THE EFFECT OF POZZOLANA ON THE PROPERTIES OF THE FINEST FRACTION OF SEPARATED PORTLAND CEMENT PART 1

RIMVYDAS KAMINSKAS, JULIUS MITUZAS, ANTANAS KAMINSKAS*

Faculty of Chemical Technology, Kaunas University of Technology, Radvilenu str. 19, LT-50254, Kaunas, Lithuania
* Institute of Thermal Insulation, Vilnius Gediminas Technical University, Linkmenu str. 28, LT-08217, Vilnius, Lithuania

E-mail: rimvydas.kaminskas@ktu.lt

This study deals with compressive strength of the fine Portland cement fraction being collected in the sleeve filters during clinker milling. This fraction has much higher amount of gypsum (12.1 wt. %) and specific surface area 1340 m^2/kg, when comparing it with ordinary Portland cement (OPC). The compressive strength of the fine fraction after 24 hours of hydration is three times higher than that of OPC. This tendency persists also after 7 days. However, after 28 days of hardening, the compressive strength of the fine fraction decreases down to 27 MPa being 1.5 times lower than that of OPC (43 MPa). This decrease is affected by high growth rate of ettringite crystal, which is initiated by elevated content of gypsum. Carbonated pozzolana additive does not change the course of hydration process. The compressive strength of the fine fraction samples with pozzolana additive is after 28 and 180 days of hardening two times lower than that of OPC samples.

INTRODUCTION

In cement production about 75 % of all electric power is used for cement milling [1]. Taking into consideration energy saving, the reduction of the cost price of the producible cement and reaching for the quality improvement, the methods how to reduce the amount of the milled cement should be looked for [2].

The installation of the closed cement milling system is one of the methods most widely used [1,2]. During the closed milling cycle the grist is passed through the mill drum. Then the elevator put up this milled mixture to the separator in which fine distinguished fraction composes a product, and a larger fraction returned to be milled again. The finest fraction is collected in the sleeve filters.

In the literature, it is possible to find related results dealing with high fineness cements. Ultra fine cement is proposed to be used in oil well cementing [3] and in injection technology [4]. Huang et al. [5] investigated the properties of wet - ground fine cement (WFC). Compared with OPC, WFC has shorter setting times, lower bleeding and compressive strength. Sarkar and Wheeler [6] analyzed the properties of ultra fine cement with a Blaine surface area > 7000 cm^2/g. Substantial increase in the specific surface area of a cement can result in two major shortcomings; namely strength retrogression at later ages and faster setting times. Both these abnormalities are attributed to finer particle size. Also Sarkar and Wheeler [6] have declared, that up to 1.0 wt.% retarder and 1.0 wt.% high - range water - reducing admixture (HRWRA) cement can be added to the benefit of the ultra fine cement. Replacement of cement with 20 wt.% superfine fly ash results in still lower amount of heat generation and improves the flowability, but the strength decreases in comparison to the other mixes. Lange and Moertel [7] have outlined that the addition of ultra fine cement increases the early strengths of the mortars. All the above-mentioned authors analyzed ultra fine cement, which is understood as more finely ground OPC, i.e. the chemical and mineralogical composition is analogous to that of OPC, and only the specific surface area is much larger.

Moreover, the finest fraction of cement collected in sleeve-type filters during cement grinding is a sphere lacking experimental research. The chemical and mineralogical composition of this fraction differs from OPC, therefore the hydration of this fraction is influenced not only by the degree of fineness but also by the particularities of chemical and mineralogical composition.

This work sets up a possibility to use the finest cement fraction received in the sleeve filters as a separate product.

EXPERIMENTAL

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

Chemical analysis and phase composition of the raw materials - ordinary Portland cement (OPC), the finest fraction collected in the sleeve filters (S) and carbonated pozzolana (O), are shown in table 1. Figure 1 presents the granulometry of the units of cement fractions.

The composition of pozzolana is (wt.%): opal 35-60, calcite 41-55, quartz 3-10, halcedonium 1-3, glauconitium 0.7-6. Pozzolana contains over 41 wt.% of calcium carbonate, that is why we denote it carbonated pozzolana. The calcite is evenly distributed in opal in form of dispersed parties and rests of microorganisms. Quartz is in form very fine particles. Hydraulic activity of pozzolana is 180 mg CaO/g.

