# Greek fly ash as a cement replacement in the production of paving blocks

**Nikolaos Koukouzas[1], Ioanna Papayianni[2], Eleni Tsikardani[3], Dimitra Papanikolaou[1], Chrisovalantis Ketikidis[1]**

[1]Centre for Research and Technology Hellas, Institute for Solid Fuels Technology and Applications, 4th km of National Road Ptolemais – Kozani, 502 00 Ptolemais, Greece, tel: +30 2463 0 53842, fax: +30 2463 0 53843,
e-mail: koukouzas@techp.demokritos.gr
[2]Laboratory of Building Materials, Department of Civil Engineering, Aristotle University of Thessaloniki, P.O. Box: 482, 541 24 Thessaloniki, Greece
[3]Department of Pollution Control Technologies, Technological Educational Institute (TEI) of Western Macedonia, 501 00 Kozani, Greece

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ABSTRACT

The fly ash produced at the power stations of the Ptolemais region in Northern Greece is rich in Ca due to the origin of the lignite burned and as a consequence it is characterized as a class C fly ash according to ASTM C 618. Because of the high Ca content its use in the concrete production and the production of concrete based products is restricted in Greece and only 10% of the produced fly ash is used for the production of cement. The remaining amount is deposited in mines causing environmental and financial concern.

In this paper a research was conducted in order to examine the possibilities of the Greek fly ash utilization in other applications than the cement production such as the production of paving blocks from concrete containing fly ash. For this reason paving blocks were produced from concrete including diverse proportions of fly ash which came from the Ptolemais Thermal Power Station. The aforementioned products were produced in the frame of the project 'k-clusters: development of new products with use of fly ash from Western Macedonia'. The qualitative characteristics of the produced products were investigated as well as their mechanical properties, characteristics which were directly correlated with the properties and the proportion of the fly ash used for cement replacement.

## INTRODUCTION

The production of fly ashes, in the year 2000, in Greece was more than 10 million tonnes. 80% of this quantity came from the Ptolemais area in Northern Greece where the main deposits of the Greek lignites are located. The most significant and systematic use of ashes (only a percentage of 10%, that is about 1 million tons/year) is that in cement industry, replacing cement clinker and aiming at the production of several CEM II types according to EN 197-1 standard. These ashes are interground with clinker and gypsum during the final grinding of cements [1, 2, 3 and 4]. The remaining quantity of fly ash is stockpiled in embankments and open cast mines around the power stations.

Beyond other uses, ashes are successfully tested in road construction, in several mortars, in cement groutings and in several environmental applications such as waste treatment, soils remediation and others.

Focusing on the use of fly ash as an additional component in concrete, despite of the technical and economical benefits, there are still some difficulties, mainly summarized to the following [5]:

- The inhomogeneity in the chemical (especially in CaO and $SO_3$ contents) and mineralogical composition, as they are by-products of a process aiming at the generation of energy and not at the quality of ash. Fluctuations occur not only between power stations but also, in the same station relating to the period of production (Figure 1 shows the fluctuation in chemical composition of the used fly ash coming from the Ptolemais Power Station during a period from January to September 2005). Remarkable differences, mainly in mineralogical characteristics, are also observed between ashes produced from the same lignite quarry but burned in different units of a power station.

- The necessity for supplementary grinding for better development of their pozzolanic and hydraulic properties. The retained on the 90 μm sieve is in the range of 15–20% while the relevant percentages on the 45 μm and the 200 μm sieves are 45–60% and 3–5% respectively.

- The elevated proportion of their free CaO as its hydration causes soundness problems as well as significant temperature increase. Ptolemais fly ashes have a remarkable free CaO ($CaO_f$) content which fluctuates between 2.7% and 8% (Table 1). The requirements for sound performance are more critical and serious as the amount and proportion of high calcium fly ash increases as part of the cementitious content of the concrete.

