Mixture of Lignite Fly Ash in Concrete: Physical and Mineralogical Characterization – Case Study from Ptolemais, Northern Greece

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ABSTRACT

The fly ash and the concrete, made by adding fly ash, were examined by means of mineralogical, chemical and physical analyses. Micro-cracks in the concrete appeared due to the reduced interconnection of the fly ash with the aggregates. Ptolemais fly ash may act as adhesive material filling the cracks of the concrete. Tests of the strength on models made by this concrete have shown comparable results in strength with reference concrete produced without ash. The use of fly ash in concrete does not affect its strength and sometimes it fills the cracks of the concrete mass.

INTRODUCTION

The Greek fly ash which is produced at the electrical power stations of Ptolemaida, Amynteon and Megalopolis belongs to type C fly ash. The type C fly ash which has high lime content (10-35%) is both pozzolanic and cementitious and presents hydraulic attributes. However Megalopolis' fly ash contains higher percentages of SiO2 in contrast with Ptolemaida's fly ash where the ratio CaO/SiO2 in fly ash content present fluctuations [1].

In Greece, previous work is mainly concentrated on the standardization of fly ash in order to be used by the construction industry [4], [3], [1].

The aim of the present work is to investigate the use of fly ash in concrete, using real conditions and trials. The mineralogical and chemical composition of the concrete produced is examined.

ANALYTICAL METHODS AND RESULTS

Selected samples of processed fly ash were collected from the electrical power station of Ptolemaida basin and were delivered to the company "Skyrodema Halkidikis Ltd." for the production of concrete essays. In parallel, the same fly ash samples were sent for mineralogical and chemical analyses at the laboratory of Economic Geology in the University of Athens. Concrete samples which were produced with fly ash, were examined for their mineralogical composition at the same Laboratory in the University of Athens, while the physical properties of the concrete were investigated in the laboratory of "Skyrodema Halkidikis Ltd".

The mineralogical composition of the samples was determined by using X-ray (XRD) diffraction, polarizing microscope and scanning electron microscope (SEM). Diffraction meter Siemens D-5005 type was used, copper tube and graphite monochromatographer. The mineralogical phases were determined by using computer and the software of Siemens Company (EVA) and the files of JCPDS. The Electron Microscope was JEOL JSM-5600 type also used for the chemical analyses of fly ash. The determination of concrete's physical properties was carried out according to the regulations of ELOT (1994) [2].

The materials used in this work for the production of concrete mixtures by cement and fly ash are described as following (Table 1):

- Cement: Type I/45 of "TITAN Ltd" company from Thessaloniki's unit.
- Aggregates: crushed limestone with a nominal size of 30mm produced by "Tagarades Quarry Ltd" which is based in Thessanoniki's area, and natural sand from Axios river.
- Fly Ash: from the electric power station of Ptolemais.

Table 1: Aggregates in concrete mixtures

Nr	Material	Quantity (kg/m^3)
1	Crushed limestone	532
2	Natural sand	570
3	Coarse Grained Aggregates	209
4	Fine Grained Aggregates	589

The replacement of fly ash to cement was made at the following rates: 10%, 20%, 30% and 40% by weight. The workability of all mixtures varied from 10cm to 11cm. The matrices which used were cubes of 15cm height made by cast iron. Five series of nineteen models were produced without fly ash of the same granulometry with the mixtures in which the concrete was replaced, 270 kg/m^3, type I/45 and of the same workability. The time of fractures was 24 hours and 3, 7, 14, 21, 28 and 60 days. Table 2 presents the number of crushed test models for each mixture and each time of fracture.

Table 2: Number of crushed test models per time.