Samples for compressive strength analysis (the prisms 4×4×16 cm) were formed following the standard LST EN 196 1-3 (cement and sand ratio was 1:3). Therefore the water and cement ratio (W/C) was selected 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 $20 \pm 1°C$ and 100% air humidity. After 24 hours of formation, the specimens were transferred into water and kept at $20 \pm 1°C$. To make a more exact estimation of the hydration process, the samples for XRD, DTA and IR - spectroscopy were prepared without usually used sand. 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 heating was carried out in air from 100 to 1000°C by a rate 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. Granulometry curves and the average grain diameter were determined using the laser granulometre FRITCH Analysette 22.

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

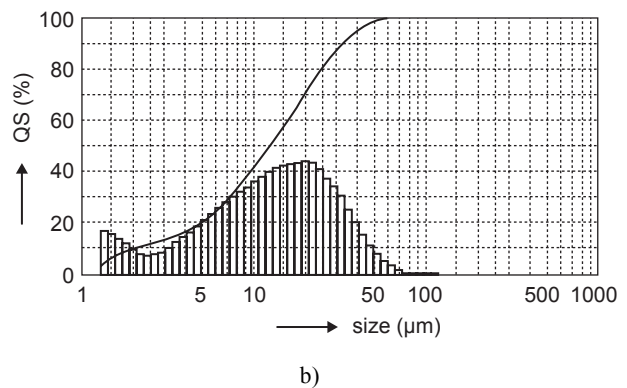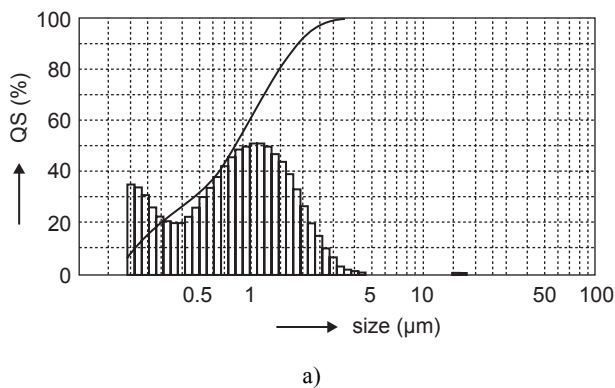| Determined Parameters	Samples		
	S	OPC	O
SiO_2	17.85	19.72	41.0
Al_2O_3	5.04	5.41	2.60
Fe_2O_3	4.36	4.21	1.53
CaO	57.24	62.76	29.80
MgO	3.77	3.41	-
Na_2O	0.26	0.16	-
K_2O	4.17	1.08	-
SO_3^{2-}	5.63	2.08	0.50
Ignition loss	1.52	0.93	23.41
Insoluble residue	0.16	0.24	1.16
Specific surface area (m²/kg)	1340	341	1323
$3CaO·SiO_2$	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	-

Figure 1. Granulometry of the finest cement fraction samples S (a) and of the ordinary Portland cement samples OPC (b).

RESULTS AND DISCUSSION

The chemical composition of the finest cement fraction (S) collected in the sleeve filters obviously differs from the composition of ordinary Portland cement (OPC) (table 1). This fraction has a much larger amount of gypsum 12.1 wt.% and specific surface area 1340 m^2/kg than OPC. Gypsum grinds better than clinker and it is easier to carry to the sleeve filter. In addition, gypsum has much lower density than clinker and larger quantity of this compound may be deposited in the sleeve filter of the separator. These characteristics have considerable effect on the hydration and strength properties of the finest fraction.

The strength analysis was performed using OPC samples (OPC), pure finest cement fraction samples (S), and with a pozzolana additive of 5, 10 and 20 wt.%. Compressive strength of the prepared prisms was measured after 1, 7, 28 and 180 days.

The results summarized in figure 2 show fundamental differences among the hardening processes of tested systems. Already after the first 24 hours hydration compressive strength of the finest fraction is three times higher (over 15 MPa) than that of OPC (5 MPa). After 7 day of hydration compressive strength of the finest fraction S samples (33 MPa) also is larger than that of OPC samples (17 MPa). However, the compressive strength of the finest fraction starts to decrease consistently during the next days. Meanwhile the compressive strength of Portland cement increases and after 28 days of hardening, it is already 1.5 times higher than that of the finest fraction. This dependence persists during the further hardening of the samples: the compressive strength of Portland cement increases, and the compressive strength of the finest fraction decreases.

