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CHEMICAL AND MICROSTRUCTURAL CHARACTERISATION OF CONCRETE MINERAL ADDITIVES

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ABSTRACT. This paper summarizes chemical and mineralogical information on concrete mineral additives such as silica fume, fly ash from Mintia and metakaolin, as well as on concrete samples that were obtained by using these additives. The experiments were performed on seven concrete mixtures, with the following composition: S-1=standard concrete, S-2=concrete with 10 % fly ash (FA), S-3=concrete with 10 % metakaolin (MK), S-4=concrete with 10 % FA+10 % MK, S-5=concrete with 10 % silica fume (SF), S-6=concrete with 10 % SF+10 % FA, and S-7=concrete with 10 % SF+10 % MK. The XRD powder diffraction patterns on all these samples indicate the presence of amorphous phases, in particular in the silica fume, besides crystalline phases in metakaolin and the fly ash. The concrete samples consist of calcium silicates, calcium aluminates and calcium ferrites hydrates, calcium hydroxide, sulphated forms of calcium aluminates and respectively phases from the aggregates and the additives used. The particle size is sub-micrometric, with ash particles being the finest. Structurally, concretes are built-up of aggregate, cement matrix with hydration components, pores and “impurities”.

Key word*: concrete, pozzolanic additives, by-products, fly ash, metakaolin, silica fume*

INTRODUCTION

One of the major challenges for the modern society is global warming. This represents a consequence of increase amounts of greenhouse gases emitted in the atmosphere. The process of fabrication of the cement clinker takes place at high temperatures (around 1450 ºC); in order to produce this heat, one must use fossil fuels with high caloric capacity (coal, oil fuel or natural

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gas). As a result, huge amounts of gases are released in the atmosphere – the cement industry being one of the major producer of greenhouse gas [1,2,3].

Researchers all over the world focus their work on obtaining performant concrete types in which cement is partially replaced by various pozzolanic additives (fly ash, metakaolin and silica fume). By using such additives in concrete, less environmental pollution results not only by the decrease of the amount of clinker needed, but also by recycling industrial by-products (wastes) that otherwise require special measures for removal and storage. Moreover, additives used alone or in combination with other components enhance some concrete properties such as density, hydration temperature, mechanical resistance, slump, alkali-silica reactions etc [4-13].

Fly ash is obtained by electrostatic or mechanical separation of solid particles from fired gases in the industrial kilns using coal powder as fuel - as such, or in mixtures. In order to be suitable as concrete raw material, fly ash has to comply with the requirements of Romanian standard SR EN 450-1. Fly ash is a fine powder including sperical glass particles with compositions dominated by SiO_2 and Al_2O_3 showing good pozzolanic properties. Silica powder is a by-product of ferrosilica; it is currently one of the most common concrete mineral additives [14].

Metakaolin is obtained through calcination of clayey raw materials at temperatures between 700 and 800 ºC [15, 16], or as waste in specific technologies [17].

Pozzolanic additives such as fly ash, metakaolin and silica fume react with water in the presence of calcium hydroxide – the latter resulted from hydration reactions of the cement's mineralogical components. The resulting phases are calcium silicates and aluminates hydrates, similar to those forming in Portland cement.

The goal of this paper is to characterize from physical-chemical and mineralogical point of view some hydraulic additives such as fly ash from Mintia steam power plant, metakaolin obtained by kaolin calcination at 780 ºC and commercial silica fume. Additionally, we have investigated concrete samples obtained by partial replacement (10 % and 20 % respectivelly) of cement with such additives.

RESULTS AND DISCUSSION

Characterisation of cement

For obtaining the concrete mixtures, we have used Portland cement CEM I 42,5R (produced by Lafarge Romania) with the main properties summarized in Table 1.

Table 1. Characterisation of Portland cement CEM I 42,5R

Chemical composition (oxides, %)							
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	PC	SO_3	Insoluble
18.49	5.01	3.51	62.27	2.44	3.15	3.03	0.80
Physical characteristics							
Surface area (cm^2/g)		Stability (mm)		Hardening time (minutes)			
				initial		final	
3709		0.50		195		247	
Mechanical characteristics							
The compressive strength after 2 days (N/mm^2)				The compressive strength after 28 days (N/mm^2)			
28.30				46.60			

Characterisation of the mineral additives

The fly ash (FA) that we have used for obtaining the experimental concrete samples is produced as waste from coal burning in the Mintia (Deva, Romania) steam power plant. In our experiments we have used the particles with < 3 mm grain size. *Metakaolin* (MK) resulted by calcination of kaolin at constant temperature (780 ºC) for 3 h 40 min. S*ilica fume (SF)* is a product of BASF The Chemical Company (commercial name: Elkem Microsilica Grade 940-U-S).