**Table 1: Free CaO in fly ash (source: Greek Public Power Corporation - PPC)**

| | January | February | March | April | May | June | July | August | September |
|---|---|---|---|---|---|---|---|---|---|
| **$CaO_f$** | 7,0 | 8,08 | 6,79 | 3,43 | 5,0 | 8,07 | 4,09 | 4,93 | 2,69 |

- The periodically elevated proportions of $SO_3$ content ($SO_3$ varies between 6.5% and 8% as depicted in Figure 1) and the upper limit of this range must be avoided because of expansion problems which may arise. Sulphates are mainly in the form of $CaSO_4$, coming from minimizing the released amount of $SO_2$, which is absorbed by the CaO, in the atmosphere.

The problems arising by the fluctuation of CaO and $SO_3$ levels in Greek fly ashes can be solved by the constitution of the 'Greek Plan of National Specifications' and the determination of limits within the composition and the characteristics of fly ash should range in order to be accepted for the use in concrete and its products. The 'Greek Plan of National Specifications', which was composed by the Technical Chamber of Greece/Department of Western Macedonia and completed with funds of the project "k-clusters: development of new products with use of fly ash from Western Macedonia" is expected to be ratified and incorporated into the Greek legislation.

Two types of fly ash exist according to the 'Greek Plan of National Specifications'. Type I refers to fly ash without any further processing and type II after grinding.

**Table 2: Categories of Greek fly ashes**

| | $R_{45}$ | $SO_3$ | $CaO_f$ |
|---|---|---|---|
| **Type I** | ≤45% | ≤7% | - |
| **Type II** | ≤30% | ≤5% | ≤3% |

Type I and type II fly ash hydrate develop significant strength capacity and their free lime content is completely bound [1]. The rate of strength development of type II is higher in comparison with that of type I. Both of them present pozzolanic character and their maximum strength level is attained at a 3-month age. Their addition to a mortar concrete mixture usually increases the water demand and slows down the rate of hardening [6].

During one research program conducted by CERTH/ISFTA with the aim of promoting the utilization the Greek fly ash a series of pilot scale production runs of paving blocks was accomplished utilizing high calcium fly ash from the Thermal Power Station of Ptolemais.

Paving blocks, which are industrial products of prefabricated unarmed concrete, having various dimensions and special morphology are used for pavement laying of residential projects carrying pedestrian and vehicular traffic such as roads, footpaths, car parks, driveways, squares etc.

The present study outlines the results of a research attempt aimed at developing and evaluating the performance of unprocessed high calcium fly ash incorporated in cement based products like paving blocks. During the pilot scale production emphasis was placed on the $SO_3$ levels of fly ash, which should not exceed the 5% threshold. Nevertheless as seen in Figure 1 this target was not possible to be met. Thus the paving blocks were produced with unprocessed fly ash. This fact led to the reduction of the cement replacement rate by fly ash because of the reduced reactivity of the unprocessed fly ash in comparison to the processed one [5, 7].

