

## Blended Cement Systems with Zeolitized Silica Fume

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In this paper the properties and the hydration of Portland cement pastes containing zeolitized silica fume were studied. Hydrosodalite was obtained by zeolitization of silica fume. XRD, DSC, SEM and energy-dispersive X-ray spectroscopy were used as investigation methods. The compressive strength of hardened cement paste was measured after 28 days. The levels of cement replacement by additives were 5 %, 10 % and 15 % by weight in the specimens. Changes in the strength of hardened cement paste were observed. The influence of additives on hydration rate and hydration temperature was also observed. Both 1Hs (hydrosodalite) and 2Hs (modified hydrosodalite) additives accelerate the hydration of the cement paste. The highest hydration temperature was achieved in a mixture with 5 wt. % 1Hs additive and with 10 wt. % 2Hs additive. The microstructure of hardened cement paste specimens with 1Hs and 2Hs additive is denser compared with reference specimens without the additives. The maximum compressive strength of the specimens with 10 wt. % of 2Hs reached up to 101 MPa under laboratory conditions.

**Keywords:** zeolitized silica fume, cement hydration, hydrosodalite.

### 1. INTRODUCTION

Zeolites are crystalline aluminosilicates, which have large quantities of reactive SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. It has been used in producing blended cements and concretes. Like other pozzolanic materials such as silica fume and fly ash, zeolite contributes to concrete strength mainly through the pozzolanic reaction with Ca(OH)<sub>2</sub>. These results are compared with those obtained from similar blended cement pastes prepared with silica fume and fly ash replacements. Supposedly C.S. Poon *et al.* [1, 2] have showed that pozzolanic effect of zeolite improved the microstructure of hardened cement paste and reduced the content of the harmful large pores, hence made concrete more impervious.

Cement mortars and concretes incorporating clinoptilolite (natural zeolite), silica fume and fly ash were investigated for changes in their physical and mechanical properties. It was found that additions of 10 % clinoptilolite and 10 % pozzolite (1:1 mixture of silica fume and fly ash) were optimal for improvement of the quality of the hardened products, giving 8 % and 13 % increases in flexural and compressive strength respectively. The specific pore volume of the mortars incorporating zeolite decreased between the 28<sup>th</sup> and 180<sup>th</sup> day to levels below the values for the reference composition [3, 4].

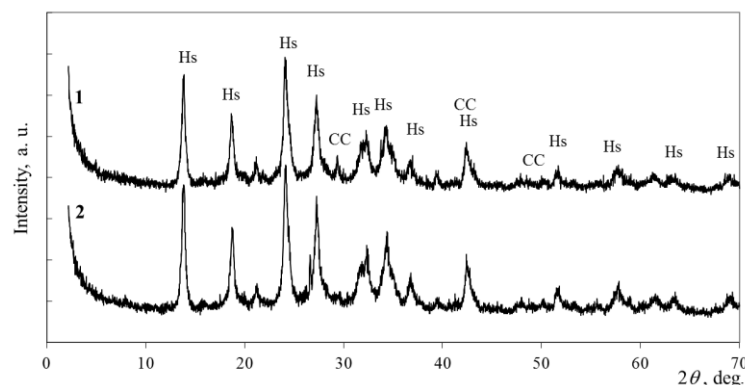
Zeolites additives in concrete increase the durability of concrete. This is due to pozzolanic reaction of zeolite with Portland cement resulting in reduction of the formed Ca(OH)<sub>2</sub> opposite to the reference PC. Ettringite and alkali–silica reaction gel formation in the microstructure of the composite against sulfate attack was limited with the usage of zeolite, fly ash and ground granulated blast

furnace slag [5]. Because zeolite is environmentally friendly, it could be a good substitute for silica fume and metakaolin. Using zeolites is more effective in enhancing the durability of concrete than lowering w/c ratio [6].

The enhanced sulfate resistance noted in the cement blended with either silica fume or fly ash indicates the usefulness of these cements in both sulfate and sulfate plus chloride environments. Maximum deterioration, due to sulfate attack, was noted in cement. The blending materials used were silica fume, slag, and calcium carbonate. Slag and calcium carbonate improve the sulfate resistance of ordinary Portland cement paste [7].