Time	24h	3d	7d	14d	21d	28d	60d
Number of Models	2	2	3	2	2	6	2

RESULTS

The fly ash from Ptolemais is a fine divided material with granulometric composition (Table 3). According to the analysis, fly ash contains material with granulometry below 45μm (≥55% of its composition) in contrast with the rest of material which has granulometry 45-90μm.
The fly ash contains glass which consists the majority of its matrix, while there are dominant phenocrystals of minerals such as quartz, feldspars, gelenite, anhydrite, lime, portlandite and chlorite (Table 4, Figure 1).

Table 3: Granulometric composition (wt. %) of fly ash from Ptolemais

Size of Granules	Fly ash samples				
	T1	T2	T5	T6	TA
< 45μm	56.1	64.7	63.3	57.7	60.6
45-90μm	43.9	35.3	36.7	42.3	39.4
Total	100.0	100.0	100.0	100.0	100.0

Table 4: Mineralogical composition of fly ash from Ptolemais by using X-ray diffraction

Mineral	Chemical formula	Fly Ash				
		T1	T2	T5	T6	TA
Quartz	SiO_2	+	+	+	+	+
Feldspars	$(Na,K)AlSi_3O_8$	+	+	+	+	+
Gehlenite	$Ca_2Al_2SiO_7$	-	+	-	-	-
Anhydrite	$CaSO_4$	+	+	+	+	+
Lime	CaO	+	+	+	+	+
Portlandite	$Ca(OH)_2$	+	+	+	+	+
Muscovite	$KAl_2(AlSi_3O_{10})(OH,F)_2$	-	-	-	+	-
Gismondine	$CaAl_2Si_2O_84H_2O$	+	-	+	+	+
Chlorite	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_9$	+	+	+	-	+

Magnetite and hematite were also determined by means of SEM. These minerals are oxides of high temperature and resulted from the combustion of lignite at temperatures of 700-800°C. Fly ash cenospheres are typical of its structure and have diameter of around 20μm. Their chemical composition is presented in Table 6. Some unburnt particles were also found in fly ash, for which microprobe analysis showed the presence of Ca, Si, Al, Fe and Mg.

