THE EFFECT OF POZZOLANA ON THE PROPERTIES OF THE FINEST FRACTION OF SEPARATED PORTLAND CEMENT. PART II

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The finest cement fraction is collected in the sleeve filters during cement clinker milling. It is estimated that after the first 24 hours of hydration the finest cement fraction is characterized by a high initial compressive strength. Moreover, in this fraction, the ettringite that is formed during the hydration due to high gypsum content reduces the strength of samples. The addition of natural pozzolana (tripoli) ensures a stable structure of cement stone. The amount of portlandite significantly decreases or completely disappears; also most of ettringite decomposes during the hardening of samples containing tripoli. After one day of hardening, the compressive strength of the finest cement fraction samples containing tripoli increases to 15-20 MPa. After 28 days of hardening, the compressive strength reached over 32.5 MPa. The finest cement fraction containing tripoli additive may be used as a separate product of cement manufacturing, distinguished by early hardening.

INTRODUCTION

The finest cement fraction is collected in the sleeve filters during cement clinker milling. This fraction contains much more SO_3^{2-} (5.63 %) and has a higher specific surface area (1340 m^2/kg) as compared to ordinary Portland cement (OPC). These essential distinctions indicate a peculiar course of hydration of the finest cement fraction. The formation of ettringite is initiated by an elevated amount of gypsum during the process of hydration [1, 2].

One of the most often analysed and used additions to Portland cement is silica fume. Condensed silica fume is a by-product of the manufacture of silicon or silicon alloys which are produced in submerged arc electric furnaces. Silica fume particles appear to be formed by the oxidation and condensation of the gaseous silicon sub-oxide SiO produced in the reaction zone. Silica fume is mainly amorphous and has an about 2000 m^2/kg surface area and thus a good pozzolanic activity [3].

Many authors claim that silica fume (SF) is an effective addition increasing the strength of Portland cement and its resistance to the sulphate attack. SF addition enhances the rate of cement hydration and accelerates both C_3S and C_3A hydration during the first few hours [4]. When silica fume is added to fresh concrete, it chemically reacts with Portlandite (CH) to produce additional calcium silicate hydrates (CSH). The benefit of this reaction is twofold: increased compressive strength and chemical resistance [5]. Silica fume replacement also causes a significant increase in sulphate resistance of a mortar even at the highest sulphate concentration [6]. Mangat and El-Khatib [7] have outlined that the sulphate resistance of concrete increases with the replacement of cement containing 9% of silica fume. The possible common factor which leads to this improved sulphate resistance is the reduced $Ca(OH)_2$ content which leads to a smaller volume of expansive reaction products containing sulphate ions.

Lee et al. [8] showed that the presence of silica fume had a beneficial effect on the loss of strength due to sodium sulphate attack. The best resistance to sodium sulphate attack was obtained with SF replacement of 5-10 %, but even then, a strength loss of 15-20 % can be expected. Vuk et al. [9] found that only the addition of silica fume to limestone cement significantly improved its sulphate resistance. Zelic et al. [10] have reported that the addition of silica fume results in less CH formed by the hydration process and consequently less gypsum and ettringite during the sulphate immersion of mortars. Moreover, silica fume can increase the resistance of quality concrete to chemical attack by several aggressive chemical environments. The key reasons for the increased resistance due to silica fume addition are permeability reduction and a reduction or a complete elimination of the free calcium hydroxide in concrete. Additional factors are that the calcium silicate hydrate paste formed with silica fume is reported to be more stable in low pH environments, and the higher polymerization of this paste enables it to tie up potentially reactive ions such as alkali and aluminum [11].

Additions of natural pozzolana may also be used for eliminating the negative effect of sulphate attack. The low basicity and permeability resulting from the presence of pozzolana increase the resistance of concrete to lime leaching, sulphate and sea water attacks and also to chloride penetration [12]. Shannag and Shaia have reported that a concrete mix containing 15% of natural pozzolana and 15% of silica fume showed the best protection in sulphate solutions and sea water. It retained more than 65 % of its strength after one year of storage in sulphate solutions and sea water. The superior resistance of that mix against sulphate attack is attributed to the pore refinement process and the further densification of the transition zone occurring due to the conversion of lime formed from the hydration of cement into an additional binding material through the lime-pozzolana reaction [13].