R. Snellings *et al.* [8] have reported that zeolites actively participate in the hydration processes of cement. Their activity in the early stage of hydration is based mainly on the large surface area of the particles while, in the later stages of activity, chemical reactions occur between the products of the hydration of cement and the soluble SiO<sub>2</sub>. It has been shown that in all cement pastes which contain zeolite additives, the quantity of portlandite is lower than that in pure cement paste or is even totally absent. Natural pozzolans can be activated in an alkaline environment to synthesize high performance cementitious construction materials. In the paper [10], the results show that pozzolan containing sodium clinoptilolite can be prepared up to high strength binder by heat treatment. Calcinations can impart disorder a constituent of pozzolan with no amorphous phase to prepare a binder. Recently many publications analyzing the performance of cementitious systems containing zeolite, silica fume as an active mineral additive have been published. However, no data was found about the effect of zeolite-like materials, made from silica fume, additive on the properties of cementitious system. The objective of the study is to investigate the effect of zeolite-like materials, made from silica fume, on the performance of cementitious systems.

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**Fig. 1.** The X-ray diffraction patterns of hydrosodalites: 1 – modified hydrosodalite (2Hs), 2 – pure hydrosodalite (1Hs); Note: Hs – hydrosodalite, CC – calcium carbonate

## 2. EXPERIMENTAL

The Portland cement CEM I 42.R was used. Chemical composition of Portland cement and silica fume showed in Table 1. In this paper the hydration of two blended cement compositions were investigated, an OPC with 0, 5, 10 and 15 % of zeolite-like materials (1Hs and 2Hs).

**Table 1.** Chemical composition of Portland cement, 1Hs, 2Hs and silica fume

Chemical composition, %	Portland cement	1Hs	2Hs	Silica fume
SiO <sub>2</sub>	20.54	38.87	40.27	88
Al <sub>2</sub> O <sub>3</sub>	5.49	37.88	37.41	1.8
Fe <sub>2</sub> O <sub>3</sub>	3.52	-	-	1.8
CaO	63.68	-	5.27	0.9
SO <sub>3</sub>	0.95	-	-	0.9
Cl <sup>-</sup>	0.001	-	-	0.3
MgO	4.31	-	-	1.8
K <sub>2</sub> O	0.52	-	-	2.0
Na <sub>2</sub> O	-	23.25	17.05	1.0
C	-	-	-	1.5
C <sub>3</sub> S	56.38	-	-	-
C <sub>2</sub> S	16.34	-	-	-
C <sub>3</sub> A	8.60	-	-	-
C <sub>4</sub> AF	10.72	-	-	-

The first additive is hydrosodalite (1Hs). This synthetic hydrosodalite was synthesized from: NaOH, Al(OH)<sub>3</sub> and silica fume (SiO<sub>2</sub> source). The molar ratio of the raw material Na<sub>2</sub>O:Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:H<sub>2</sub>O was 2:1:2:10. Low-temperature (105 °C) zeolite synthesis was performed in the unstirred suspension at 3 hours isothermal curing. The final product of synthesis was filtered, dried at ~60 °C temperature and sieved through a 0.5 mm-mesh sieve. The second additive (2Hs) was obtained by a modification of the first.

The X-ray curves of investigated samples before and after the modification were carried out. Both curves have a similar character and almost identical to visible peaks. The curves of X-ray diffraction analysis show that the diffraction peaks with interplanar distances (d) of 0.628; 0.363; 0.281; 0.256; 0.290; 0.174 nm (Fig. 1), are characteristic of hydrosodalite (1Hs). After ions exchange reaction the structure of hydrosodalite crystals was noticed to be stable because the shape of the X-ray diffraction patterns (Fig. 1, curve 2) did not change. Before modification crystalline phase consists 84.1 % and 15.9 %