Chemical composition

The chemical compositions obtained by traditional wet chemistry analyses of the fly ash, metakaolin and silica fume are presented in Table 2.

Table 2. Chemical composition (oxides %) of the concrete mineral additives

Oxides (%)/Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_4^{2-}	LOI
Fly ash, FA	49.67	26.33	7.66	2.42	3.68	0.13	10.11
Metakaolin, MK	58.77	36.22	1.20	1.16	0.43	0.12	2.10
Silica fume, SF	94.75	1.92	0.50	0.71	0.50	-	1.62

Mineral additives such as fly ash, metakaolin or silica fume are mainly consisting of silica, aluminium and iron oxides that react with $Ca(OH)_2$ resulted from the hydration of the cement components, leading to the generation of new calcium silicates, aluminates and ferrites hydrates respectively. Fly ash is relatively richer in MgO which may further be hydrated, thus negatively influencing the concrete properties. However, our XRD patterns show that MgO is not present as oxide, but chemically bond in magnesium silicates.

Mineralogical composition

The main mineral components of the Portland cement CEM I 42,5R, as calculated by using the Bogue equations based on its oxide composition are presented in Table 3.

Table 3. Mineralogical composition of the cement CEM I 42,5R

Component	C_3S	C_2S	C_3A	C_4AF
(%)	65.59	3.62	7.35	10.67

The mineralogical composition of the pozzolanic additives was investigated by X-ray diffraction on powders. The XRD patterns for the fly ash, metakaolin and silica fume are illustrated in Fig. 1.

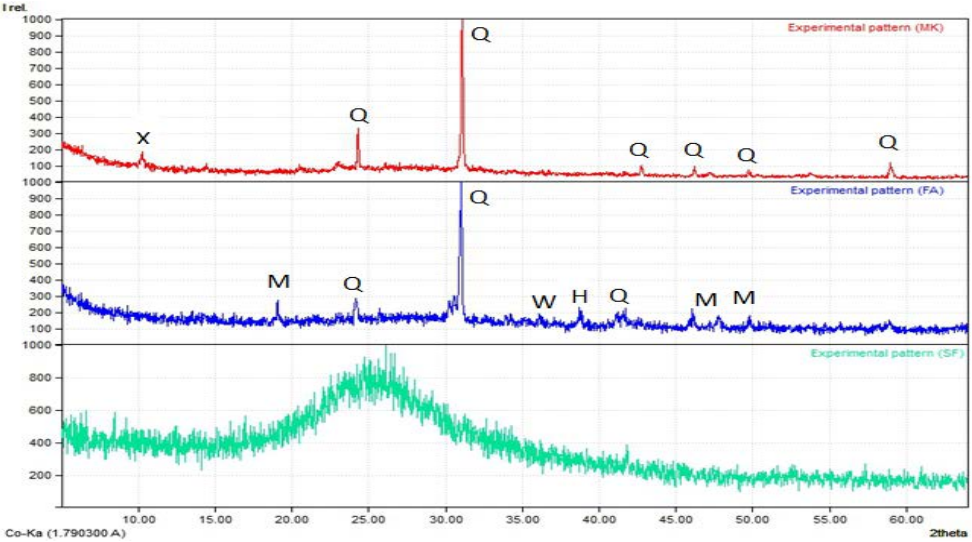

Figure 1. X-ray powder diffraction patterns of metakaolin (MK), fly ash (FA) and silica fume (SF). Q-quartz, M-mullite, H-hematite, W-wollastonite, X-$(K,NH_4,Na)Al_2(Si, Al)O_{10}(OH)_2$)

The metakaolin (MK) XRD pattern shows the peaks of high-temperature quartz (SiO_2) accompanied by less developed peaks of partly-transformed muscovite, $(K, NH_4, Na)Al_2(Si, Al)_4O_{10}(OH)_2$. These components are related to the “impurities” present in kaolin and they were not transformed during the thermal treatment. It is worthy to mention that the transformation products of kaolinite and the free oxides (SiO_2 and Al_2O_3) are mainly amorphous, the characteristic peaks being absent in the XRD pattern. This feature determines metakaolin to be highly reactive.