This work aimed at investigating the influence of silica fume and natural pozzolana (tripoli) on the properties of the finest cement fraction.

EXPERIMENTAL

The finest cement fraction samples were selected from the sleeve filters by grinding the quickly hardening Portland cement (CEM I R (LST EN 197), with up to 5 % of limestone added to this cement during grinding. Samples of ordinary Portland cement were prepared in a laboratory grinding-mill by grinding cement clinker with a 4.47 % additive of gypsum up to a specific surface area - 341 m²/kg.

Tripoli was used as natural pozzolana. Tripoli, a sedimentary rock, basically consisting of amorphous silica, represents a grey, light porous material. About 85 % of tripoli composition consists of opal mineral. Also small amounts of quartz, chalcedony, calcite, glauconite are found in tripoli. Hydraulic activity of pozzolana is 290 mg CaO/g.

Silica fume "Fesil" was used as synthetic pozzolana. "Fesil" consists of microgranules, thus its specific surface area is quite small (S = 141 m²/kg). Meanwhile the hydraulic activity of silica fume is high and equals 340 mg CaO/g.

The chemical analysis and phase composition of the raw materials - ordinary Portland cement (OPC), the finest fraction collected in the sleeve filters (S), silica fume (SF) and natural pozzolana - tripoli (T) - are shown in Table 1.

Samples for compressive strength analysis (prisms 4×4×16 cm) were formed following the standard LST EN 196 - 1÷3 (cement and sand ratio was 1:3 by weight). Therefore the water and cement ratio (W/C) was determined to be 0.6, as the standard water content (W/C = 0.5) is too small to form the samples. During the first day, the samples are kept in forms at 20 ± 1°C and 100% air humidity. After 24 hours of formation, the specimens were transferred into water and kept at 20 ± 1°C. To make a more exact estimation of the hydration process, the samples for XRD, DTA and IR-spectroscopy were prepared without sand usually used. The conditions of keeping the samples were analogous to those applied during strength test.

Thermal analyzer Du Pont 990 with computerized control and data recording was applied for differential thermal analysis (DTA) studies. The heat test was conducted in open-air and ranged from 100 up to 1000°C with increments of 10°C/min. The aluminum crucibles and Al_2O_3 as inert material were used. The X-ray powder diffraction data were colleted with DRON-6 powder X-ray diffractometer with Bragg-Brentano geometry using Ni filtered CuK_α radiation, operating voltage 30 kV and emission current -24 mA. The step-scan covered the angular range 5-60° (2θ) in steps of 2θ = 0.02°. IR spectra have been measured by the spectrometer Perkin Elmer FT–IR system Spectrum X. Samples were prepared by mixing 1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range 4000 ÷ 400 cm⁻¹ with spectral resolution of 1 cm⁻¹.

Table 1. Chemical and mineralogical composition of the starting materials, (wt.%).

Determined Parameters	Samples			
	S	OPC	SF	T
SiO_2	17.85	19.72	96.7	77.6
Al_2O_3	5.04	5.41	0.31	7.02
Fe_2O_3	4.36	4.21	0.22	1.9
CaO	57.24	62.76	0.9	5.61
MgO	3.77	3.41	0.24	0.97
Na_2O	0.26	0.16	0.18	0.3
K_2O	4.17	1.08	0.55	0.46
SO_3^{2-}	5.63	2.08	-	-
Ignition loss	1.52	0.93	0.7	5.0
Insoluble residue	0.16	0.24	0.2	1.14
Specific surface area, m²/kg	1340	341	141	1112
$3CaO·SiO_2$	57.21	63.19	-	-
$2CaO·SiO_2$	8.02	8.87	-	-
$3CaO·Al_2O_3$	5.98	7.21	-	-
$4CaO·Al_2O_3·Fe_2O_3$	13.27	12.81	-	-
Hydraulic activity, mg CaO/g.	-	-	340	290

RESULTS AND DISCUSSION

In the initial stage of the study, the influence of silica fume addition on the properties of the finest cement fraction was determined. Strength analysis was performed using pure finest cement fraction samples with the addition of silica fume of 0, 5, 10 and 20 wt.%. The compressive strength of the prepared prisms was measured after 1, 7, 28 and 180 days. The results are provided in Figure 1.

