APPLICATION OF MICROSCOPIC TECHNIQUES FOR STUDYING MICROSTRUCTURE OF AIR-ENTRAINED CONCRETES CONTAINING HIGH CALCIUM FLY ASH

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ABSTRACT

The possibility of using the high calcium fly ash (HCFA) as type II concrete additive is not well established, especially in relation to the durability of concrete structures in aggressive environment. The paper presents results of microstructural characterization of air-entrained concrete containing high calcium fly ash from lignite combustion. Frost resistant concretes were designed with different content of fly ash use for cement replacement by 15% and 30%. Different kinds of HCFA were used: raw (unprocessed) and grinded during 10, 15 and 28 minutes. The evaluation of the microstructure was performed using SEM and optical microscopy on thin sections and plane sections. All thin sections were impregnated with epoxy containing fluorescent dye and were examined using ordinary light, crossed polarized light and UV light. The thin section evaluation involved petrographic characterization of aggregates and examination of paste quality. Automatic air-void analysis on plane sections revealed air-content, specific surface, spacing factor and the content of micropores in the hardened concrete. Significant differences in particle shape and size before and after grinding of the HCFA were revealed by SEM analysis. The results of thin section analysis of the high calcium fly ash concrete showed that its microstructure was more dense than that of the ordinary concrete. The influence of specific surface of fly ash on air void content in HCFA concrete was found.

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1. INTRODUCTION

Lignite is one of the most common fuels used for power generation in European countries, especially in Middle and East Europe. The high calcium fly ash, a by-product of lignite burning, captured by electrostatic precipitators. It is very fine powder, exhibiting not only the pozzolanic properties but also hydraulic properties, originating from the presence of highly active constituents, such as reactive lime, reactive silica and alumina. The CaO content is within the range from 10 to 40% and therefore the so-called self-setting is observed, where CaO from fly ash plays a role of pozzolanic reaction activator or binding agent. For this reason high calcium fly ash is considered as a pozzolanic and hydraulic material, [1, 2]. HCFA also contain significant amounts of calcium aluminate glass which is more soluble than the glass in low-calcium fly ash and may slowly release calcium and aluminum into solution, [3].

According to ECOBA (European Coal Combustion Products Association) statistics, the amount of high calcium fly ash in Europe is more than 50% of the total fly ash produced by burning hard coal and lignite. The amount of high calcium fly ash produced in Poland is about 5 Mtons per year that corresponds approximately to 30% of the current cement production. Previous research [1,2, 4-6] suggest that there is considerable variability in the characteristics and hydration behavior of high calcium fly ash, and the subject deserves further investigations. Grinding is one of the most common method of the homogenization of fly ash.

The most widely known standards for the use of HCFA mineral admixture are the American ones, ASTM C618-08, [7] in which they were classified as category C and the relevant ASTM C311-90, [8] for sampling and testing. Canadian standards CAN3-A23.5-M82, [9] also cover the use of HCFA, [10]. In Europe it is beyond the scope of EN 450-1, [11] and EN 206-1, [12].

The objective of this investigation was to study the influence of high calcium fly ash, coming from selected power plant in Poland, on the microstructure of air-entrained concrete. Tests were carried out on several concrete mixes designed with a constant water to binder ratio and with substitution of a part of the cement by HCFA in such a way as type II additions are used according to EN 206-1, [12].

2. MATERIALS AND LABORATORY TEST METHODS

Materials, mixing and curing

The ordinary concrete without fly ash was made as reference concrete. High calcium fly ash concrete was made using 15% and 30% replacement of cement by HCFA. The coefficient of efficiency for HCFA was assumed $k = 0.4$. The chemical composition and loss on ignition of the cement and high calcium fly ash from combustion of lignite is presented in Table 1. Two kinds of HCFA were tested from different deliveries from the power plant, namely I – spring time, March 16th, 2010 and II – summer time, May 19th, 2010. The phase composition of fly ash was determined on the basis of XRF method. Totally six kinds of HCFA were used: ordinary (I) and grinded during 10 min (I/10), and 28 min. (I/28) from the first delivery, and ordinary (II) and grinded during 15 min (II/15) from the second delivery. The physical characteristics of the grinded high calcium fly ashes is presented in Table 2.