After 180 days exposure the finest cement fraction (S) (curve 1) and Portland cement (OPC) (curve 5) have the lowest and the highest compressive strength, respectively.

The samples with 5 wt.% of pozzolana additive reach the compressive strength maximum after 7 days but afterwards starts consistently to decrease (figure 2, curve 2). After 28 days of hardening the compressive strength remains the same up to 6 months of hardening. The curves with 10 and 20 wt.% of pozzolana are analogical until the 28 days of hardening, then the strength increases. The compressive strength of the samples with 10 wt.% of the additive (figure 2, curve 3) stops to increase after 28 days of hardening and remains stable until 180 days. When the amount of pozzolana additive is increased up to 20 wt.% (figure 2, curve 4), the compressive strength of samples steadily increases within studied time interval. However, the strength of the sample containing 20 wt.% of pozzolana is two times lower when comparing it with OPC samples after both 28 and 180 days of hardening.

Different hydration and hardening courses may be explained by several facts. Sudden change of the compressive strength of the finest cement fraction after 24 hours of hardening may be explained by a large number of small cement particles; the largest particle in the finest fraction samples has diameter 5 μm, when the average diameter is 0.95 μm (figure 1a). The particles of this size hydrate quickly, influencing a fast increase of the initial strength. The decrease of the finest fraction strength observed after 7 day is probably affected by several times greater amounts of gypsum (table 1) in comparison with conventional Portland cement. Larger amounts of gypsum influence fast growth of ettringite $(3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O)$ crystals, which deform cement stone.
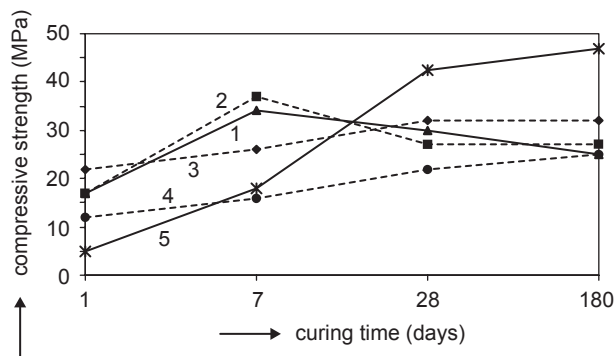

Figure 2. Compressive strength of samples vs. curing time: 1 - pure samples of the finest cement fraction (S); 2 - finest cement fraction samples with 5 wt.% of pozzolana; 3 - finest cement fraction samples with 10 wt.% of pozzolana; 4 - finest cement fraction samples with 20 wt.% of pozzolana, 5 - samples of the ordinary Portland cement (OPC).
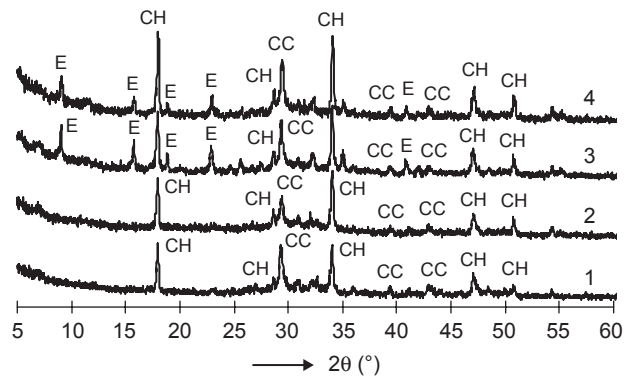

Figure 3. XRD patterns of pure finest cement fraction samples cured for: 1-1 day; 2-7 days; 3-28 days; 4-6 months. Indexes: E - ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; CH - portlandite Ca $(OH)_2$; CC - calcium carbonate $CaCO_3$.

In order to confirm the hypothesis and to understand the impact of carbonate pozzolana on the hydration of the finest fraction of cement, X-ray powder diffraction, DTA and IR-spectroscopy examinations were carried out.

XRD patterns of the samples at different periods of hardening are showed in figures 3 and 4. After the first day of hardening, the formation of portlandite (*d*-spacing: 0.493, 0.262, 0.179 nm) and the peaks of calcium carbonate (*d*-spacing: 0.386, 0.332, 0.209 nm) conditioned by additive of limestone are observed (figure 3, curve 1). However, the peaks of non-hydrated cement minerals are not identify in the samples (S). It should be noted that in the OPC only 70 % of the C3S is reacting during 28 days of hardening [21]. The character of XRD patterns does not change after 7 days of hardening, only the intensity of CH slightly increases (figure 3, curve 2). After 28 days of hardening a large amount of ettringite (*d*-spacing: 0.973, 0.561, 0.388 nm) is identified (figure 3, curve 3). It should be noted that this compound remains stable in the samples even after 180 days of hardening (figure 3, curve 4).