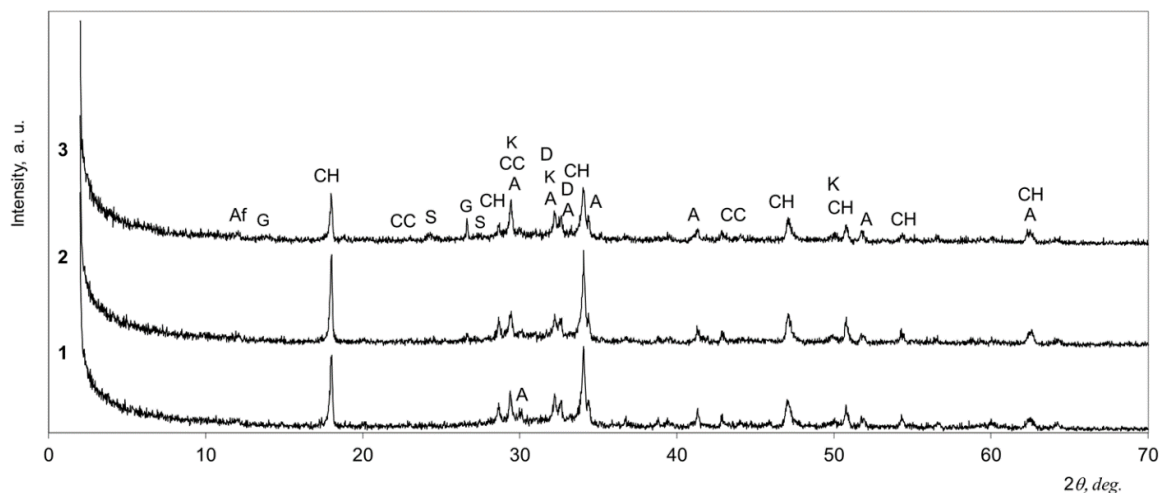
of amorphous phase is in the 1Hs material. After modification (2Hs) crystalline phase slightly decreases till 83.9 % and an amorphous phase increases till 16.1 %. The chemical composition of 1Hs and 2Hs showed in Table 1.

The X-ray powder diffraction data were collected with DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu K $\alpha$  radiation and graphite monochromator, operating with the voltage of 30kV and emission current of 20 mA. The step-scan covered the angular range 2–70° (2 $\theta$ ) in steps of 2 $\theta$ =0.02°. Calculations of crystalline and amorphous phases was done with the EVA program. Thermal analysis (differential scanning calorimetry-DSC and thermogravimetry-TG) was also employed for measuring the thermal stability and phase transformation of products at a heating rate of 15 °C/min, the temperature ranged from 30 °C up to 1000 °C under the air atmosphere. The test was carried out on a Netzsch instrument STA 409 PC Luxx. The ceramic sample handlers and crucibles of Pt-Rh were used there. The structure of hardened cement paste was studied by scanning electronic microscopy. A high resolution scanning electron microscope FEI Quanta 200 FEG with a Schottky field emission gun (FEG). Chemical compositions of zeolite were investigated by an energy-dispersive X-ray spectrometer (EDS) with silicon type drift droplet detector. The cement paste hydration temperature measurements were performed with 8-channel USB TC-08 Thermocouple Data Logger (temperature measurement range from – 270 to + 1820 °C). In all test sample constant flow was stable and the ratio of water and solid material was constant and equal to W/S = 0.3. The contents of 1Hs or 2Hs were 0; 5; 10 and 15 % mass. Silica fume, 1Hs and 2Hs have surface areas of about 20.59 m<sup>2</sup>/g, 21.85 m<sup>2</sup>/g and 22.05 m<sup>2</sup>/g (Blaine), respectively. The formed test samples, 2×2×2 cm sized cubes, were hardened for 28 days. The test procedure of hardened cement paste compressive strength was applied according to the EN 196-1.

## 3. RESULTS AND DISCUSSION

### 3.1. The effect of 1Hs additive synthesized with silica fume on cement hydration

X-ray diffraction patterns of hardened cement paste specimens revealed that Ca(OH)<sub>2</sub> decreased with the increase of 1Hs additive (Fig. 2).