Table 1. Chemical compositions of cement CEM I 42.5 R and HCFA from two different deliveries

Constituent	CEM I 42.5R	Calcareous fly ash	
		I	II
SiO_2, (% by mass)	22.2	33.47	35.4
Al_2O_3, (% by mass)	5.3	19.19	21.86
Fe_2O_3, (% by mass)	3.0	5.37	6.11
$\Sigma\ SiO_2 + Al_2O_3 + Fe_2O_3$ (% by mass)	30.5	58.03	63.37
CaO, (% by mass)	66.3	31.18	25.58
SO_3, (% by mass)	0.6	4.33	4.22
CaO free, (% by mass)	1.3	3.43	1.24
MgO, (% by mass)	1.3	1.84	1.49
Loss on ignition, (% by mass)	0.2	2.56	3.43

High calcium fly ashes from both deliveries have similar chemical composition. Since that sum of contents $SiO_2 + Al_2O_3 + Fe_2O_3$ is lower than 70%, the tested calcareous fly ash does not meet the standard requirements of EN 450-1, [11]. However, the loss on ignition is quite low, as required.

In physical characteristics HCFA I and II differed from each other significantly. The specific surface of fly ash I was similar to specific surface of the ordinary cement Type I, but that of fly ash from the second delivery II was more than two times higher.

Table 2.Physical characteristic of the two high calcium fly ashes – I and II

No. of specimen	Specific gravity	Fineness – rest on the sieve 45 μm	Blaine's specific surface
	[g/cm^3]	[%]	[cm^2/g]
I/0*	2.62	38.0	2860
I/10*	2.77	23.0	3500
I/28*	2.75	10.5	3870
II/0*	2.58	35.4	4400
II/15*	2.70	13.3	6510

* consecutive numbers correspond to the grinding time in min., ex. 28 – grinding during 28 min.

The ordinary Portland cement CEM I 42.5R, siliceous sand fraction 0÷2 mm and the amphibolite as a coarse aggregate (two fractions 2÷8 mm and 8÷16 mm) were used. The air entraining admixture and the high rate water reducing admixture (HRWRA) were used to obtain,

respectively, a target air content between 5% and 8% and the slump between 110-150 mm. All concrete mixes were made with constant *w/b* ratio equal to 0.45, but the binder content was calculated as *b=c+k*fa* (*k*-coefficient of efficiency, content of: *b* – binder, *c*- cement, *fa* – fly ash). The composition of all concrete mixes and the basic properties of mixes are given in Table 3. The amount of chemical admixtures was adjusted to meet the designed slump and the designed air content.

Table 3. Composition of the concrete mixes and mix properties

Mix	Cement	HCFA		Aggregate	Water	HRWR	AEA	Slump	Porosity
		Origin/grinding time	content						
	$[kg/m^3]$	time	$[kg/m^3]$	$[kg/m^3]$	$[kg/m^3]$	$[l/m^3]$	$[l/m^3]$	[mm]	[%]
A-0	350	-	0	1890	158	2.1	0.5	140	8.0
A-15	298	I/0	133	1800	158	3.2	1.1	100	6.4
B-15	298	I/10	133	1800	158	3.2	2.5	120	6.0
C-15	298	I/28	133	1800	158	2.3	4.5	170	7.4
A-30	245	I/0	263	1710	158	7.4	3.0	200	7.0
B-30	245	I/10	263	1710	158	6.0	4.3	150	5.0
C-30	245	I/28	263	1710	158	5.0	6.0	200	5.0
D-15	298	II/0	133	1800	158	10.0	4.5	110	5.0
E-15	298	II/15	133	1800	158	6.0	7.4	140	5.0

HRWR- high range water reducer polycarboxylate ethers based, AEA- air-entraining admixture based on polyethylene glycol

The same mixing procedure was used for all concretes.
1. Dry mixing of aggregate for 3 min.,
2. Half the amount of water was added,
3. Cement and optionally high calcium fly ash was added and mixed for 1 min.,
4. Finally the rest of water with admixtures was added and mixed for 3 min.