The fly ash has a complex XRD diffraction pattern that includes the characteristic peaks for quartz (SiO_2), hematite (Fe_2O_3), mullite ($Al_6Si_2O_{13}$), wollastonite ($CaSiO_3$) and a Mg and Fe silicate solid solution, $(Mg,Fe)_2SiO_4$.

The silica fume (SF) diffractogram evidences an amorphous material with no indication of crystalline phases. This explains the high reactivity of SF with the calcium hydroxide in the cement paste, with the formation of calcium silicates hydrates (C-S-H) and the enhancement of some properties of the concrete containing silica fume, such as hardening time and mechanical resistance.

Grain size distribution

Mineral additives are used in concrete compositions due to their reaction with $Ca(OH)_2$ resulting from the hydration of the clinker's mineral components in Portland cements. This reaction leads to the formation of new quantities of calcium aluminates and silicates hydrates that improve the mechanical properties of concretes. The reaction takes place at the contact surfaces between the particles. The smaller the particles, the larger their surface area and thus, the faster and more complete the chemical reaction. Also the fine pozzolanic additives determine the compaction of concrete due to pore filling processes – also leading to an enhanced mechanical resistance. Moreover, the increase in density also results from the crystallization of new phases in the larger pores, the pore surfaces triggering the crystallization of calcium hydrated components. The particle grain size distribution curves for the three studied additives are illustrated in Fig. 2.

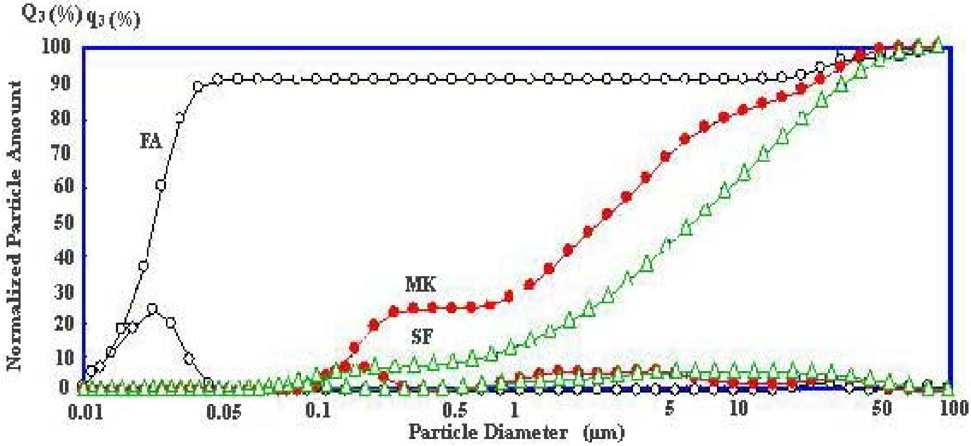

Figure 2. Grain size distribution of additives: FA- fly ash; MK – metakaolin; SF – silica fume

Fly ash, FA shows the finest grain size, with about 92 % of the grains being 0.041–0.010 μm, the rest of 8 % being 61–21 μm in size. The average grain diameter is 0.021 μm.

Metakaolin shows a wide grain size distribution in the 41–0.123 μm interval. Three sub-intervals can be separated: ~20 % of the grains are in the 41–12 μm range, ~50 % in the 10–1 μm range, while ~30 % in the 1–0.123 μm range. The average grain diameter is 2.5 μm.

Silica fume, SF consists of ~80 % grains with sizes in the 57–1 μm interval, while the rest are in the 1–0.90 μm interval; the average diameter is 6.69 μm.

Based on the particle size distribution and the resulting reactivity, one would expect the highest mechanical resistance values in the concrete samples obtained by using fly ash, FA. Nevertheless, reactivity is also controlled by the crystallinity degree of the pozzolanic material used. In our case, the best combination is present in the silica fume, SF – that is diffractometrically amorphous and shows micrometer-size grains. The expected higher reactivity was experimentally obtained in the concrete samples with silica fume as additive: these concretes show high mechanical resistivity even after short hardening times. In spite of their small particle sizes, the fly ash, FA and the metakaolin, MK show relatively lower reaction speeds with $Ca(OH)_2$ as a result of their higher crystallinity degree. This correlates with longer hardening times for achieving high mechanical resistance [18].