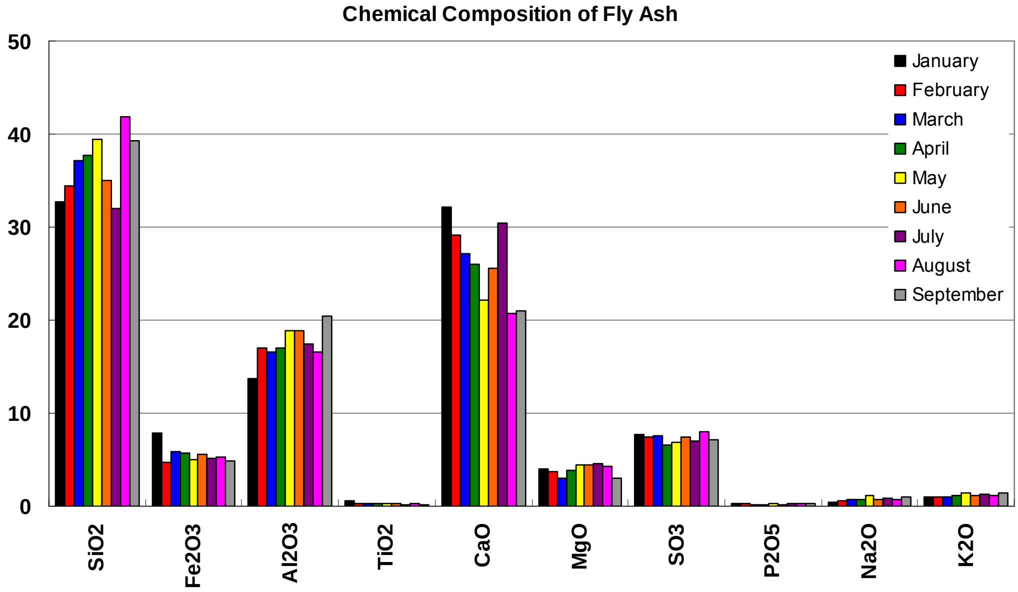



**Figure 1: Chemical Composition of fly ash during a specified period (January – September 2005, Source: PPC)**

Mineralogical analyses of the used fly ash were performed by means of X-Ray Diffraction procedures, using a Siemens D-500 spectrometer with copper Kα radiation.

The morphology was observed using a JSM-6300 JEOL Scanning Electron Microscope (SEM) operated with the typical accelerating voltage of 20 kV. The microscope was equipped with an Energy Dispersive X-ray Spectrometer with a Oxford Link ISIS system.

The main mineralogical phases identified in fly ash were: quartz, gehlenite, anhydrite and calcite.

A representative portion of each fly ash sample was sprinkled onto a double-sided carbon tape mounted on a SEM stub. This grain mount enables the analyst to determine the particle morphology, external surface structure and external elemental distribution of individual fly ash particles.

Each fly ash sample was characterized by randomly selecting 3-4 fields of view and examining all the fly ash particles observed within the selected fields. The elemental composition and morphology were noted for each particle and compiled for each sample.

Figure 2 shows a secondary electron image of a mapped region followed by nine elements (Na, Mg, Al, Si, S, K, Ca, Ti and Fe) chosen such that the fly ash particles could be identified from the maps. The SEM-EDX elemental profiles indicated a general increase in the content of Al, Si, Ca and Fe.