For each of the series 150x150x150 mm cubes were cast. All specimens were demoulded one day after casting and placed in the moist room (95±2% relative humidity) for curing. At the end of the curing period of 28 days the specimens were removed from the moist room and prepared for the microscopic analysis.

Test methods

Scanning Electron Microscope

The samples was examined using Zeiss-SPURA Scanning Electron Microscope (SEM) in the secondary electrons (SE) mode using an acceleration voltage of 15 kV. The powder preparation was made from the fly ash samples. The preparations were coated with a thin layer (10 nm) of carbon using a Baltec SCD 005. The surface of analyzed preparations were at least 1.0 cm^2 (10x10mm).

Plane sections

Air-content *A*, specific surface *α*, spacing factor $\overline{L}$ and the content of micropores below 0.3 mm A_{300} in the hardened concrete specimens were measured with the PN-EN 480-11, [13] method on plane sections after 28 days. Technique of careful preparation of specimen surface was used and described in [14]. Flat specimens of planar dimensions 100×100 mm were polished with SiC

powders of different gradation. After polishing and before acceptance of the preparation the surface was inspected using a stereomicroscope to avoid acceptance of the surface with processing defects. The next step was coloring the surface with a blue marker, which is followed by filling the air voids by white, contrast paste. The surplus of the paste was removed and finally the surface was cleaned and protected using oil. At the end, the quality of preparation, especially the accuracy of the air-void filling by the white paste was controlled again under the microscope. If the quality of the surface was poor the whole treatment had to be repeated. A special program for automated air void analysis was used based on the linear traverse method was used. Each specimen was tested using 45-traverse lines. Digital image analysis of plane sections was performed using stereomicroscope Nikon SMZ 800 and Image Pro Plus image analysis software.

Thin sections
The fluorescent epoxy impregnated thin sections used for this study were prepared according to [15]. The concrete samples were cut in small blocks measuring 40 x 50 mm. The blocks were vacuum impregnated using a low viscous yellow fluorescent. After hardening one face of the block was ground using grinding equipment, which ensured plane parallel grinding throughout the process. After grinding the block was impregnated a second time, in order to ensure proper impregnation of the capillary porosity. After hardening the excess epoxy and part of the concrete beneath the impregnation surface was removed by grinding. An object glass was then glued onto the fully impregnated concrete and the block cut in such a way that about 1 mm of the impregnated concrete was left on the glass. The concrete slice was ground to thickness of 20-25 μm. The thickness was controlled manually by watching the birefringence change of quartz in crossed polarized light. As the last step a cover glass was glued onto the section prior to analysis, [15]. Thin section analysis were prepared using optical polarizing microscope Olympus BX51 connected with digital camera. The thin sections were examined in ordinary light, crossed polarized light (also with lambda plate) and fluorescent light.

4. RESULTS

Images from Scanning Electron Microscope
All the tested high calcium fly ash samples contained mainly spherical particles and conglomerates of spherical grains. Unprocessed fly ash form first delivery (I/0) contained spherical particles with predominant grain size between 8 and 12 μm and conglomerate both, spherical and irregular shape, mainly bigger from spheres, size from 60 to 70 μm. Fly ash after 10 minutes of grinding (I/10) was characterized by the same shape of particles as above, but it differed by the particles size. Fly ash I/10 contained spheres with main size from 10 to 16 μm and conglomerates – up to 50 μm. Occasionally, the parts of the spheres filled up with smaller regular and irregular shape particles have been seen. The HCFA after 28 minutes of grinding contained the smallest size of particles. Spherical grains – from 4 to 12 μm, and conglomerates – from 25 to 30 μm.