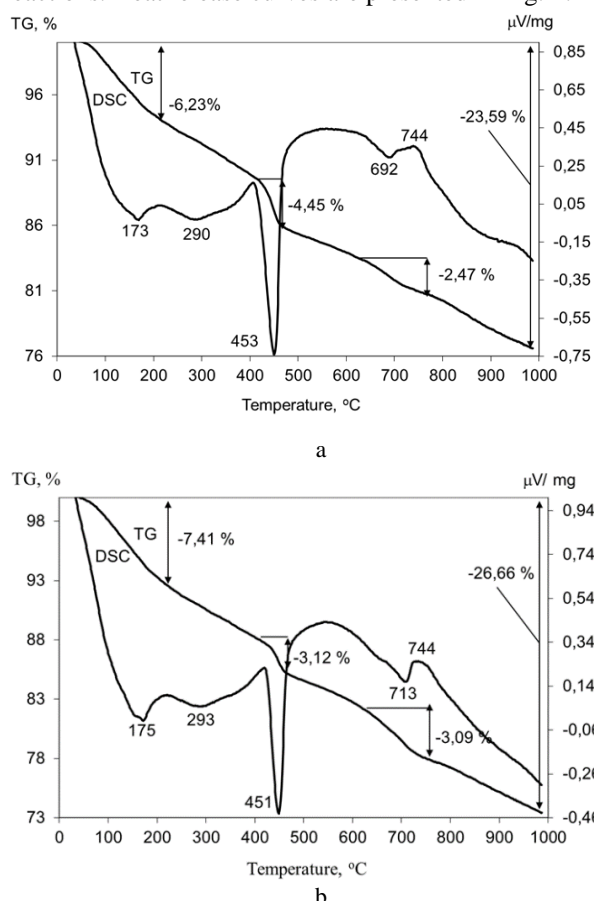
**Fig. 2.** X-ray diffraction patterns of hardened cement paste after after 28 days. 1Hs addition content accounts for 0 % (1); 5 % (2); 15 % (3). Notes: CH – portlandite; A – alite; K – calcium silicate hydrate; D – belite; E – ettringite; CC – calcite; G – calcium aluminum silicate hydrate, S – sodium aluminum silicate hydrate, Af – monosulfoaluminate

The highest typical peak of  $\text{Ca}(\text{OH})_2$  (0.493 nm) is the most intense when the additive is not used by comparing three curves. After 28 days of hydration no hydrosodalite peaks were identified after 28 days of hydration. When zeolitic additive is present in the cement and water mixture, high pH of the zeolite causes disintegration and depolymerization of the aluminosilicate frame. During the depolymerization  $[\text{SiO}(\text{OH})_3]^-$  and  $[\text{Al}(\text{OH})_4]^-$  ions enter the solution and react with  $\text{Ca}^{2+}$  ions thus forming hydrated calcium silicates and calcium aluminates, very similar to those compounds, which develop during the hydration of ordinary cement [11].

Thermal analysis is an important experimental procedure used to study the cement hydration and consumption of portlandite due to pozzolanic reactions. TG and DSC curves of hardened cement paste with 1Hs are shown in Fig. 3. In the temperature range 173 – 175 °C, and in the range up to 300 °C the complex dehydration of calcium silicates, aluminates and calcium aluminosilicates is observed. An endothermic peak in the temperature range 451 – 453 °C is attributed to decomposition of  $\text{Ca}(\text{OH})_2$ . This peak decreases with the increased amount of 1Hs (consumption of  $\text{Ca}(\text{OH})_2$  by zeolite). In specimens with 1Hs the weight loss associated with  $\text{Ca}(\text{OH})_2$  decomposition decreased till 3.12 % after 28 days of hydration, compared with reference specimen without additive (4.45 %). This decrease of portlandite quantity can be attributed in particular to pozzolanic reactions. The result is the formation of calcium silicate hydration (C–S–H) phases and aluminates. The last endothermic peak at 692 – 713 °C temperature is attributed to  $\text{CaCO}_3$  decomposition. The DTA curve of the tested specimens shows an exothermic peak at 744 °C temperature, which is typical of the recrystallization of C–S–H(I).