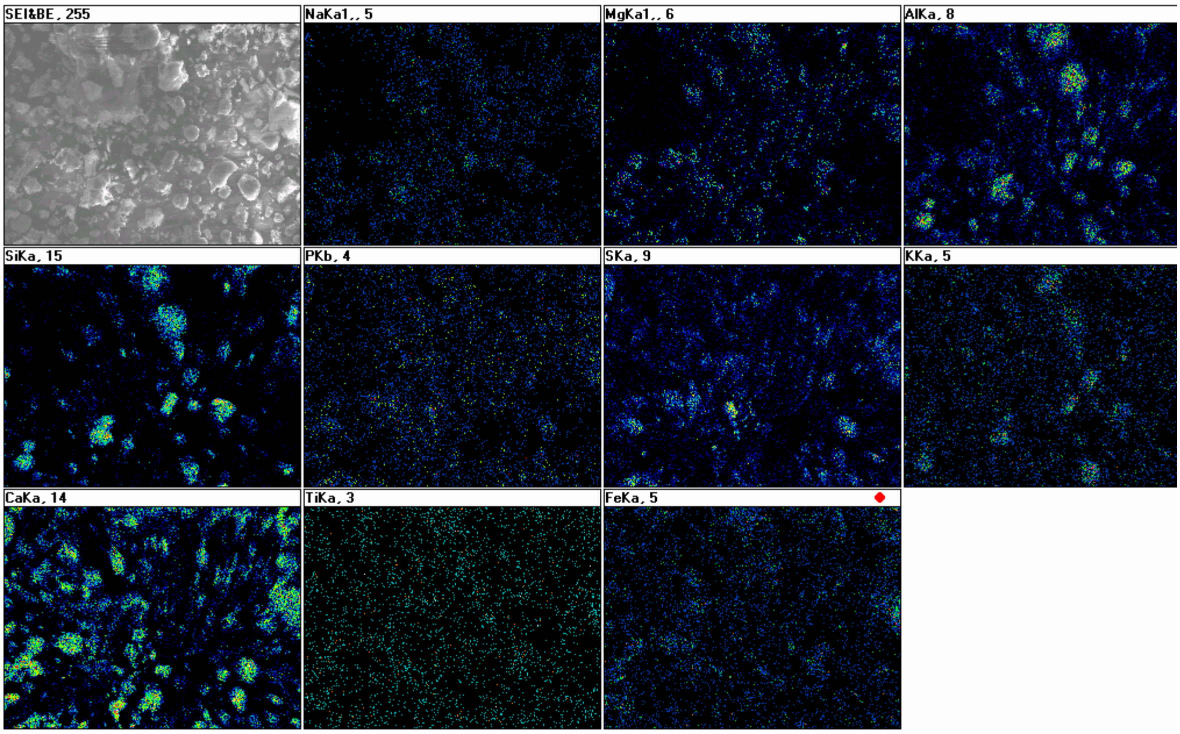
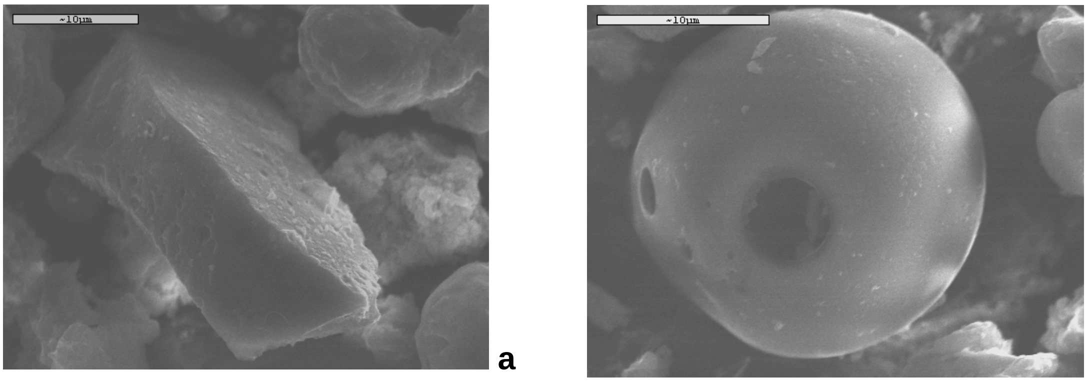



**Figure 2: SEM-EDX mapping. Secondary electron image of a randomly selected region and distribution of the selected elements Na, Mg, Al, Si, S, K, Ca, Ti and Fe**

The existence of certain mineral phases identified by XRD is confirmed by SEM procedures. Figure 3a shows quartz while Figure 3b an aluminosilicate phase containing calcium.



a b

**Figure 3: a) Quartz and b) Aluminosilicate phase rich in calcium**

PILOT SCALE PRODUCTION OF PAVING BLOCKS

For preparing the paste and mortar specimens a normal setting cement (CEM II 42.5 according to EN 197-1) was used. The mixing took place in a rotating blender (without any grinding of the fly ashes) until homogeneity of the blends was reached. A mix as given in Table 3 with fly ash replacing solely cement and not concrete and the incorporation of fly ash was used to produce a batch of 50 paving blocks. The specimens produced are designated here as Block 1 – Block 4 and Standard Block (conventional block for commercial use). The paving blocks were fabricated at a block factory in steel moulds having a rectangular shape and internal dimensions of 200 mm in length, 100 mm in width and 60 mm in depth. They were moulded in an automatic mechanized block-making machine, under a combined vibration and compacting force. The formed blocks were afterwards removed from the moulds and first cured under wet linen fabrics at room temperature for 10 days and further cured in air at room temperature until the age of 28 days.