The particles of the high calcium fly ash from the second delivery, both ordinary II/0 and milled during 15 minutes II/15 have mainly spherical shape. Fly ash II/0 contains the particles with the average size of 10 μm and irregular grains shape larger than spheres, size 40 μm – 60 μm. It has been observed that surface of the spheres is smooth. The milled fly ash II/15 characterizes smaller spherical particles – 5 μm and conglomerate of both spheres and irregular

shape grains, 10 μm – 20 μm. The surfaces of the spherical particles differs from each other from in their morphology. The example of the SEM micrographs of the high calcium fly ash is shown in Fig. 1.

It seems that grinding of HCFA affected mainly irregular particles while glassy spherical particles were not crushed.
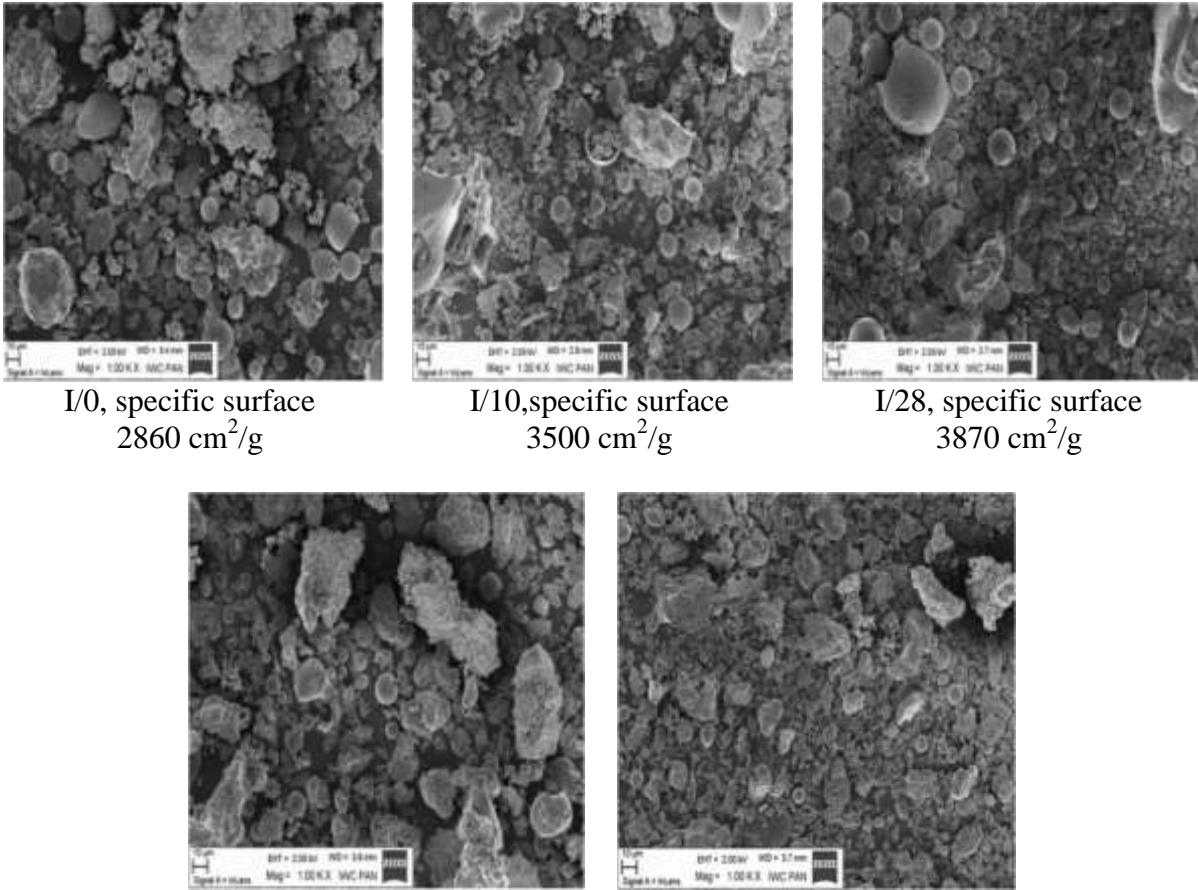
I/0, specific surface 2860 cm^2/g   I/10,specific surface 3500 cm^2/g   I/28, specific surface 3870 cm^2/g