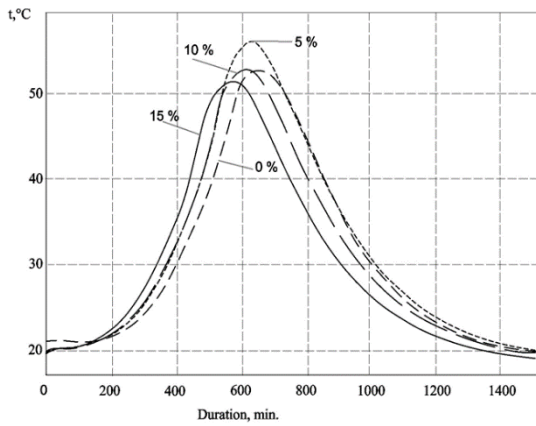
These data confirm the argument that hydrosodalite and portlandite participate in pozzolanic reaction by forming secondary calcium silicate hydrates and hydro aluminates. It was found that 1Hs in the cement paste affect the temperature of hydration process. Higher hydration temperature intensifies the chemical reaction and

the greater amount of heat is released during these reactions. Heat release curves are presented in Fig. 4.



**Fig. 3.** TG and DSC curves of hardened cement paste after 28 days. 1Hs addition content accounts for 0 % (a) and 15 % (b)

The hydration of cement paste was faster in all specimens with 1Hs (5, 10 and 15 wt. % of cement). The hydration rate is a function of additive amount, i.e. the hydration rate increases with the higher additive content. The highest hydration temperature was observed in specimens where cement was replaced with 5 wt. % of 1Hs.



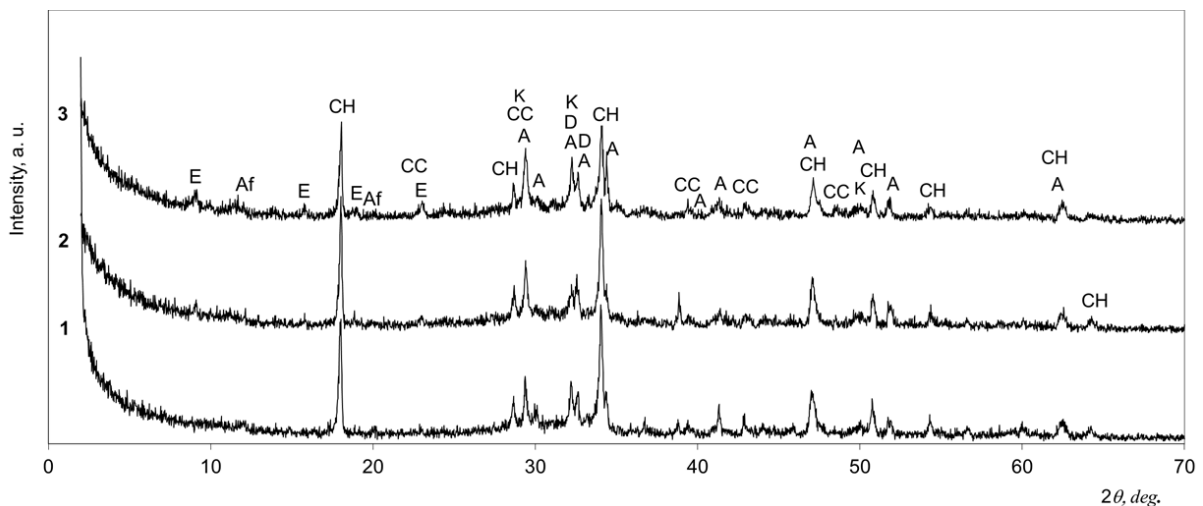
**Fig. 4.** The dependence of hydration temperature of cement paste on the quantity of 1Hs