However [8], the disadvantages of using fly ash in structural concrete can be avoided in concrete mixtures for mechanized moulded concrete blocks. This is because in manufacturing concrete blocks using a mechanized moulding machine, the mixed materials are moulded under a combined vibrating and compacting action. The requirement for maintaining a workable mix is not so important. Only a minimal amount of water is needed to make the mixture fluid enough to be fed into the moulding machine [9]. This reduces the difficulties of controlling the water/cement (w/c) ratio and workability. Also, the low water content of the concrete mixtures for the moulded blocks significantly reduces the creep and shrinkage of the hardened products.

During the production of the blocks the water to cement ratio was varied in order to facilitate the workability of the fresh concrete.

**Table 3: Mix proportions for paving blocks incorporated with unprocessed fly ash**

| Mix notation | Ratio of aggregates (0-1,5 mm : 1,2-2,5mm) | Cement (kg) II BW (S.P.W) 42,5N | Fly Ash (kg) | Blended cement and fly ash (kg/m$^3$) | Water (kg) | Cement substitution by fly ash (%) |
|---|---|---|---|---|---|---|
| **Block 1** | 5:1 | 40 | 15 | 285 | 16 | 20 |
| **Block 2** | 5:1 | 40 | 20 | 295 | 17 | 20 |
| **Block 3** | 5:1 | 35 | 15 | 280 | 16 | 30 |
| **Block 4** | 5:1 | 35 | 20 | 285 | 17 | 30 |
| **Standard Block** | 5:1 | 30 | 0 | 280 | 19 | 0 |

MECHANICAL PROPERTIES OF THE PAVING BLOCKS

Mechanical properties were determined partly at the age of 28 days and mainly at the age of 120 days. The produced blocks were subjected to tests conforming to the Greek standard EN1338 (paving blocks made of concrete – requirements and methods of testing). In general the early age strength is expected to be lower in the case where fly ash replaces cement [10].

Greek ashes [5] and especially those of Ptolemais origin are classified according ASTM as type C [11]. According to literature Ptolemais fly ashes have not only pozzolanic but also hydraulic behaviour [12, 13]. In all cases the sum of $Al_2O_3 + SiO_2 + Fe_2O_3$ is greater than 50% but less than 70%. Furthermore, the level of $SiO_2$ is higher than $CaO_f$ and the greater this difference is, the more is the tendency for the pozzolanic reaction between the constituents of fly ash (mainly reactive $SiO_2$) and the $Ca(OH)_2$ produced during the hydration of the mineral phases of clinker. It must be emphasized that the mineralogical composition and especially the amorphous siliceous and aluminous phases, in relation to the fineness of fly ash, determine how fast this material can react with lime [1, 14 and 15].

A series of tests were conducted to determine the compressive strength of the 28 day age and 120 day age specimens. All the below mentioned tests were conducted only on the specimens of 120 days age.

- compressive strength
- transverse strength (flexural strength)
- rupture strength

Compressive strength measured at 28 and 120 days revealed values slightly lower for blocks containing fly ash in comparison to the standard block without fly ash addition (Table 4). The strength of blocks containing fly ash can gradually increase with the time of hardening [16]. The compressive strength of block 4 measured at 28 days is lower than that of the other blocks (Figure 4) due to the higher content of fly ash. Thus its strength increasing rate, comparing the values of day 28 and day 120, is higher compared to the respective ones of the other blocks, a fact which is beneficial for its future strength development. The strength increasing rate is due to the reaction of $Ca(OH)_2$ with active silica and active alumina contained in fly ash which produces considerable amounts of hydrated calcium silicate (the main carrier of strength in hardened cement) and hydrated calcium aluminate.

The strength gain of the standard block can be compared to block 2 and this is because the early hydration rate of clinker contained in cement is accelerated by the fly ash addition and $Ca(OH)_2$ [17, 18]. Part of water can be absorbed by dehydrated clay minerals and free CaO which decreases the water to binder ratio. A low water to binder ratio is advantageous for the strength of cement. Thus for blocks with high ash contents (block 3 and 4) the decrease in strength is due to the reduction of the cement proportion in the mixture and the excessive $Ca(OH)_2$ generated from the reaction of free CaO with water a fact which is disadvantageous for the mechanical properties of cement.