II/0, specific surface 4400 cm^2/g   II/15, specific surface 6510 cm^2/g
Figure 1. SEM micrographs showing the morphology of the HCFA particles

Plane section analysis
The result of the of air-voids characteristics in hardened concrete is showed in Table 5.

Table 4. Air-void structure parameters in hardened concrete specimens according to EN 480-11

| Mix	Type of HCFA	cement replacement	paste content by volume	A	α	$\bar{L}$	A_{300}
		[%]	[%]	[%]	[mm^{-1}]	[mm]	[%]
A-0	none	0	27.1	7.36	22.49	0.16	2.80
A-15	I, grinded during 0 min	15%	30.5	4.17	18.64	0.30	1.36
B-15	I, grinded during 10 min	15%	30.5	2.59	17.76	0.39	0.92
C-15	I, grinded during 28 min	15%	30.5	3.35	20.90	0.30	1.04
A-30	I, grinded during 0 min	30%	33.8	2.73	33.25	0.21	1.43
B-30	I, grinded during 10 min	30%	33.8	2.27	27.56	0.28	1.21
C-30	I, grinded during 28 min	30%	33.8	3.10	24.13	0.28	1.44
D-15	II, grinded during 0 min	15%	30.5	3.73	25.82	0.23	1.86
E-15	II, grinded during 15min	15%	30.5	3.77	17.26	0.34	1.11

I, II – calcareous fly ash from first and second delivery, respectively

As it is given in Table 3, the addition of the high calcium fly ash caused of the reduction of the air content in the fresh mix. The air content in the hardened concrete was significantly lower. In reference concrete without HCFA the difference between air content in fresh mix and in hardened concrete was almost unnoticeable – 8% and 7.34%. With the prolongation of the grinding time of HCFA air content both in the mix and in hardened concrete were decreasing. In the fly ash from first delivery (I) the highest differences in porosity values were noticed for HCFA grinded during 10 minutes. The HCFA from the second delivery (II) did not show the significant differences in porosity between fresh mix and concrete.

In the Figure 3, the example of air void distribution in three concretes is presented. A commonly observed relationship between the increasing content of HCFA and the decreasing the air-void content in concrete is visible. There is also a tendency for increasing the specific surface of air voids for HCFA concrete. The analysis of the air-void microstructure of the high calcium fly ash concretes on the plane sections did not show any other particular relationship between content of the fly ash and air-voids characteristics.
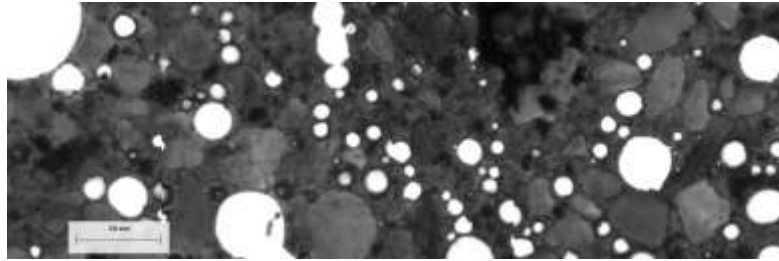
A-0, reference concrete without any addition of fly ash, A= 7.36%
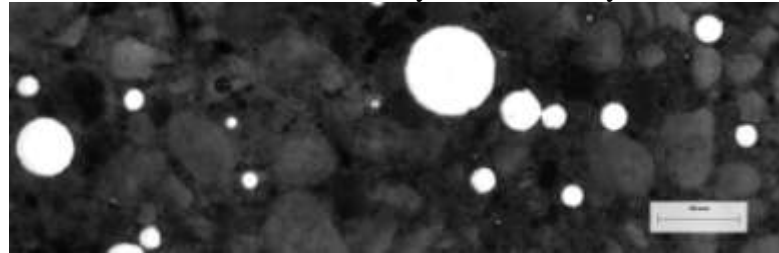
A-15, 15% of high calcium fly ash without milling, A= 4.17%
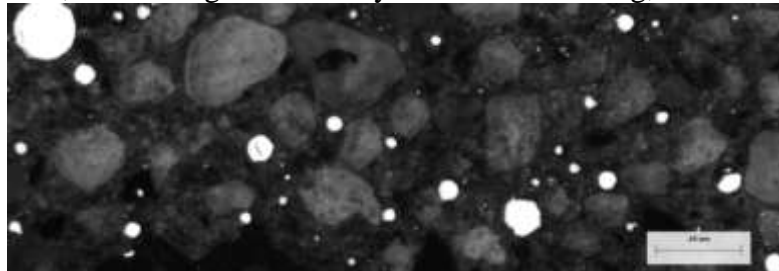
A-30, 30% of high calcium fly ash without milling, A= 2.73%