The strength of samples is increasing up to 7 days (figure 2, curve 1) of hardening until ettringite was not observed in the XRD patterns. Meanwhile, after 28 days of hardening the strength of the samples (S) decreases (from 38 MPa to 27 MPa); at the same time ettringite already dominates in the XRD patterns. Thus, the XRD data shows that large crystals of ettringite are formed already in the stiffened system and destroys the structure of cement stone. Consequently, one would conclude that the formed structure is getting coarser and compressive strength drops with time of curing.

As can be seen from the XRD patterns (figure 4a, b) both after 28 days and after 6 months of hardening, ettringite is identified almost in all samples, except OPC

samples. The intensity of ettringite main peaks in the samples of the pure finest cement fraction is a little higher than in that samples with pozzolana. Even in samples with 20 wt.% of pozzolana (figure 4, curves 5), the strength of which constantly increased, ettringite was identified after both 28 and 180 days of hardening. Thus, we may confirm that addition of pozzolana does not change the hydration process of the finest cement fraction - ettringite is identified in all samples. The XRD patterns of OPC samples after 28 days of hardening shows a significant amount of CH and the formation of purely crystallized CSH (I) type calcium silicate hydrates (figure 4a, curve 1) is also identified. The essential difference in the XRD patterns of the finest cement fraction with and without addition of carbonate pozzolana and OPC samples are: in the OPC sample ettringite was not identified and non-hydrated C_3S is observed (*d*-spacing - 0.274, 0.277, 0.260, 0.218 nm); meanwhile, non-hydrated C_3S was not found in the sample (S) already after 1 day of hydration and ettringite dominates in all samples after both 28 and 180 days of hydration.

Moreover, the intensity of CH peaks in the samples with pozzolana constantly decreases when the amount of pozzolana increases. Therefore, it is not accidental that basic reflections of CH in the samples with 20 wt.% pozzolana are lowest and only insignificant responses are observed after 6 months of hydration (figure 4b, curve 5). Thus, the increase of strength of the samples with 20 wt.% pozzolana is related to $Ca(OH)_2$ reaction with amorphous SiO_2 upon secondary calcium silicate hydrates formation [8, 9, 21].

The sequence of hydration reaction can be different when $CaCO_3$ is added into Portland cement. The effect of limestone incorporation on the Portland cement has
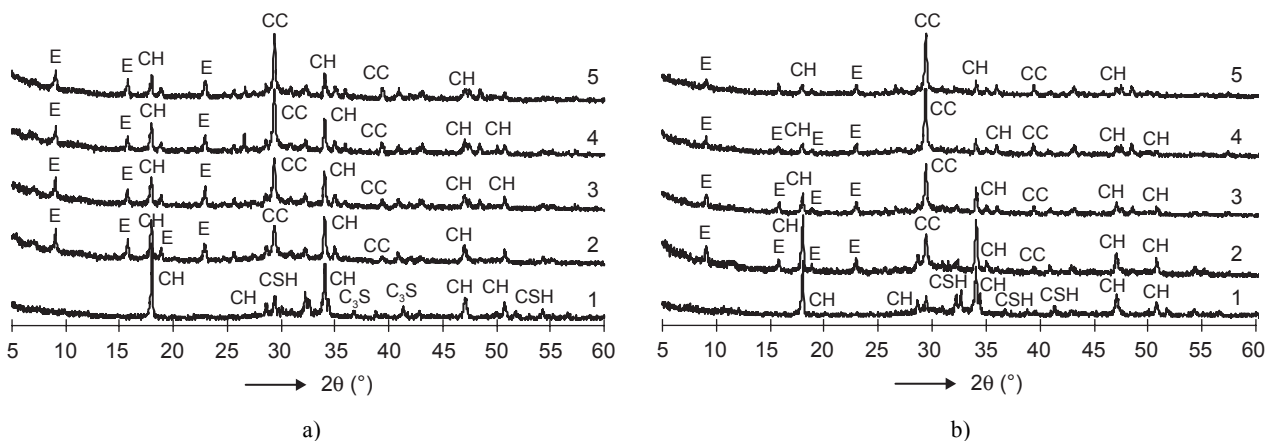