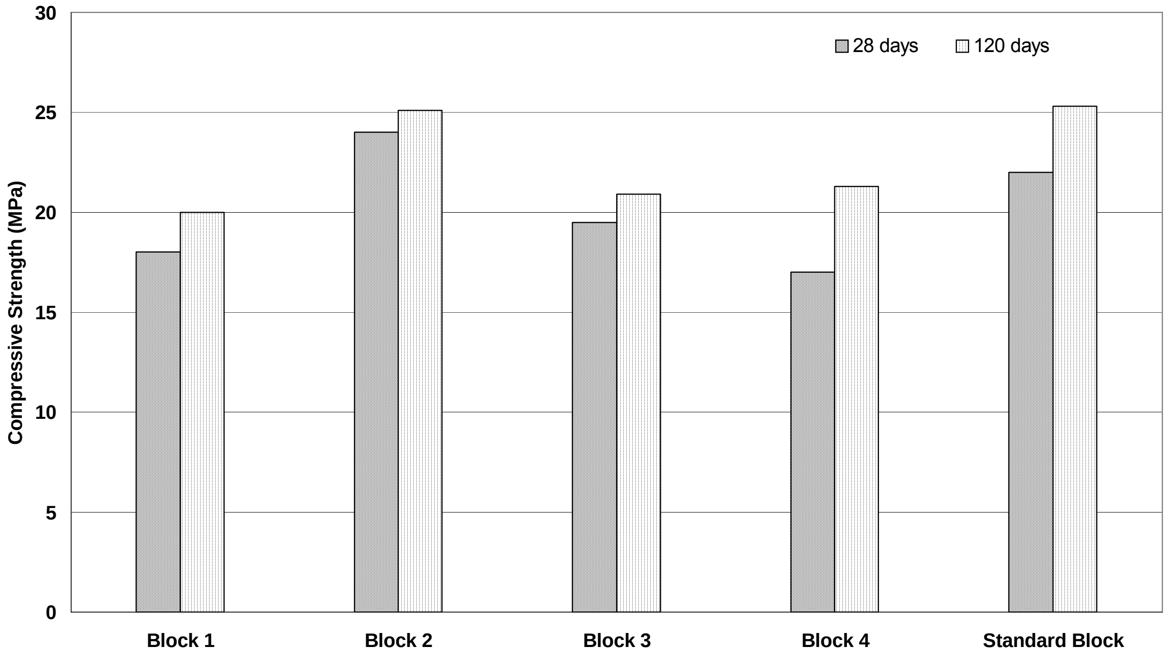



**Figure 4: Compressive strength gain of mixtures within time**

**Table 4: Compressive strength (%) of examined blocks compared to the standard block**

| Mix notation | 28 days | 120 days |
|---|---|---|
| **Block 1** | 83 | 80,0 |
| **Block 2** | 103 | 99,25 |
| **Block 3** | 89 | 82,6 |
| **Block 4** | 77,5 | 84,2 |

Flexural and rupture strength of the blocks are shown in Table 5. The variation in flexural and rupture strength correlated to the fly ash content was entirely consistent with the earlier remarks in the case of compressive strength.

**Table 5: Flexural Strength, Rupture Strength**

| Mix notation | Flexural Strength (MPa) | Rupture Strength (MPa) |
|---|---|---|
| **Block 1** | 2,6 | 1,0 |
| **Block 2** | 3,4 | 1,3 |
| **Block 3** | 2,8 | 1,3 |
| **Block 4** | 3,2 | 1,1 |
| **Standard Block** | 3,3 | 1,3 |

The ph of the blocks with fly ash (Figure 5) is in general lower than that of the standard block, a fact which is attributed to the bonding of $Ca(OH)_2$ by the reactive silicon of fly ash.