Figure 3. The example of the air-void microstructure taken on plane section

The content of micro air-voids (the diameter less than 300 μm), which play important role to provide the frost resistance of concrete is from 30% to 50% of total air-voids content. This results suggest that during the concrete mixing time mostly the large air-voids escaped and small ones were stabilized as required. The differences in the content of the air-voids in concretes made with HCFA from 2.27% to 4.17% influenced the spacing factor values which varied from 0.21 mm to 0.39 mm.

Additionally the content of the air-entraining admixture with reference to the specific surface of the high calcium fly ash has been studied, Fig. 4. For both 15% and 30% content of high calcium fly ash the content of the AEA increasing with increasing of the fineness of fly sh. The relationship between the content of air-entraining admixture and content of high calcium fly ash is found to be close to linear.
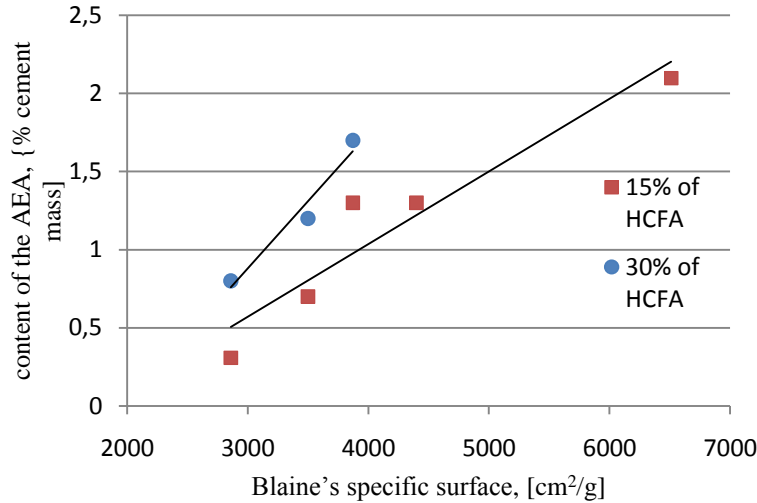
Figure 4. Content of the air-entraining admixture vs. specific surface of the HCFA for concretes made with 15 and 30% of fly ash

Thin section analysis

The tested concretes have been examined in ordinary light, crossed polarized light (also with lambda plate) and fluorescent light.