Characterisation of concrete samples

Mineralogical composition of the matrix

X-ray diffraction patterns were collected on mixtures of cement paste with additives, in the absence of coarse aggregate material. S-1 represents the standard composition for the cement paste without additives. S-2, S-3 and S-5 contain 10 % fly ash (FA), metakaolin (MK) and silica fume (SF) respectively. In the S-4, S-6 and S-7 mixtures, the cement was partly substituted as follows: 10 % fly ash and 10 % metakaolin in S-4, 10 % fly ash and 10 % silica fume in S-6, and respectively 10 % silica fume and 10 % metakaolin in S-7.

In all the studied mixtures, the water/cement+additives ratio was 0.4, while the amount of superplastifier (Adium 150) used was 3.15 l/m3 of concrete.

In order to identify the hydration phases formed in the hardened cement paste, the cement mixtures with pozzolanic additives but without SiO_2-containing aggregates were submitted to the same hardening conditions as the aggregate-containing concretes. After 28 days, ground powder samples were submitted to X-ray diffraction.

The XRD powder diffraction patterns for the studied mixt compositions are illustrated in Fig. 3.

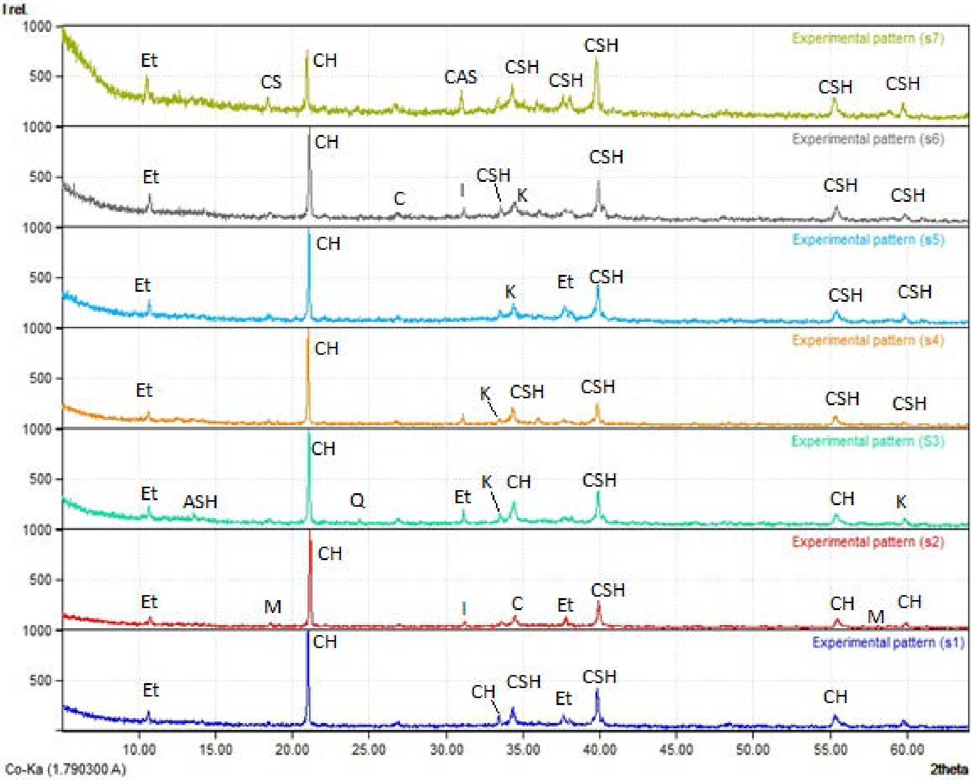

Figure 3. XRD powder diffraction patterns for the studied concrete samples (Et-ettringite, CH-portlandite, CSH-calcium silicate hydrate, CAS-calcium aluminosilicate, I-illite, C-calcite, K-kaolinite, M-mullite)

The XRD patterns reveal the mineral components in each of the studied concrete samples. In the references sample S-1 we have identified hydration products of calcium silicates ($Ca_{1.5}SiO_{3.5}xH_2O$, $Ca_3Si_2O_7 \cdot H_2O$), calcium aluminates ($Ca_4Al_6O_{13} \cdot 3H_2O$), calcium ferrites ($Ca_3(FeO_3)_2 \cdot 6H_2O$), calcium aluminoferrites ($Ca_{12}Al_{13,86}Fe_{0,14}O_{32}(OH)_2$), sulphated forms of calcium aluminates ($Ca_4Al_2SO_{10} \cdot 12H_2O$) and ettringite $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), besides $Ca(OH)_2$ resulted from the hydration of the mineral components.