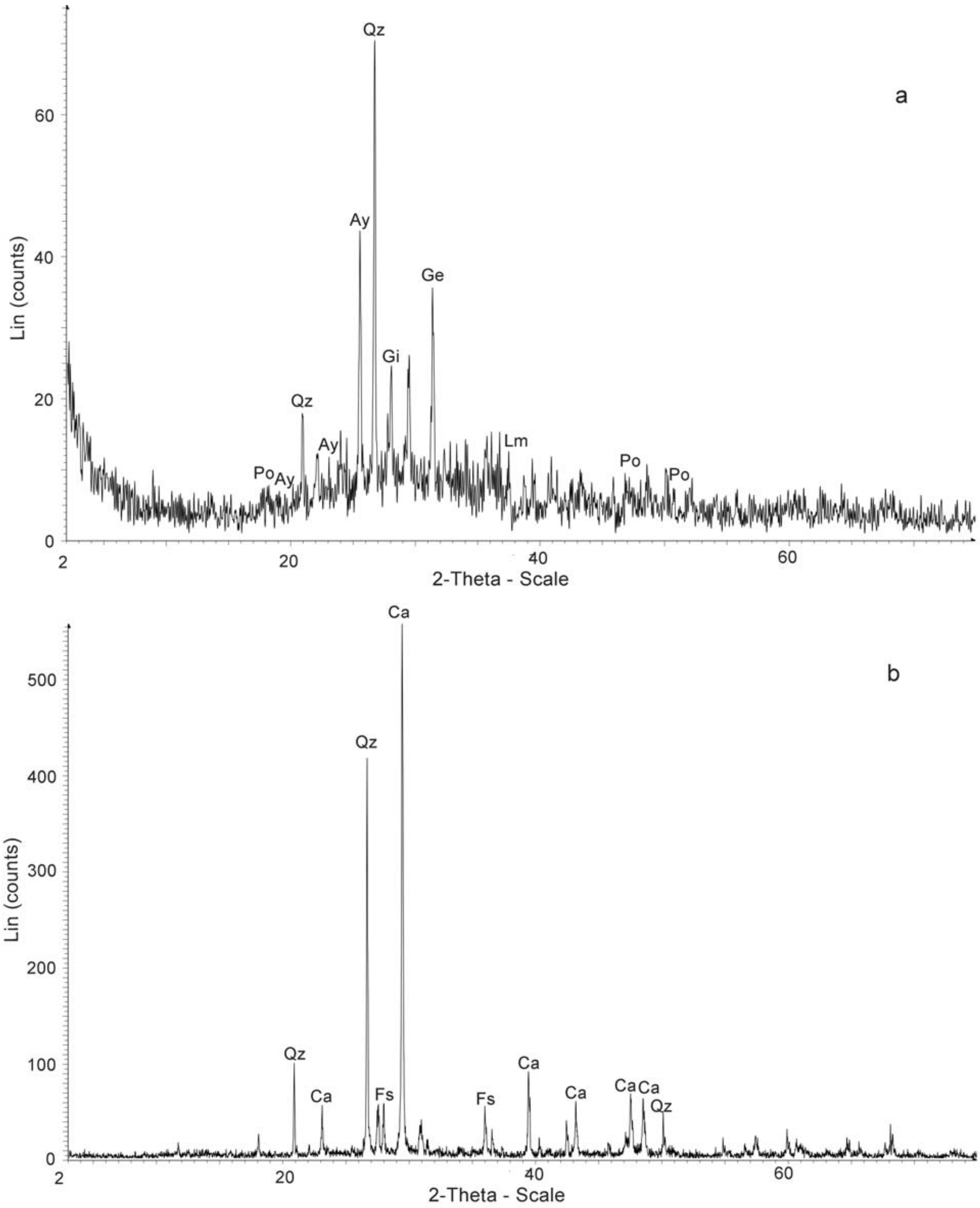

Figure 1: X-ray diffraction patterns .(a): Fly ash from Ptolemais, (b): Concrete with the fly ash (40%). Qz: Quartz, Ca: Calcite, Fs: Feldspars, Po: Portlandite, Lm: Lime, Ay: Anhydrite, Ge: Gehlenite, Gi: Gismondine

Table 5: Mineralogical composition of concrete, by optical microscopy of thin sections.

Mineral	Chemical formula	Concrete			
		1	2	3	4
Quartz	SiO_2	+	+	+	+
Feldspars	$(Na,Si)AlSi_3O_8$	+	+	+	+
Epidote	$Ca_2(Al,Fe)Al_2Si_3O_{12}(OH)$	+	+	-	-
Chlorite	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_9$	+	+	-	-
Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	+	+	+	+
Calcite	$CaCO_3$	+	+	+	+
Glass		+	+	+	+

Table 6: Chemical composition (wt. %) of fly ash.

	T1	T2	T3	T4	T5	T6	TA	Mean	Standard Deviation
SiO_2	30.11	28.55	28.93	29.10	30.54	31.84	33.78	30.41	1.8640
Al_2O_3	17.40	16.85	17.50	16.70	17.02	16.74	16.92	17.02	0.3168
TiO_2	1.01	0.52	1.36	0.89	0.80	0.94	0.85	0.91	0.2518
Fe_2O_3	7.34	6.19	6.16	5.82	6.71	7.01	6.04	6.47	0.5615
MgO	3.18	3.94	3.03	3.72	3.05	3.00	2.78	3.24	0.4221
CaO	26.85	26.02	27.69	27.78	26.22	23.91	22.57	25.86	1.9474
Na_2O	1.42	1.30	2.10	2.11	1.80	1.55	1.93	1.75	0.3275
K_2O	1.19	1.75	1.18	1.12	1.21	1.72	1.77	1.42	0.3071
SO_3	8.62	11.36	8.53	10.32	9.39	9.56	9.84	9.66	0.9816
Total	97.12	96.48	96.48	97.56	96.74	96.27	96.48		