Figure 4. XRD patterns of samples cured for 28 days (a) and for 6 months (b). 1 - Portland cement (OPC); 2 - pure finest cement fraction (S); 3 - finest cement fraction with 5 wt.% of pozzolana; 4 - finest cement fraction with 10 wt.% of pozzolana; 5 - finest cement fraction with 20 wt.% of pozzolana; Indexes: E - ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$; CH - portlandite $Ca(OH)_2$; CC - calcium carbonate $CaCO_3$; C_3S - tricalcium silicate; CSH - calcium silicate hydrate.

been the subject of several studies [10-12]. The elevated amount of limestone increases the heat of hydration and enhances the compressive strength at early ages [13,14]. Two forms of carboaluminate have been reported, which correspond to the high and low sulfate variants of calcium sulfoaluminate hydrates. The calcium monocarboaluminate $C_3A \cdot CaCO_3 \cdot 11H_2O$ and $C_3A \cdot 3CaCO_3 \cdot 32H_2O$ were observed during early hydration stages [15,19,21].

Growing crystals of mentioned complexes together with carbonate fill form a stable crystal structure and the strength of the cement stone increases at the same time [16].

In other hand, Kakali et al. [17] have reported that in pastes containing $CaCO_3$ the ettringite's transformation to monosulfate is delayed. Also Bonaveti et al. [18] have found that in limestone-blended cements, calcium monocarboaluminate is immediately detected after the begining of hydration and the transformation of mono-

sulfoaluminate to monocarboaluminate occurs at 28 days, while the conversion of ettringite to monosulfoaluminate is deferred.

It should be underlined that new complexes with calcium carbonate were not identified in the samples with pozzolana (*d*-spacing: 0.757; 0.941 nm). This statement is also proved by the fact that during the whole period of hardening the intensity of $CaCO_3$ peaks remains nearly unchanged, i.e. the carbonate part of pozzolana does not participate in the hydration reactions.

It is obvious from the DTA analysis that the nature of curves for both the pure finest cement fraction samples and the samples with 10 wt.% of pozzolana hardly differs after 28 and 180 days of hardening. Three significant endothermic peaks at 200, 490 and 750°C are observed in these curves (figure 5a).