The pure samples of the finest cement fraction reach their maximum of compressive strength after 7 days of hydration, but afterwards it starts to consistently decrease (Figure 1, curve ▲). The compressive strength of samples containing silica fume additive depends on the amount of this addition. The curves containing 5 and 10 wt.% silica fume additive are similar, because until the 28th day of hardening the strength increases. However, after 28 days of hardening the compressive strength starts to decrease (Figure 1, curves ■, ◆), as in the case of pure samples. When the amount of silica fume additive was increased up to 20 wt.% (Figure 1, curve ●), the compressive strength of samples steadily increased within the time interval studied. Samples containing any content of silica fume had a higher compressive strength than did samples without additions after both 28 and 180 days of hardening; the only exception was the sample with 20 wt.% silica fume after 28 days of hardening.

After the first day of hardening (Figure 2a) formation of portlandite (*d*-spacing: 0.493, 0.262, 0.179 nm) and peaks of calcium carbonate (*d*-spacing: 0.386, 0.332, 0.209 nm) caused by the limestone additive were observed. However, peaks of non-hydrated cement minerals were not identified in any of the samples. Thus,

cement minerals were fully hydrated during the first day of hydration. An extremely rapid process of hydration may be explained by a large amount of small cement particles [2].

In pure samples of the fine fraction, the intensity of CH peaks during the entire process of hydration remained almost unchanged. Moreover, the intensity of CH peaks in samples containing silica fume continuously decreased when the amount of silica fume and the duration of hydration increased. The basic reflections of CH in the samples containing 20 wt.% silica fume were lowest, and only traces were observed after 6 months of hydration (Figure 2d, curve 3). This fact is related to the reaction of $Ca(OH)_2$ with amorphous SiO_2 and the formation of amorphous secondary calcium silicate hydrates.

The decrement of strength of the pure finest cement fractions, or compounds containing 5 and 10 wt.% of silica fume additives is related to the formation of ettringite during the process of hydration. In all the samples ettringite was found as soon as after 28 days of hardening (Figure 2c), although after 7 days of hardening (Figure 2b) no peaks of ettringite were identified. Thus, ettringite is already formed in the stiffened system and destroys the structure of cement stone. In the samples even containing 20 wt.% of silica fume, in which the strength was constantly increasing, ettringite was identified both after 28 and 180 days of hardening. In these samples the formation of ettringite did not reduce the strength of samples. The main reason is the large amount of calcium silicate hydrates which increase the strength of samples and reduce the destructive effect of ettringite. It should also be noted, that the compressive strength of these samples after 28 days of hydration was considerably lower and did not reach 30 MPa. Thus, granular silica fume does not change the hydration process of the finest cement fraction.

The observed data differ from those reported in the references [3, 4, 5], which indicate that silica fume increases the resistance of cement to the sulphate attack. Our results can be explained by the formation of ettringite in the finest cement fraction because if an excessive amount of gypsum in this fraction, but not because of sulphates getting in from the outside. Formation of ettringite proceeds faster than the reaction of Portlandite containing the active SiO_2. It is possible that this reaction is delayed because silica fume has considerably smaller specific surface area, as compared with the finest cement fraction. For this reason, another pozzolana additive (tripoli) was tested.

The analysis was performed using OPC samples, pure finest cement fraction samples, and containing a tripoli additives of 5, 10 and 20 wt.%. The compressive strength of the prepared prisms was measured after 1, 7, 28 and 180 days.
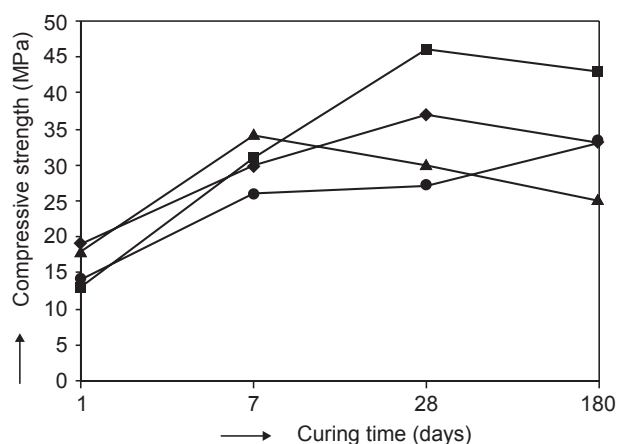

