical University of Athens, KTESK and the Institute of Geological Research and Studies.

From October 2007 the National Specifications are in force (FEK551). The two categories of HCFA prescribed in Table 3, concern actually a raw HCFA EIT1 mainly for low strength concrete applications and a processed one EIT2 for conventional or high strength concrete products. For facilitating the users the structure and format of EN450 for Low Calcium Fly Ashes was followed. In the Hellenic Specifications Soundness and reactivity by compressive strength tests are suggested not only for the cement / fly ash mixtures of EN196-2 but for cement/fly ash 50/50 mixtures. A complete list of methodologies of testing these fly ashes has been attached for the convenience of the specification users.
Table 3. Categories of HCFA according to the Hellenic Specifications

<table>
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<tr>
<th></th>
<th>(R_{45})</th>
<th>(SO_3)</th>
<th>(CaO_f)</th>
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<tbody>
<tr>
<td>EIT1</td>
<td>(\leq 45%)</td>
<td>(\leq 7%)</td>
<td>-</td>
</tr>
<tr>
<td>EIT2</td>
<td>(\leq 30%)</td>
<td>(\leq 5%)</td>
<td>(\leq 3%)</td>
</tr>
</tbody>
</table>

The specifications have been loaded at the site www.evipar.org.

The limits in sulfates were decided after recording the fluctuations of this Constituent. In raw fly ash and in preselected (by following a very simple way [12]) fly ash Fig.1,2,3). It seems that a percentage only of 30% of the analyzed fly ash samples present sulfates lower than 7%. Among them the 30% have sulfates lower than 5% by mass. The testing of EIT1 calcareous fly ash as a constituent for hydraulically bound mixtures was very encouraging for the use of this fly ash in soil stabilization [13].
CONCLUSIONS

It is obvious that the existing standards, national specifications concerning the use of HCFA in construction are inadequate for the promotion of the Utilization of these fly ashes in construction which is very low in comparison to that of siliceous fly ashes. A regulative frame more flexible, based on the performance type criteria should be developed orientated to the final application field. A classification of HCFA is necessary concerning the most reactive constituents of it, lime, silica, sulfate as well as fineness. To this direction the Workgroup of ECOBA Calcareous Fly Ashes has been activated for more than two years to elaborate a record (data base) concerning HCFA and in particular production, characteristics, utilization fields, harmonization of definition and finally to propose a classification system. By this work, is expected to open the way for standardization of HCFA(s) at European level.

REFERENCES