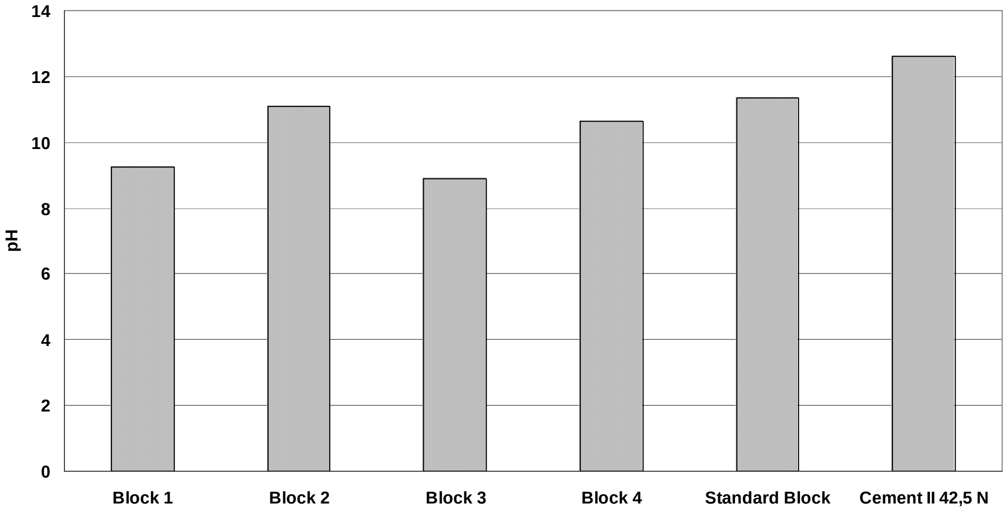



**Figure 5: pH of mixtures**

MICROSTRUCTURAL ANALYSES OF PAVING BLOCKS

The fly ash which was used for the pilot scale production was rich in $SO_3$ (~7%) and free calcium oxide (~6%). This chemical constitution could cause expansion problems, therefore the microstructure was investigated. According to literature [19] high free CaO and sulphur content may affect volume stability and concrete durability.

Small fractured samples of all compositions were subjected to stereoscopical analysis after a circle of drying and hydration of the blocks. Based on visual observation crystals of sulphates were not developed in the pores.

 a  b

**Figure 6: Stereoscope image of a) block 1 and b) standard block (magnified x25)**

According to the differential thermal analysis (DTA) of the blocks the free CaO has been totally bound by the reactive $SiO_2$ [7] of the used fly ash and is therefore absent from the TG-DTA diagram. This leads to the conclusion that free lime does not create any expansion or cracks in concrete.

Finally the absence of free calcium oxide in the cement products is identified by the XRD analysis of the blocks. Furthermore none of the blocks (except of block 4) contained ettringite, which is considered [20] as a mineral causing expansion problems, with concomitant formation of cracks, and thus leading to a reduction in strength development.

## CONCLUSIONS

The results obtained show that fly ash without any processing could replace cement up to 20% by weight. This replacement does not negatively affect the mechanical features of the cement products.

The unexpected positive results of the pilot process production were important because the project presupposed that ground fly ash was used in order to assure constant quality with elevated reactivity due to the grounding. Nevertheless the production supply with fly ash of specified quality should be aimed at. For the present study we were restricted to the fly ash utilization from unit IV of the Ptolemais Power Station during a limited period of time (not more than one month) something which restricts the inhomogeneity factors. It is also apparent that fly ash of fine grinding (above 45% remaining on the $R_{45}$ sieve) like the one applied can replace cement.

In addition the content of fly ash in free calcium oxide and sulphates does not seem to affect the strength of the blocks (for up to 20% cement replacement). The fly ash which was used can be classified as Type I according to the ‘Greek plan of National Specifications’ except of the criterion of fineness, which does not confine with the plan because the remaining percentage on the $R_{45}$ sieve is slightly above the specified level (57% instead of 45%).

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