The aggregate used in this research was siliceous sand (fraction $0 \div 2$ mm) and amphibolite (fractions $2 \div 8$ and $8 \div 16$ mm). The observation made in the transmitted cross polarized light seemed to correlate with the mix design. The fine aggregate consist mainly of quartz which has smooth, rounded grains and very dense structure. The coarse aggregate, Fig. 5, amphibolite, consists mainly of amphibole, pyroxenes, plagioclase and biotyte. The structure of the grains is very dense.
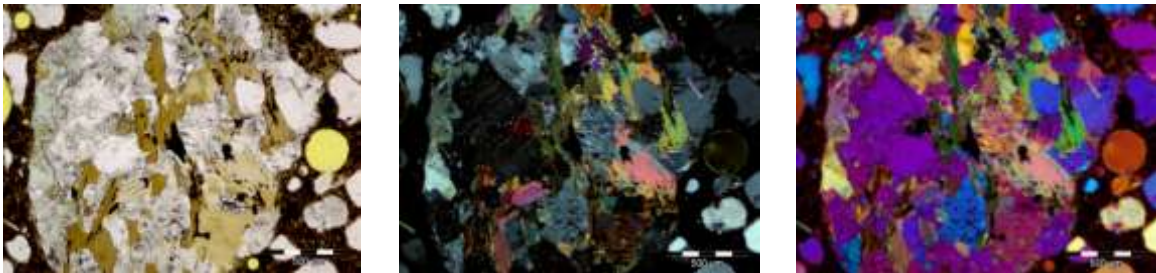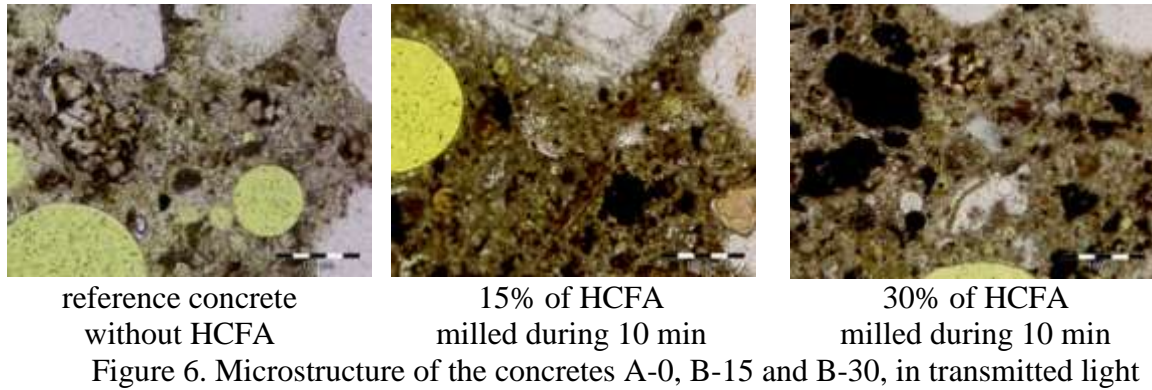

Figure 5. Images of concrete microstructure the coarse aggregate grain from concrete A-15; transmitted, cross polarized and cross polarized with gypsum plate light

All concretes appeared sound with a dense dark paste. The reference concrete contains the higher amount of cement grains conglomerates with visible alite, belite and ferrite grains than concretes made with HCFA. The content of the unburned carbon particles increases with the increasing of the addition of the high calcium fly ash, Fig. 6, so the color of the paste comes darker. Fly ash particles are observed in the paste in concretes with HCFA.

| reference concrete | 15% of HCFA | 30% of HCFA |
| without HCFA | milled during 10 min | milled during 10 min |

Figure 6. Microstructure of the concretes A-0, B-15 and B-30, in transmitted light