Figure 1. Compressive strength of samples vs. curing time: ▲ - pure samples of the finest cement fraction(S); ■ - finest cement fraction samples with 5 wt.% of silica fume; ◆ - finest cement fraction samples with 10 wt.% of silica fume; ● - finest cement fraction samples with 20 wt.% of silica fume.
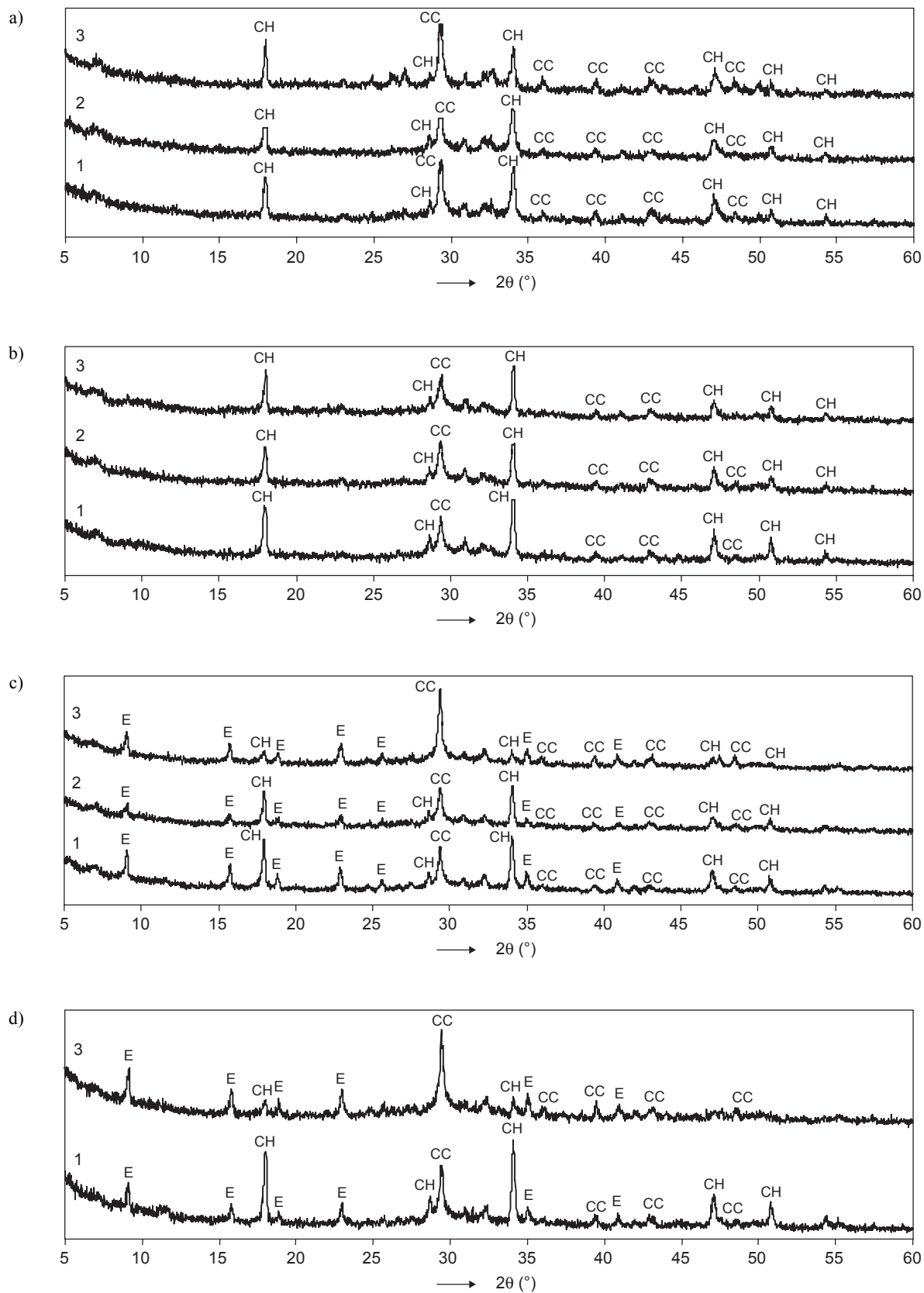
Figure 2. XRD patterns of samples cured for: 1 day (a); 7 day (b); 28 days (c) and 180 days (d). 1 - pure finest cement fraction (S); 2 - finest cement fraction with 10 wt.% of silica fume; 3 - finest cement fraction with 20 wt.% of silica fume. Indexes: E - ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; CH - portlandite $Ca(OH)_2$; CC - calcium carbonate $CaCO_3$.
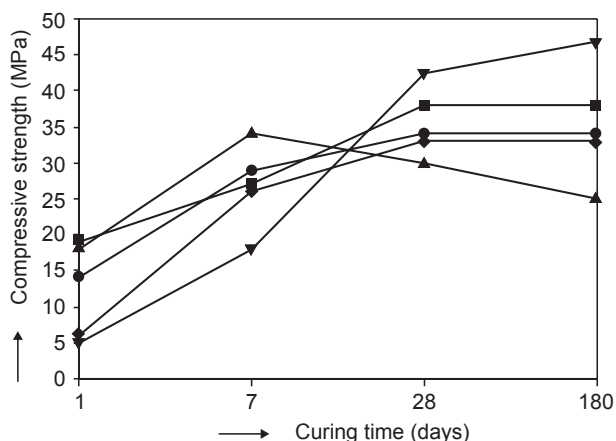
Figure 3. Compressive strength of samples vs. curing time: ▲ - pure samples of the finest cement fraction (S); ■ - finest cement fraction samples with 5 wt.% of tripoli; ● - finest cement fraction samples with 10 wt.% of tripoli; ◆ - finest cement fraction samples with 20 wt.% of tripoli; ▼ - samples of the ordinary Portland cement (OPC).