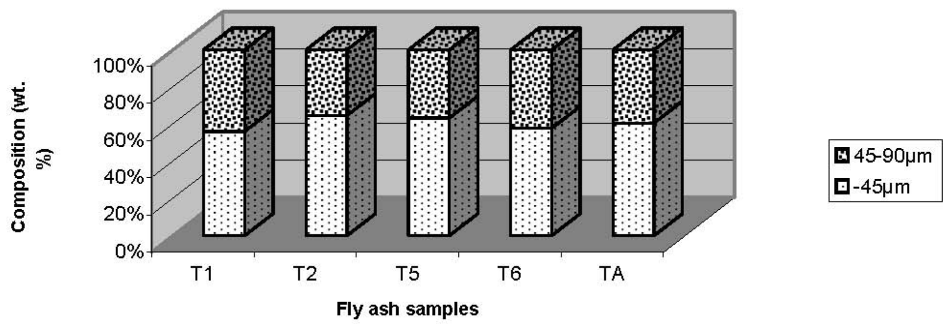

Figure 3: Granulometric composition (wt. %) of fly ash from Ptolemais

The concrete with high content of fly ash presents microcracks in the places where phenocrystals of minerals, such as quartz, are occurred. These microcracks are presented around the mineral crystals and in between them producing sometimes network of cracks in concrete (Figures 2d, 2e and 2f).