The air content of the samples were visually estimated and all in all seemed to correlate with the plane section analysis, Fig. 7. The volume of air-voids decreased with the content of the high calcium fly ash.
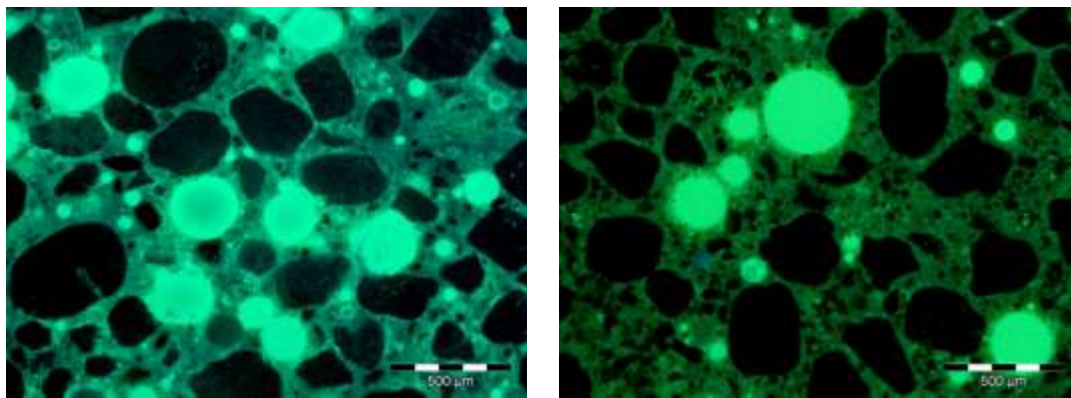
A-0, reference concrete without HCFA   A-15, 15% of HCFA without milling

Figure 7. Examples of the air-voids microstructure of concretes with HCFA, UV light

Additionally, ettringite needles have been observed in air voids in concrete C-15 (15% of HCFA after 10 minutes of milling), Fig. 8. The ettringite filled completely small air-voids (< 80 µm) and partially the larger air-voids. The air-voids with ettringite deposit are localized in whole thin section. It is not clear why such ettringite deposition have not been seen in other HCFA concrete specimens. This phenomenon could influence the frost resistance and scaling of concretes.
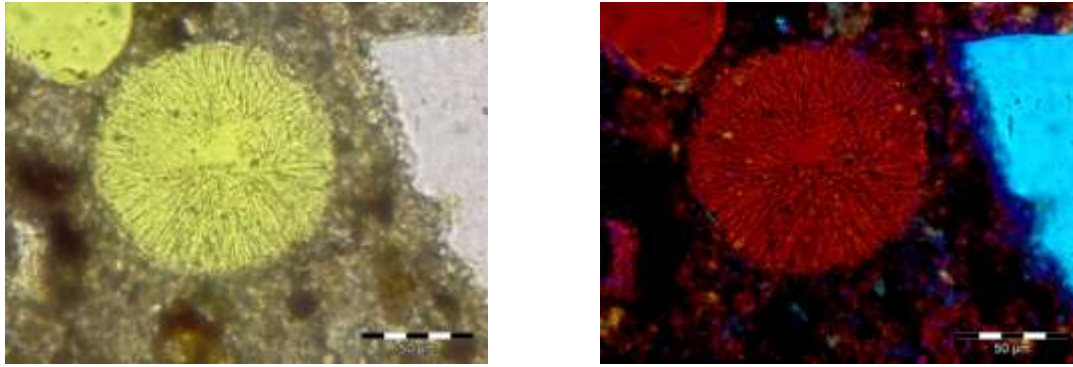
Figure 8. Concrete C15, the ettringite needles filing the air-void, picture taken in the optical microscope in transmitted light (left photo) and in crossed polarized light with gypsum plate (right photo)

5. CONCLUSIONS

The use of high calcium fly ash as type II addition in air entrained concrete was obstacle due to higher water demand and instability of air void system.

Application of microscopic techniques revealed the following features of concrete microstructure:

The thin section analysis revealed more dense microstructure of the cement paste in HCFA concrete than in the reference concrete. The content of the unburned carbon particles increased with the increase of the amount of the high calcium fly ash. Ettringite needles has been observed only in one concrete (15% of HCFA after 10 minutes of grinding) in air-voids, but the ettringite deposits were evenly distributed.

Plane section analysis revealed a decreased air-void content and spacing factor in hardened concrete due to the use of HCFA as type II addition.

SEM analysis revealed both spherical particles and irregular agglomerates particles of HCFA. Grinding of HCFA did not reduce significantly the content of spherical, glassy particles. A relation between specific surface of grinded HCFA and the amount of air entraining admixture needed achieve the target air content in the mix was close to linear.

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