The results summarized in Figure 3 shows that the compressive strength of samples containing tripoli additive clearly differs from that of pure fine fraction samples. The compressive strength of samples containing tripoli, irrespective of tripoli content, increased during the entire hardening period. After the first day of hydration, the maximum compressive strength was shown by samples containing 5 wt.% of tripoli (Figure 3, curve ■). Also, the compressive strength of samples containing 10 wt.% additive (Figure 3, curve ●) was three times higher (15 MPa), than that of OPC samples (5 MPa). After 7 days of hydration, the maximum compressive strength was shown by the pure finest cement fraction samples (Figure 3, curve ▲), while the compressive strength of samples containing tripoli remained 1.5 times higher than of OPC samples. During 7 days of hardening, the compressive strength of samples containing tripoli increased intensively, but later on the increase in strength was slower than in OPC samples. Samples of the finest fraction (without additives)
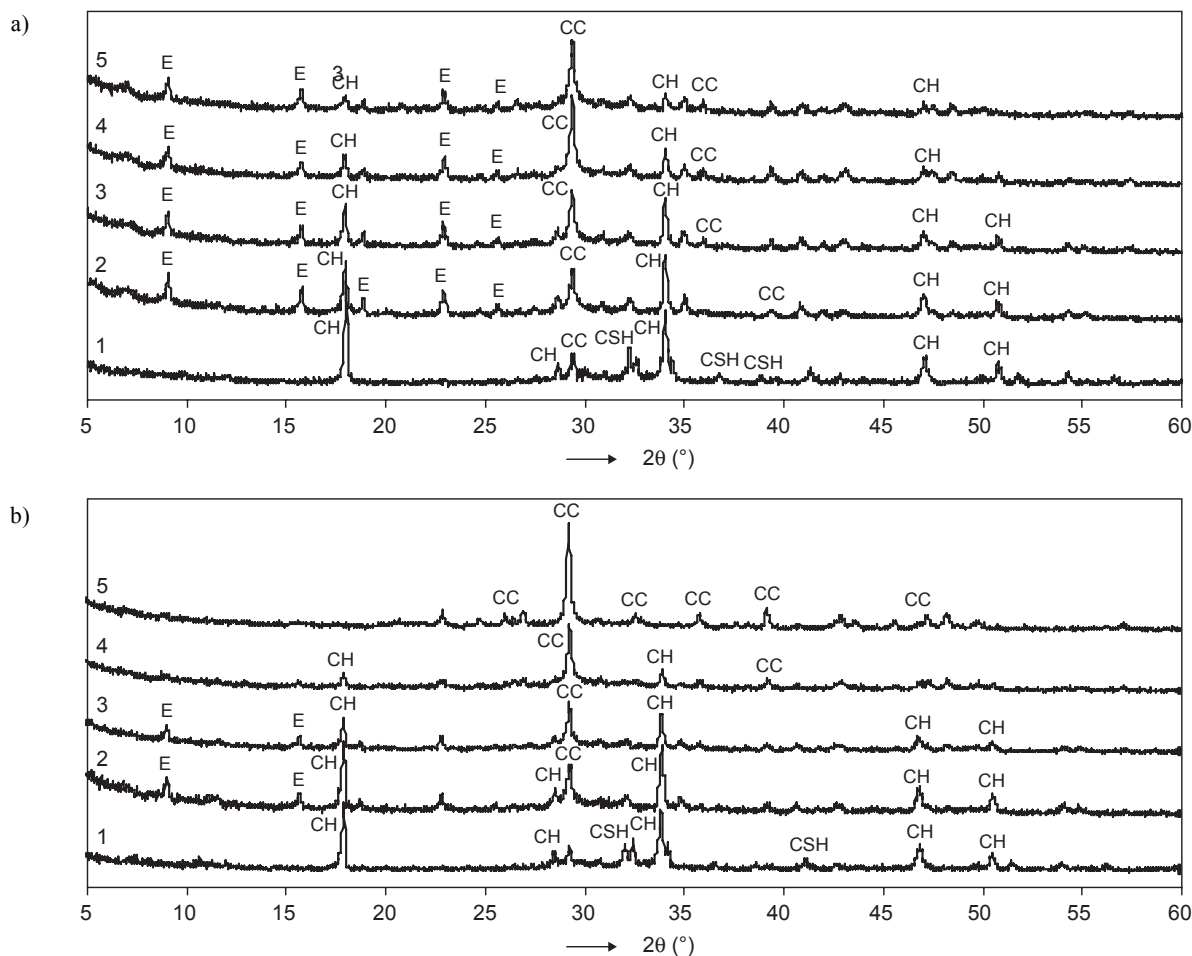