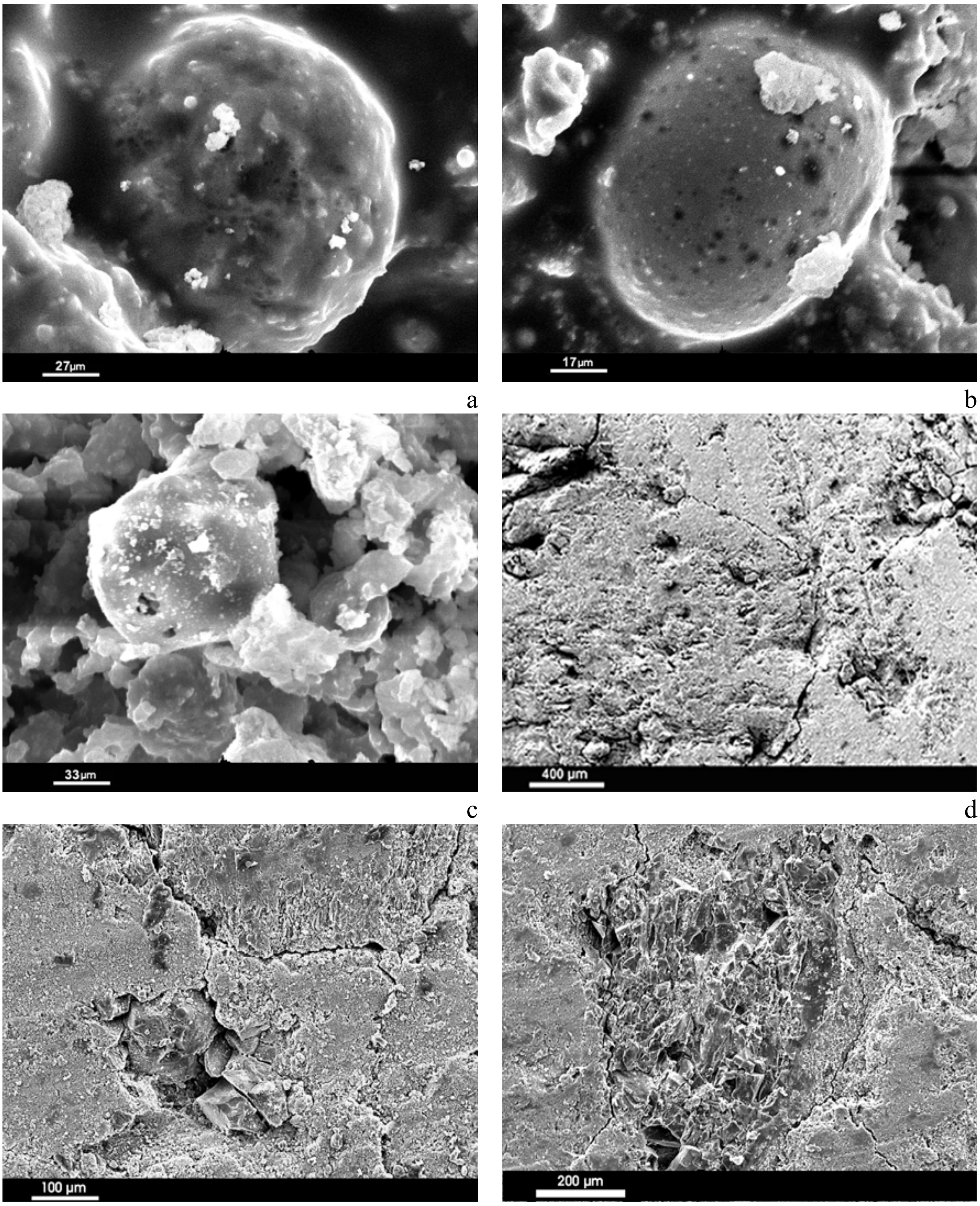

Figure 2: SEM images of fly ash and produced concrete. (a), (b): Typical shape of cenospheres in the fly ash of Ptolemais, (c): Crystalline phase in the fly ash, (d): Network of microcracks in the ground mass of concrete containing fly ash from Ptolemais, (e): Microcracks in the mass of the concrete which are due to the quartz crystals (center). The ground mass of the concrete is calcareous showing good assimilation of the fly ash and the other components, (f): The microcracks in the central part of the picture are originated around the quartz-calcite crystals assemblage.

Table 7: Chemical composition (wt. %) of cenospheres in fly ash.

	K1	K2	K3	K4	Mean	Std
SiO_2	47.17	43.43	43.59	34.95	42.29	5.1854
Al_2O_3	23.75	25.71	33.13	17.48	25.02	6.4458
TiO_2	0.67	0.31	0.22	2.90	1.02	1.2671
Fe_2O_3	6.39	5.00	3.08	7.21	5.42	1.8085
MgO	2.81	3.57	1.82	4.98	3.29	1.3298
CaO	10.93	6.80	6.65	25.55	12.48	8.9352
Na_2O	1.10	3.58	1.11	1.21	1.75	1.2211
K_2O	3.33	7.32	7.38	0.74	4.69	3.2441
SO_3	1.97	3.30	0.78	0.61	1.66	1.2484
Total	98.12	99.02	97.76	95.63		

Table 8: Mean values of compressive strength (kg/cm^2) of concrete mixtures produced by cement and fly ash (FA).

No	Percentage of FA in the Mixture	Compressive strength (kg/cm^2).							
		24 h	3d	7d	14d	21d	28d	60d	7d/28 d
1	10%	89,5	144	190	223,4	249	254,4	301	0,747
2	20%	62	115	162,3	194,6	199	245	276,3	0,663
3	30%	39,5	101,7	135,6	174	208	221,8	269	0,611
4	40%	40	80,5	111	143,7	162,8	191	216,9	0,581
5*	0%	97,7	168,7	221,4	251,8	280	288,9	304,6	0,766

* 5: Mean values of compressive strength (kg/cm^2) of reference.mixture.

Table 8 shows the mean values of compressive strength (kg/cm^2) of concrete mixtures produced by cement and fly ash. In all mixtures where fly ash is mixed in the cementious material, no problem was indicated. For the 30% of the models, the compressive strength test was carried out even after the maximum value and a model of two opposite cones was produced. As the percentage of fly ash used in the cementious material is increased, the water demand is also increased in order to achieve the required workability (Table 9). Mixtures with fly ash presented greater values of compressive strength after 28 days compared with the normal concrete. As the percentage of fly ash is increased, compressive strength is reduced at early time.