### 3.2. The effect of 2Hs additive on cementitious system

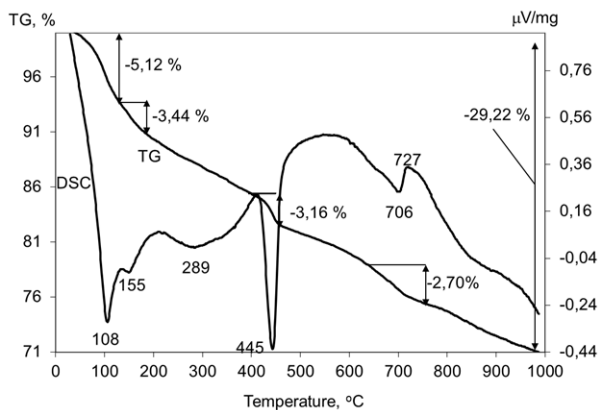
XRD patterns of hardened cement paste specimens with 2Hs additive are shown in Fig. 4. After 28 days of hydration, portlandite, calcium hydrosilicate, ettringite, non-hydrated alite, belite and the peaks of calcium carbonate, which forms when CO<sub>2</sub> present in the ambient

air reacts with calcium hydroxide, were identified. The intensity of portlandite peak decreases with the increase of additive as a result of pozzolanic reaction between 2Hs and Ca(OH)<sub>2</sub>. The endothermic effect observed in the thermogram (Fig. 6) at 108 and 155 °C temperature is mainly due to the dehydration of CSH (tobermorite-like phase) as well as ettringite. Thus, the endothermic peak at 155 °C temperature in the curve of this specimen may be specifically attributed to the high content of C-S-H. From Fig. 6 it can be seen that the amount of C-S-H gel is the greatest when 2Hs additive is used, when compared to the specimen without additives or to specimens with 1Hs additive (Fig. 3).

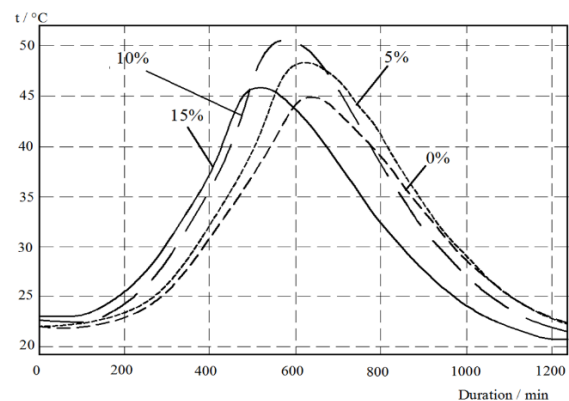
The next endothermic peak at 289 °C is related to the dehydration of calcium silicate and calcium aluminosilicate hydrates. DSC curves of hardened cement paste show decomposition of Ca(OH)<sub>2</sub> at 455 °C temperature. After 28 days of hardening, Ca(OH)<sub>2</sub> decomposition peak was weaker (Fig. 6) in specimens containing 15 wt.% of 2Hs additive compared to the control specimen without additives (Fig. 3). The endothermic peaks at 706 °C indicate CaCO<sub>3</sub> decomposition and the exothermic peak at 727 °C is typical of the recrystallization of C-S-H(I).



**Fig. 5.** X-ray diffraction patterns of hardened cement paste, after 28 days. 2Hs addition content accounts for 0 % (1); 5 % (2); 15 % (3). Notes: CH – portlandite; A – alite; D – belite; K – calcium silicate hydrate; E – ettringite; CC – calcite, Af – monosulfoaluminate