Figure 4. XRD patterns of samples cured for: 28 days (a) and 180 days (b). 1 – Portland cement (OPC); 2 – pure finest cement fraction (S); 3 – finest cement fraction with 5 wt.% of tripoli; 4 – finest cement fraction with 10 wt.% of tripoli; 5 – finest cement fraction with 20 wt.% of tripoli. Indexes: E – ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; CH – portlandite $Ca(OH)_2$; CC – calcium carbonate $CaCO_3$, CSH – calcium silicate hydrate.

reached the maximum compressive strength after 7 days of hardening, but afterwards the strength started decreasing consistently. After 28 days of hydration, the maximum compressive strength was shown by the OPC samples (43 MPa), while the weakest was the pure finest cement fraction sample S (30 MPa). The compressive strength of all the samples containing tripoli additive after 28 days of hydration increased to 32.5 MPa. This dependence persisted during the further hardening of samples: the compressive strength of OPC and samples containing tripoli additive increased, while of finest cement fraction samples without additives it decreases. Therefore we may state that the tripoli additive make conditions for the formation of a stable structure of the finest cement fraction stone.

XRD patterns of the samples at different periods of hardening are shown in Figure 4.

In pure finest cement fraction samples (Figure 4a, b, curve 2), the intensity of CH peaks both after 28 and after 180 days of hardening remained almost unchanged, while the amount of ettringite (d - 0.973 nm., etc.) was considerable. In samples containing tripoli, the intensity of CH peaks decreased when the amount of

tripoli increased. In samples containing 20 wt.% of tripoli after 28 days of hardening (Figure 4a, curve 5) very small CH peaks (d-spacing: 0,493 nm, 0,262 nm, etc.) were observed, while after 6 months of hydration (Figure 4b, curve 5) CH peaks disappeared. Ettringite decomposes through the same time span the peaks of ettringite are not observed in XRD patterns after 180 days of hydration (Figure 4b, curves 4, 5). The crystal structure of the product of ettringite decomposition is formless, and its identification by XRD methods is complicated.

The endothermic peak below 200°C is mainly due to the dehydration of CSH (tobermorite-like phase) as well as ettringite. DTA curves of OPC and pure samples of the finest cement fraction (Figure 5, curves 1-3) show decomposition of $Ca(OH)_2$ in the temperature range 490-505°C. However, in samples containing 10 wt.% tripoli after 28 days of hardening, the $Ca(OH)_2$ decomposition peak was weaker (Figure 5, curve 4), while in samples containing 20 wt.% additive after 6 months of hardening (Figure 5, curve 5) no endothermic peak was observed. It is possible that secondary calcium silicate hydrates form in samples containing tripoli and these compounds affect the strength of the samples.