In sample S-2, besides the cement hydration components we noticed also crystalline components from the fly ash: quartz, mullite and calcite. In sample S-3, the characteristic peaks of quartz are accompanied by those of calcite and clay minerals (kaolinite). The presence of kaolinite can be explained by an incomplete decomposition at the given firing temperature or by a partial hydration of metakaolin during the preparation of the cement mix. Kaolinite was also identified in sample S-4, which could be the cause for the lowest mechanical resistance at all hardening times for this type of experimental concrete.

In sample S-5, besides the typical hydration compounds we noticed diffraction peaks of calcium orthosilicate (Ca_2SiO_4); this can represent a still unhydrated clinker phase that needs longer time for reacting. Such a composition may explain the relatively higher mechanical resistance in concrete after long hardening times.

Calcium orthosilicate is present also in samples S-6 and S-7, besides crystalline phases from the additives (unhydrated iron phases, gehlenite or even kaolinite, the latter in sample S-7).

Optical microscopy

The optical microscopic study in polarized light performed on thin slices (20-25 micrometer thick) obtained from the concrete samples allowed us to identify and characterize some structural-textural and additional compositional features.

From structural point of view, the studied concrete samples consist of a relatively coarse aggregate (grain sizes between 0-16 mm) embedded in a fine matrix resulted by hydration reactions involving the Portland cement components, or additionally when it is the case, the ones in the mineral additive (FA, MK and SF). The structure is inequigranular, porphyroclastic[1], being characterized by the combination of relatively large aggregate particles and the fine matrix (Fig. 4).

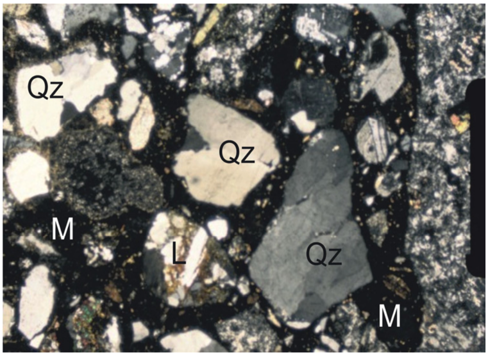

Figure 4. Porphyroclastic structure in sample S-3 with 10 % MK (N+). (Qz- quartz; L- aggregate clast, M – matrix) Scale bar=0.5 mm.

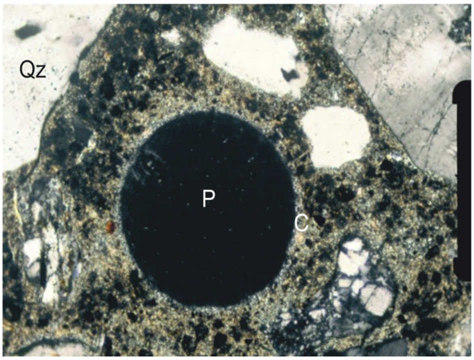

Figure 5. Spherical pore in sample S-1 – standard concrete (N+). (Qz-quartz, C-rim of posthydrating crystals Scale bar=0.5 mm.)

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[1] The structural term “porphyroclastic” is used here according to its petrographic meaning, concerning natural rocks: the “*porfiro”* prefix points to the presence of clasts (fragments) that are larger than the particles in the matrix, or the fundamental mass of the studied material.

The main textural feature is the presence of pores typically displaying spherical morphologies (Fig. 5). The pores in concrete provide the environment for the crystallization of the hydration products or for secondary alteration processes (carbonation). It is common that calcite is present along the inner pore walls or close to them, as a result of the carbonation process (Fig. 6). In later stages of this process, the matrix may be impregnated with secondary calcite; this may also crystallize on the surface of the aggregate particles (Fig. 7).