**Fig. 6.** The thermal analyze of hardened cement paste after 28 days. 2Hs addition content accounts for 15 %

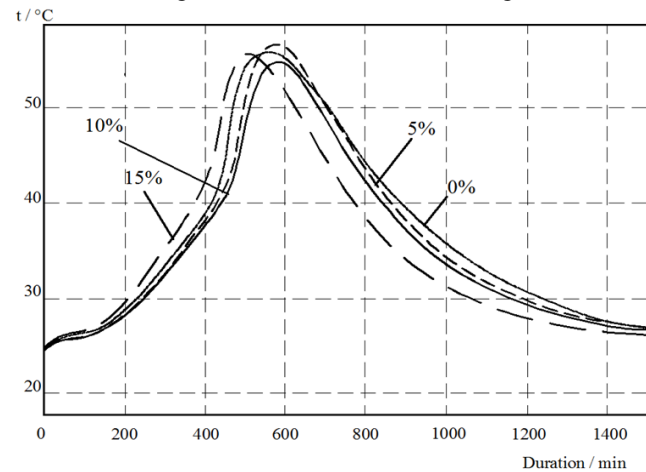


**Fig. 7.** The dependence of hydration temperature of cement paste on the quantity of 2Hs additive. Cement paste producing without zeolite and with 5 %, 10 % and 15 % of 2Hs

The increase in specimen strength and the release of higher hydration temperature can also be attributed to active  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  present in hydrosodalite (2Hs additive). Therefore, 2Hs additive added at 15 wt.% accelerates the hydration reaction (Fig. 7).

### 3.3. The comparison of the effect of used additives on cementations systems

Studies have demonstrated that the three investigated pozzolanic additives – 1Hs, 2Hs and silica fume – have a distinctive influence on the properties of cementations systems. The effect of additives 1Hs, 2Hs had bigger effect on the hydration temperature of the cement paste than silica fume additive (Fig. 4, Fig. 7, Fig. 8). The effect of silica fume on the cement paste hydration temperature influence is insignificant, as can be seen in (Fig. 8).



**Fig. 8.** The dependence function of cement paste hydration temperature on the type of additive after 28 days of hydration. Note FeSi – silica fume

Specimens with 5 wt.% 1Hs additive had the highest compressive strength (84 MPa) under the test conditions. The highest compressive strength was recorded in specimens with 10 wt.% of 2Hs additive (101 MPa). The increase in compressive strength may be related to active  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  present in 1Hs and 2Hs additive. The highest compressive strength of 80 MPa after 28 days of hardening was observed in specimens of hardened cement paste with 5 wt. % silica fume additive.

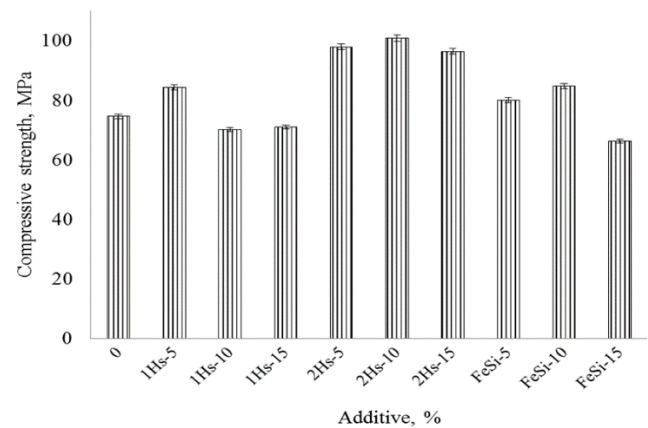
Higher compressive strength was obtained by using 1Hs and 2Hs additives (Fig. 9). Up to 20 % increase in compressive strength of cementitious systems can be achieved by using 2Hs added at 10 wt.%.

### 3.4. Microstructure of hardened cement pastes

The micro-structural study on hardened cement paste with zeolitic additives revealed that the soluble  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  could react with  $\text{Ca}(\text{OH})_2$  to produce calcium silicates hydrate and calcium aluminates hydrate which densified the hardened cement paste matrix.

Pozzolanic effect of these additives improved the microstructure of hardened cement paste and reduced the content of the harmful large pores [11–13]. This is explained by the formation of new crystal and amorphous phases and crystallization of the solution. The majority of new CSH compounds and calcium aluminate hydrate

(AFm) are formed in pores, the number of pores decrease with the crystallization and densification of new compounds. Needle-shaped ettringite, hexagonal laminated crystals of  $\text{Ca}(\text{OH})_2$ , reticulated type crystals of calcium silicate hydrates are seen in SEM images (Fig. 10 a).