The endothermic peak below 200°C is mainly due to the dehydration of interlayer of CSH (tobermorite-like phase) as well as ettringite or monosulphate and carboaluminate hydrates. The decomposition of ettringite or monosulphate is occurred at lower temperature and overlapped by the CSH [20]. C-S-H (I) type calcium silicate hydrates recrystallise into wollastonite at the temperature range of 800 - 860°C and DTA curves show a exothermic peak [21]. This exothermic peak is not observed in any DTA curves of the samples of pure finest cement fraction and the finest cement fraction with pozzolana. Meanwhile, this peak it is observed in the curves of OPC sample (OPC) after 28 and 180 days of hardening (figure 5, curve 5, 6). It is possible to
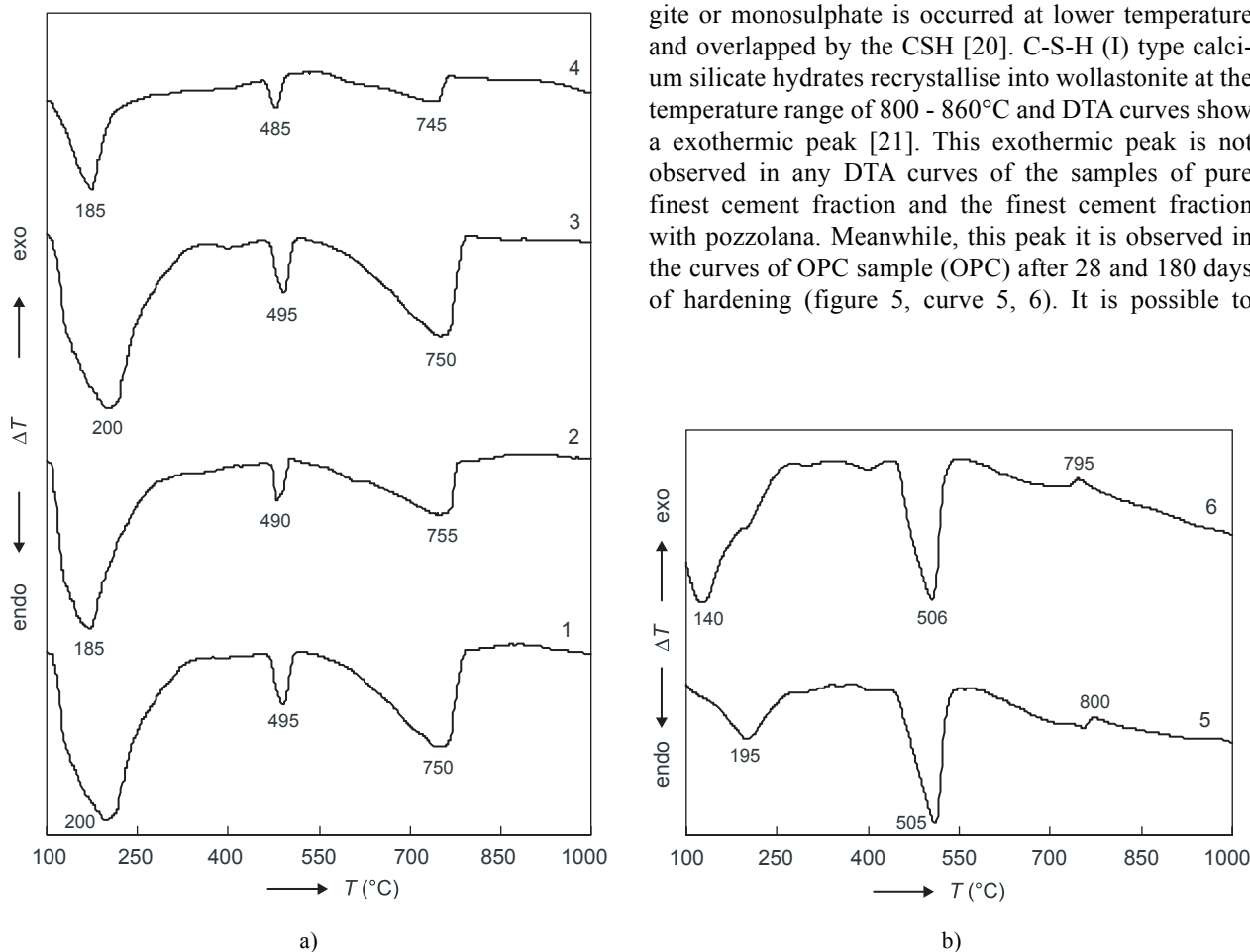

Figure 5. DTA curves of finest cement fraction samples (a) and OPC samples (b): 1 - the pure finest cement fraction, curing time 28 days; 2 - the pure finest cement fraction, curing time 180 days; 3 - the finest cement fraction with 10% of pozzolana, curing time 28 days; 4 - the finest cement fraction with 20 wt.% of pozzolana, curing time 180 days; 5 - Portland cement, curing time 28 days; 6 - Portland cement, curing time 180 days.

assume that in the samples of finest cement fraction a higher basic CSH is formed, which is identified only by dehydration at 120-200°C. Higher CSH basicity may be related to the fact that part of Ca^{2+} ions, getting into the stiffening system with larger content of gypsum, inserts into CSH structure.

The endothermic peak at 485-495°C corresponds to the decomposition of $Ca(OH)_2$. This peak intensity is higher in the pure samples of the OPC and lower in the samples with pozzolana. This is especially well seen in the thermograms after 6 months of hardening (figure 5a, curve 4).

The endotherms at 745-755°C indicate the decomposition of $CaCO_3$. The intensity of these endothermic peaks in samples with pozzolana slightly decreases during hardening. This may be related to the partial participation of fine dispersive calcite in the hydration reactions.

Figure 6 compares IR spectra of the finest cement fraction with and without pozzolana addition. The absorption bands in the range 1430 and 875 cm^{-1} characteristic for calcium carbonates [19, 21] are clearly seen