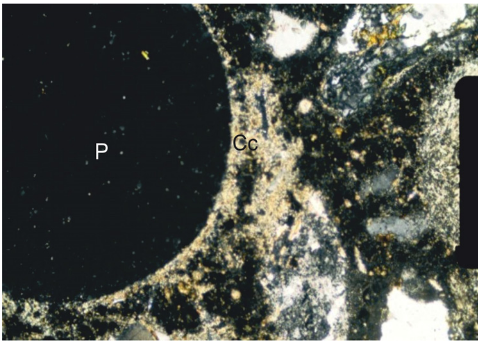

Figure 6. Detailed view of calcium carbonate (calcite-Cc) formed on the pore walls (P) in sample S-3 with 10 % MK, (N+). Scale bar=1.0 mm

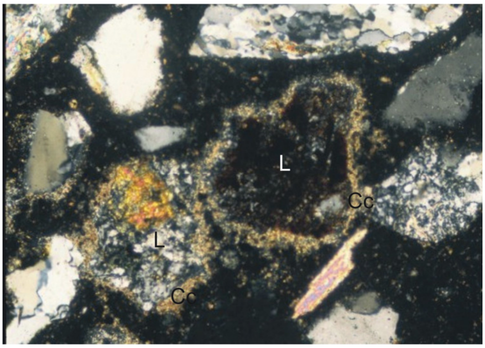

Figure 7. Calcite rim (Cc) on aggregate clasts (L) in sample S-5 with 10 % SF, (N+). Scale bar=0.5 mm

From compositional point of view, two main groups of components can be noticed in concrete: the aggregate, and the matrix.

The aggregate consists of fragments of minerals and rocks (the latter are called lithic fragments). The mineral fragments consist of quartz (Fig. 8), plagioclase feldspars, micas (muscovite), pyroxenes (Fig. 9), hornblende etc. The lithic fragments are represented by quartzites (dominating), volcanic rocks (dacites) and crystalline schists (*e.g.*, quartzitic schist; Fig. 9).

The investigated samples show a microcrystalline matrix consisting of calcium silicates, aluminates, ferrites, aluminoferrites hydrates etc accompanied by sulphated forms of calcium aluminates and ettringite, as well as portlandite. The latter phases are related to the mineralogical components of cement. The matrix also contains phases from the mineral additives, as well as products of the reactions between the cement components and water. Because of their very small sizes, the exact composition of the matrix grains cannot be defined by optical microscopy in polarized light; XRD patterns are more relevant in this respect.

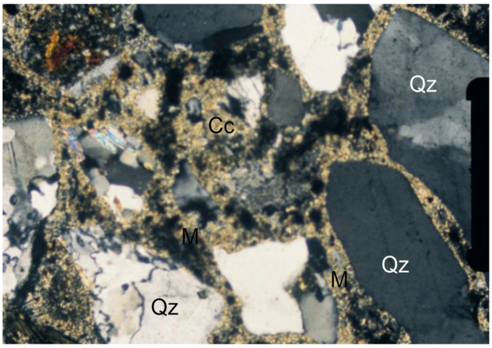

Figure 8. Aggregate components consisting of quartz clasts (Qz) embedded in intensely carbonated microcrystalline matrix (M) in sample S-4 with 10 % FA+10 % MK (N+). Scale bar=0.5 mm

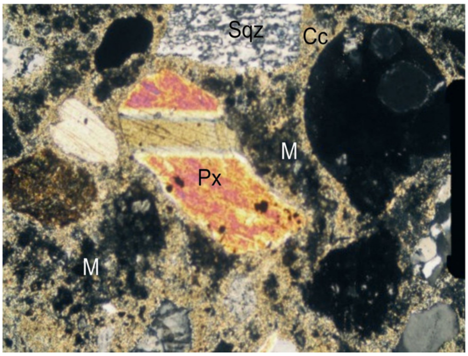

Figure 9. Pyroxene (augite) (Px) and quartzitic schist fragments (Sqz) embedded in intensely carbonated microcrystalline matrix (calcite-Cc) in sample S-4 with 10 % FA+10 % MK (N+). Scale bar=0.5 mm