Only the DTA curve of OPC samples (Figure 5, curve 1) shows an exothermic peak in the temperature range 800-860°C, which is typical of the recrystallization of C–S–H (I) into wollastonite.

Calcium silicate hydrate is identified in thermographs by loss of water (i.e. endothermic peak) in the temperature range 120-150°C. In pure finest cement fraction samples, the C–S–H endothermic peak may be overlapped by the ettringite dehydration peak. Meanwhile, in the XRD patterns of samples containing 20 wt.% tripoli after 6 months of hardening no ettringite was identified. Thus, the endothermic peak in the temperature range 180-200°C in the curve of this sample may be attributed exactly to the high content of C–S–H. The endotherms at 745-755°C indicate $CaCO_3$ decomposition. In samples containing 20 wt.% of tripoli, the endothermic peak at 640°C can be attributed both to $CaCO_3$ decomposition (due to fine cement the fine-grained $CaCO_3$ is formed) and a full dehydration of C–S–H.

The absorption bands in the range 1440, 875 and 713 cm⁻¹, characteristic of calcium carbonates, are seen in all samples. In the IR spectrum of samples containing tripoli (Figure 6, curve 2, 3) a single, broad band in the range 975-985 cm⁻¹ characteristic of calcium silicate hydrates is clearly seen. The absorption band at 3640 cm⁻¹ is characteristic of portlandite; it is seen in the OPC sample (Figure 6, curve 1), but is not identified in the curves of the finest cement fraction samples containing tripoli. In the curve of finest cement fraction sample containing 20 wt.% of tripoli, after 28 days of
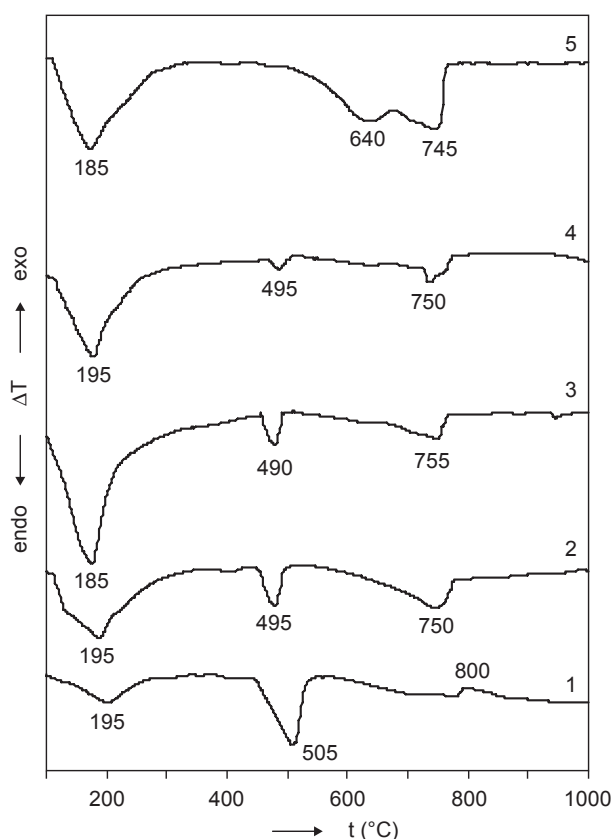

Figure 5. DTA curves of samples cured for: 1 - ordinary Portland cement (OPC), 28 days; 2 - the pure finest cement fraction (S), 28 days; 3 - the pure finest cement fraction (S), 180 days; 4 - the finest cement fraction with 10 wt.% of tripoli, 28 days; 5 - the finest cement fraction with 20 wt.% of tripoli, 180 days.

hydration (Figure 6, curve 2), a shoulder at 1120 cm^{-1}, characteristic of ettringite is observed. Meanwhile, in the curve of the finest cement fraction sample containing 20 wt.% of tripoli, after 180 days of hydration (Figure 6, curve 3) and in the OPC sample (Figure 6, curve 1), a shoulder is observed at 1100 cm^{-1}, which is characteristic of monosulphoaluminate. A complex band near 1140 cm-1 and a simple band near 667 cm^{-1} are common to gypsum. The band at 1140 cm^{-1} is overlapped by a broad peak characteristic of calcium silicate hydrates. In samples containing tripoli, a low intensity band at 667 cm^{-1} confirm an inconsiderable amount of gypsum (Figure 6, curves 2, 3).