after both 28 and 180 days of hydration of finest cement fraction with pozzolana addition (figure 6a, curves 1, 2). In addition, calcium carboaluminate hydrates readily detectable in the range of 2990 cm^{-1} [19] are not present in these samples. This confirms relative $CaCO_3$ inertness during hydration. On the other hand, ettringite is clearly identified in the absorption band in the range 3435-3445 and 1120 cm^{-1} [19, 21] both in the mentioned samples and in the sample of pure finest cement fraction (figure 6, b, curve 4). Meanwhile, in OPC sample, only a shoulder is observed in the range 1100 cm^{-1} showing the existence of monosulfoaluminate [21]. The absorption band at 3640 cm^{-1} being characteristic to portlandite [19] is the largest in OPC sample after 28 days of hardening (figure 6b, curve 3), whereas this band almost diminished in the sample with pozzolana additive. After 6 months of hydration portlandite already was not observed in the sample with pozzolana additive (figure 6a, curve 2). This is the result of reaction between portlandite and pozzolana when secondary CSH is formed. This compound is identified as CSH(II) at 975-985 cm^{-1} [21].
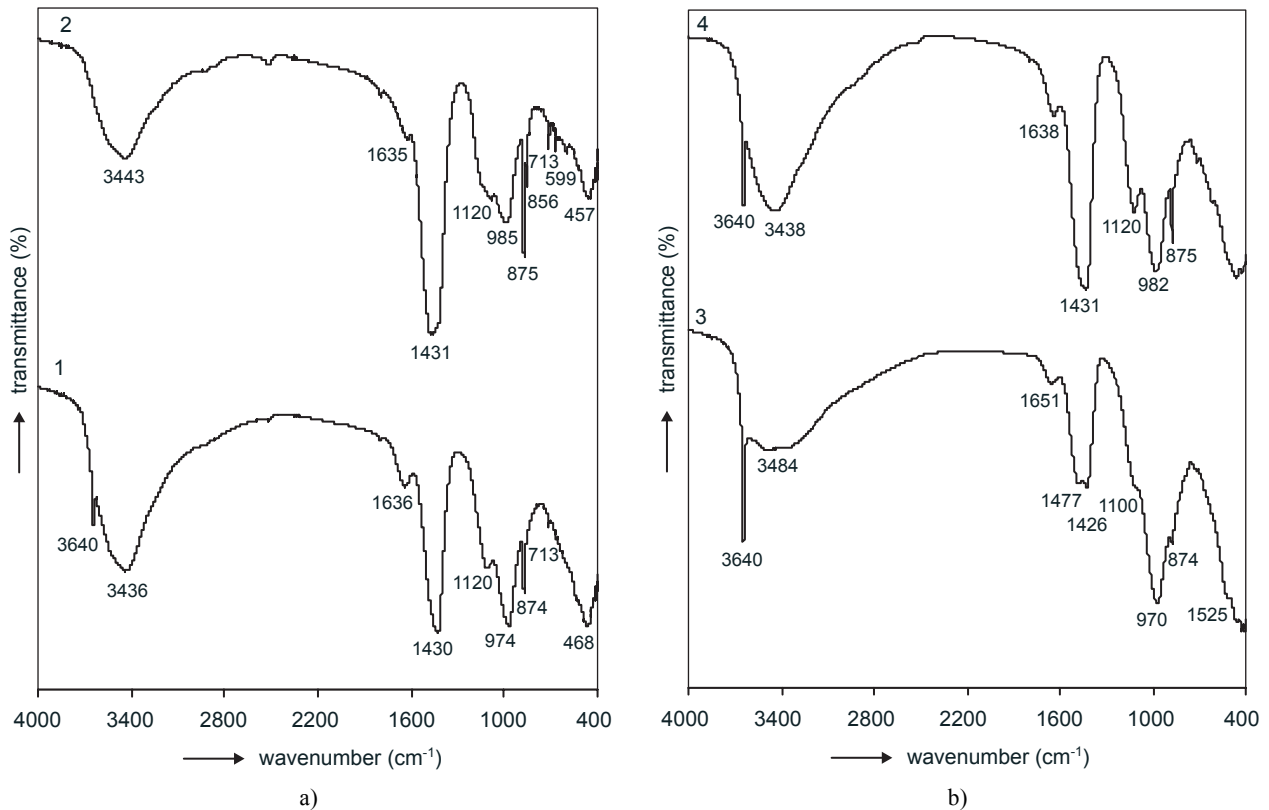

Figure 6. The IR - spectra of the finest cement fraction with pozzolana (a) and pure samples (b): 1 - 10 wt.% of pozzolana, curing time 28 days; 2 - 20 wt.% of pozzolana, curing time 180 days; 3 - Portland cement (OPC), curing time 28 days; 4 - finest cement fraction (S), curing time 28 days.