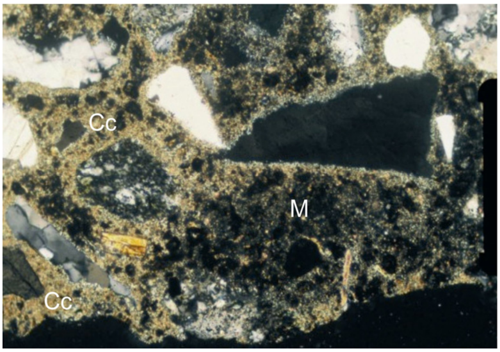

Figure 10. Fine crystalline matrix (M) impregnated with calcite (Cc) in sample S-2 with 10 % FA. (N+). Scale bar=0.5 mm

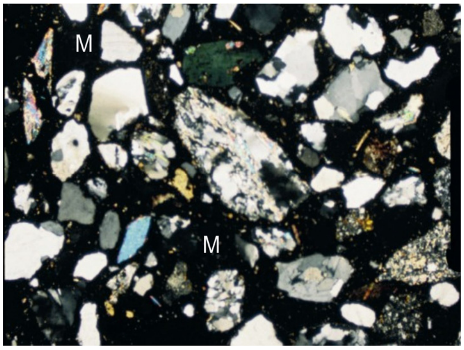

Figure 11. Isotropic matrix (M) with opacitization features in sample S-6 with 10 % SF+10 % FA (N+). Scale bar=0.2 mm

The matrix also contains calcite as secondary phase deposited along the pore walls, as rims on the aggregate clasts, or as impregnations in the matrix (Fig. 10). In some cases, the matrix is optically isotrope (due to the presence of hydration gels), with local opacitization trends (Fig. 11).

CONCLUSIONS

Hydraulically active cementoid additives such as fly ash, silica fume and metakaolin are used in concrete in order to improve its physical-mechanical characteristics, through reactions involving their mineralogical components.

By partial (10 % or 20 %) replacement of cement with such additives, the concrete performs better both fresh, and after hardening. The effect on the concrete properties is closely related to the characteristics of the additives. The studied additives contain high amounts of poorly crystallized, or even amorphous silica and aluminium oxides, which enhance their pozzolanic reaction with the $Ca(OH)_2$ resulting from cement hydration.

The grain size of the studied mineral additives is in the micrometer and nanometer range, thus determining their high reactivity with portlandite in the cement matrix.

The mineral components of the cement matrix are similar to those of a standard cement without additives; nevertheless, the relative content of free $Ca(OH)_2$ is lower, while new hydration phases are also present.

From microstructural point of view, the concrete consists of cement matrix, aggregate and pores. The matrix is dominated by the cement hydration products and by those resulted from the reaction with the pozzolanic additives. The aggregates consist of fragments of minerals and rocks. The mineral clasts are mainly represented by quartz, plagioclase feldspars, micas (muscovite), pyroxenes, and hornblende. The lithic fragments are dominantly quartzites, but also volcanic rocks (dacites) and crystalline (quartzitic) schists.

The pores in concrete provide the environment for the crystallization of hydration or secondary alteration (carbonation) products: on the inner pore walls or close to them calcite forms, as result of the carbonation process.

EXPERIMENTAL

The concrete samples were prepared in a cement mixer. The aggregates were successively added, in decreasing grain size order: 8-16 mm, 4-8 mm and finally 0-4 mm. After ~30 seconds of mixing, half of the water amount is added. Mixing continues for another 90 seconds. The rest of the cement and the mineral additives are then included in the composition and mixed in for 3 minutes. Then the rest of the water, including the additive is mixed together with the rest for 6 minutes. The final mixture is poured into standard moulds for mechanical tests. The moulds are covered with a foil and kept as such for ~24 h, after which the concrete samples are released from the moulds. These samples are then preserved in water at $20\pm2\ ^0C$ for 28 days. Samples from the resulting materials are ground as micrometer-sized powders and submitted to X-ray diffraction for the mineralogical investigation of the hydration products. For this, we have used a Bruker D8 Advance diffractometer with Co anticathode, in the 2 theta interval $5 - 65^o$.

From the concrete samples S-1, S-2, S-3, S-4, S-5, S-6 and S-7 we have obtained 25-30 micrometers thin sections that we used for the optical study with polarized light under a Nikon Eclipse E 200 microscope.

The grain size distribution for the cementoid additives (fly ash, silica fume and metakaolin) was studied by using a Counter Coulter WING-SALD 7101 granulometer.

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