CONCLUSION

The finest cement fraction provides for the greatest compressive strength during the first days of hydration, but later the compressive strength starts to decrease. This is the result of ettringite crystals' growth initiated by the higher content of gypsum in this fraction. From both the active mineral additives studied, only tripoli protected a stable structure of the cement stone. During the hardening of samples containing tripoli, portlandite reacts with active SiO_2, and formation of secondary calcium silicate hydrate is observed. At the same time, the amount of portlandite significantly decreases or

completely disappears. Also, the largest part of ettringite decomposes and in the hydration products monosulphate and a small amount of gypsum are formed. The extremely high initial strength is characteristic of the finest cement fraction containing tripoli, because after one day of hardening the compressive strength of samples increased to 15-20 MPa. After 28 days of hardening, the compressive strength reached over 32.5 MPa. The finest cement fraction containing tripoli additive may be used as a separate cement manufacturing product, distinguished by early hardening.

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VLIV PUCOLÁNU NA VLASTNOSTI NEJJEMNĚJŠÍ FRAKCE SEPAROVANÉHO PORTLANDSKÉHO CEMENTU - ČÁST II

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Nejjemnější cementová frakce se shromažďuje v pouzdrových filtrech během mletí cementového slínku. Odhaduje se, že po prvních 24 hodinách hydratace se nejjemnější cementová frakce vyznačuje vysokou počáteční pevností v tlaku. Kromě toho v této frakci snižuje pevnost vzorků etringit, který se vytváří během hydratace v důsledku vysokého obsahu sádry. Přidání přírodního pucolánu (tripoli) zajišŹuje stabilní strukturu cementových dlaždic. Objem obsaženého portlanditu se významně snižuje nebo zcela mizí; rovněž většina etringitu se rozkládá během vytvrzování vzorků obsahujícího tripoli. Po jednom dni vytvrzování se pevnost v tlaku nejjemnější cementové frakce obsahující tripoli zvyšuje na 15-20 MPa. Po 28 dnech vytvrzování dosáhne hodnota pevnosti v tlaku více než 32,5 MPa. Nejjemnější cementová frakce obsahující aditivum tripoli se může použít jako samostatný produkt pro výrobu cementu, který se vyznačuje rychlým vytvrzováním.
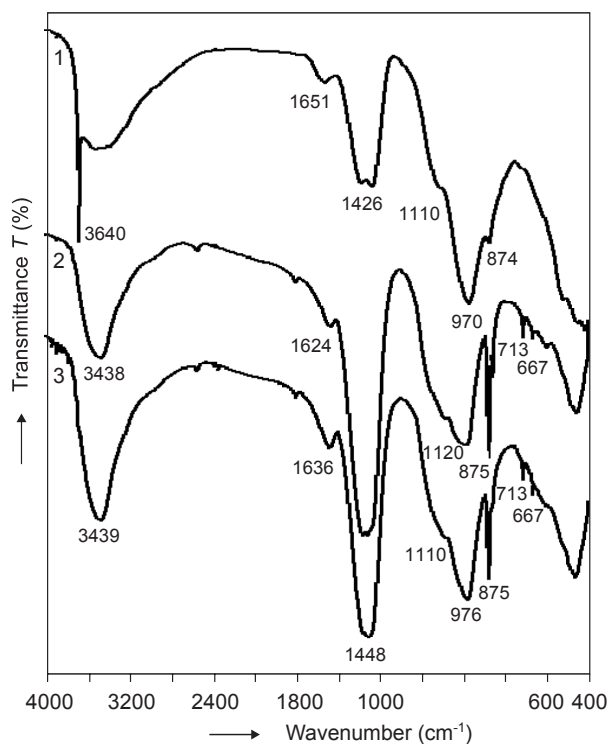

Figure 6. The IR - spectra of the samples cured for: 1 - ordinary Portland cement (OPC), 28 days; 2 - the finest cement fraction with 20 wt.% of tripoli, 28 days; 3 - the finest cement fraction with 20 wt.% of tripoli, 180 days.