Table 9: Ratio of water (N) to cement (T + IT) and sedimentation

	Reference. Mixture (0% FA)	10% FA	20% FA	30% FA	40% FA
N / (T + IT)	0,797	0,811	0,825	0,860	0,865
Sedimentation (cm)	10,5	10,5	11	10,75	10

DISCUSSION-CONCLUSIONS

The fly ash consists of well crystallized rombohedral calcite microcrystals which are rich in Ca (calcite) (Fig. 4). The concrete's microstructure which is full of calcite, is the result of aggregate's cracking. The aggregates consist of limestone and therefore during the concrete's production the spaces in concrete covered by calcite.

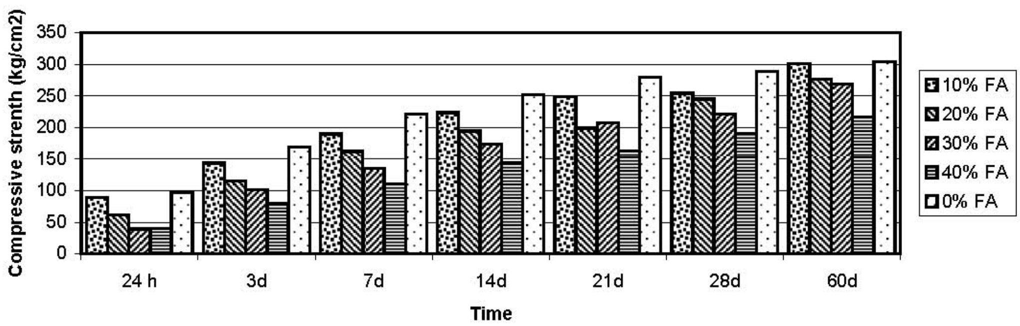

Figure 4: Mean values of compressive strength of the concrete mixtures produced by cement and fly ash (FA)

The appearance of fly ash, in small quantities, in between calcite assemblages indicates that the mixture was well developed resulting to the filling of all concrete's spaces. Quartz and feldspar crystals are heavily cracked and of ubnormal size, while biotile crystals are of short length and cracked, as well. Quartz and feldspar phenocrystals are of large size with diameter over 10 mm. Iron oxides are of spheroidal assemblage, and calcite is presented in large ubnormal crystals of diameter up to 3.5 cm. In the concrete which includes lower amount of fly ash, the matrix is not well-structured as result of the big participation of aggregates in the matrix.

Limestone aggregates result to well-structured matrix of concrete compared with this containing aggregates from metamorphic rocks and contain minerals such as quartz, feldspars and chlorite. This is due to the fact that calcite presents very good porosity and consequently ability to include large amounts of fly ash and cement during the production of concrete. On the contrary, quartz, feldspars and other minerals cannot easily agglomerated with the concrete's matrix.

Microcracks in between aggregates and the matrix (fly ash and cement), which appear in some parties of the concrete, are filled in with fly ash and well-oriented microcrystals of iron minerals. This indicates that these microcracks were developed at the early stage of concrete's production and fly ash and iron oxides covered the spaces and holes made later. This structure might be beneficial for concrete's strength.

However, small pores of diameter up to 30 μm and spherical shape were found in the limestone aggregates and might be resulted from microfossils. Smaller pores are presented in concrete's matrix. This indicates that concrete's materials are not homogenized and might be resulted to problems in the final product's strength. Nevertheless, the fly ash and cement well-covered all concrete's spaces and holes. As far as the compressive strength of the concrete is concerned, it is achieved later compared with the concrete without fly ash as result of the low interaction between fly ash and $Ca(OH)_2$. As the percentage of fly ash in concrete is increased, the compressive strength is decreased at early time.

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