**Fig. 9.** The dependence of hardened cement paste compressive strength on the type of additive after 28 days of hydration

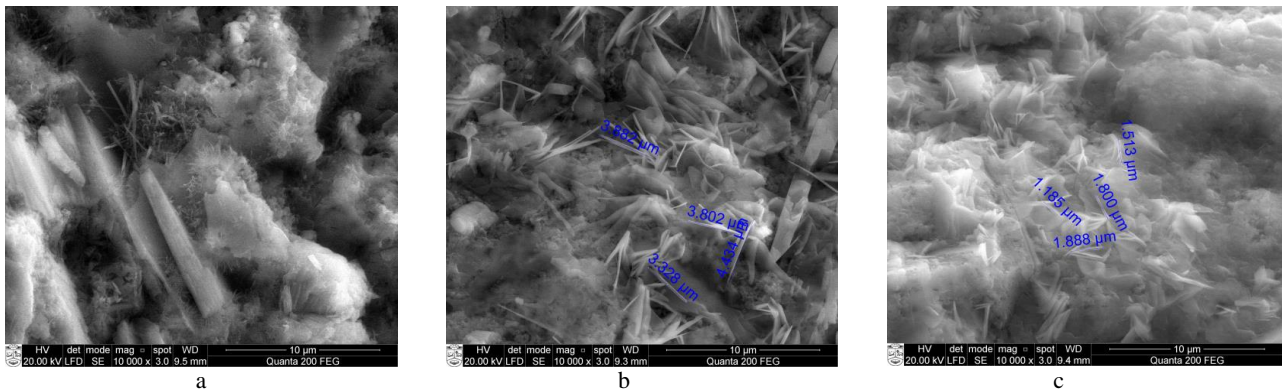
Newly formed calcium hydro-silicate C-S-H compounds have small needle-shaped crystals seen in SEM image (Fig. 10 b, c). Monosulfoaluminate preparations give apparently single phase preparations with relatively coarse hexagonal plate morphology (see Fig. 10 b, c).

When 15 wt.% of additive 1Hs is used, the hexagonal platy AFm phases are about  $4.43\text{--}3.33\ \mu\text{m}$  in size; when additive 2Hs is used, these platy hexagonal AFm phases are smaller,  $1.88\text{--}1.51\ \mu\text{m}$  in size. Therefore, specimens with 2Hs additive have smaller surface area.

## 4. CONCLUSIONS

Instrumental analysis has revealed that with higher content of the investigated additives the content of portlandite in the mineral composition of hardened cement paste reduces. According to the thermal analysis results, after 28 days the mass loss in specimens with 1Hs and 2Hs due to  $\text{Ca}(\text{OH})_2$  decomposition is lower by 3.12 %, 3.16 % respectively compared with the reference specimen (4.45 %). This decrease in portlandite content can be attributed to the result of pozzolanic reaction. The result is the formation of calcium silicate hydrated (C-S-H) phases and aluminates. The highest compressive strength of 84 MPa is observed in specimens of hardened cement paste with 5 wt.% of 1Hs additive, whereas in specimens with 10 wt.% of 2Hs additive the highest compressive strength was 101 MPa. 20 % higher compressive strength was reached by using 2Hs additive. Under the test conditions both 1Hs and 2Hs additives accelerate the hydration of the cement paste.

The highest hydration temperature was achieved in a mixture with 5 wt.% 1Hs additive and with 10 wt.% 2Hs additive. The pozzolanic effect of investigated additives 1Hs and 2Hs improved the microstructure of hardened cement paste. The formation of additional quantity of small needle-shaped CSH compounds and hexagonal plate monosulfoaluminate hydrate (AFm) phases was observed in the specimens with investigated additives.



**Fig. 9.** SEM picture of hardened cement paste samples: a – without additives; b – with 15 % of additives 1Hs; c – 2Hs

Results show that, in general, the additive 2Hs is slightly more active as additive 1Hs or silica fume, although it could be used as a substitute for pozzolans because it has better strength characteristics and is environmentally friendly as well. So, this zeolite could be a good substitute for silica fume.

### Acknowledgment

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