CONCLUSION

The finest cement fraction collected in the sleeve filter containing three times higher gypsum (12.1 wt.%) than ordinary Portland cement and having specific surface area 1340 m^2/kg and the largest particle size 5 μm (average diameter 0.95 μm) has the biggest strength during the first days of hydration, but later on the strength decrease. This is the result of ettringite crystal growth, which is initiated by elevated content of gypsum in this fraction. Carbonated pozzolana additive does not change the hydration process of the finest cement fraction, and after 28 and 180 days of hardening the strength of samples with additive is two times lower in comparison with OPC samples.

References

1. Breitschmidt K., Fisch H.: *Optimization of Grinding Systems*, VA 85/5212/E (1986).
2. Jankovic A., Valery W., Davis E.: Mineral Engineering *17*, 1075 (2004).
3. Clark W. J., McNally A. C.: Proc. Low. Perm. Res.Symp., pp. 291 - 298 (1993).
4. Geymayer H., Tritthart J., Guo W., Reinmann C.: ZKG Int. *2*, 86 (1995).
5. Huang Z., Chen M., Chen X.: Cem.Concr.Res. *33*, 729 (2003).
6. Sarkar S.L., Wheeler J.: Cem.Concr.Res. *31*, 119 (2001).
7. Lange J., Moertel H.: ZKG Int. *12*, 661 (1995).
8. Maropolou A., Cakmak A., Labropoulos K. C., Van Grieken R., Torfs K.: Cem.Concr.Res. *34*, 1 (2004).
9. Massazza E.: Cem.and Concr.Comp. *15*, 185 (1993).
10. Barret P., Bertrandie D., Beau D.: Cem.Concr.Res. *13*, 789 (1983).
11. Bensted J.: World Cement Technol. *11*, 395 (1980).
12. Bobrowski G. S., Wilson J. L., Daugherty K. E.: Rock Prod. *80*, 67 (1977).
13. El-Alfi E., Darweech H., El-Didamony H.: Ceramics-Silikáty *44*, 109 (2000).
14. El-Didamony H., El-Alfi E.: Ceramics-Silikáty *44*, 146 (2000).
15. Feldman R. F., Ramachandran V. S., Sereda P. J.: J.Am.Ceram.Soc. *48*, 25 (1965).
16. Kaminskas R., Mituzas J. in: *Technology watch and Innovation in the Construction Industry*, pp. 211 - 221, Brussel 2000.
17. Kakali G., Tsivilis S., Aggeli E., Bati M.: Cem.Concr. Res. *30*, 1073 (2000).
18. Bonavetti V. L., Rahhal V. F., Irassar E. F.: Cem.Concr. Res. *31*, 853 (2001).
19. Ramachandran V. S.: *Handbook of Analytical Techniques in Concrete Science and Technology*, New York 2001.
20. Heikal M., Helmy I., El-Didamony H., El-Raoof F. A.: Ceramics-Silikáty *48*, 49 (2004).
21. Taylor H. F. W.: *Cement Chemistry*, Second edition, Oxford 1997.

VLIV PUCOLÁNŮ NA VLASTNOSTI JEMNÉ FRAKCE PORTLANDSKÉHO CEMENTU ČÁST 1.

RIMVYDAS KAMINSKAS, JULIUS MITUZAS, ANTANAS KAMINSKAS*

*Faculty of Chemical Technology,
Kaunas University of Technology,
Radvilenu str. 19, LT-50254, Kaunas, Lithuania
*Institute of Thermal Insulation,
Vilnius Gediminas Technical University,
Linkmenu str. 28, LT-08217, Vilnius, Lithuania*

Tato studie se zabývá pevností v tlaku jemné frakce portlandského cementu nashromážděné v rukávových filtrech během mletí slínku. Tato frakce má mnohem vyšší obsah sádrovce (12,1 hmot.%) a specifický povrch ve srovnání s běžným portlandským cementem (OPC). Pevnost v tlaku jemné frakce je po 24 hodinách tuhnutí třikrát vyšší než u OPC. Tato tendence přetrvává i po 7 dnech. Po 28 dnech tuhnutí však pevnost v tlaku jemné frakce klesá na 27 MPa, což je hodnota 1,5krát nižší než u OPC (43 MPa). Tento pokles je způsoben vysokou rychlostí růstu krystalů ettringitu ovlivněnou vysokým obsahem sádrovce. Karbonizovaný pucolán průběh hydratačního procesu neovlivňuje. Pevnost v tlaku jemné frakce s přísadou pucolánu je po 28 a 180 dnech tuhnutí dvakrát nižší než u OPC vzorků.