

## Blended Cements Produced with Synthetic Zeolite Made from Industrial By-Product

Danutė VAIČIUKYNIENĖ<sup>1\*</sup>, Vitoldas VAITKEVIČIUS<sup>1</sup>, Aras KANTAUTAS<sup>2</sup>, Aurelijus KARTOVICKIS<sup>1</sup>, Žymantas RUDŽIONIS<sup>1</sup>

<sup>1</sup> Faculty of Civil Engineering and Architecture, Kaunas University of Technology, Studentų str. 48, LT-51367 Kaunas, Lithuania

<sup>2</sup> Faculty of Chemical Technology, Kaunas University of Technology, Radvilėnų Rd. 19, LT-50254 Kaunas, Lithuania

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Zeolites are appropriate supplementary cementitious materials in cement and concrete industry. In the present work synthetic zeolites were used as supplementary material in hardened cement paste and some properties as well as its influence on Portland cement hydration was determinate. X-ray powder diffraction, scanning electronic microscopy and energy-dispersive X-ray spectroscopy, FTIR spectroscopy were used as investigation methods. The compressive strength of hardened cement paste was measured at day 3, 28 and 60. The instrumental analysis showed that zeolite A(Na) dominates and unreacted Al(OH)<sub>3</sub> remains in the investigated synthetics zeolites, made from thermal and mechanical treated AlF<sub>3</sub> production waste. The Chapelle test showed that both zeolites have good pozzolanic properties. The samples compressive strength remained close to the control samples compressive strength, reducing the amount of Portland cement, i. e., changing it by zeolite. After 60 days, the compressive strength was the best in the samples where 5 % of Portland cement was replaced by the synthetic zeolite. The compressive strength of the samples increased by 9 % compared with control samples. This research provides a real opportunity to save cement thus disposing the waste.

**Keywords:** blended cements, synthetic zeolite, by-product.

### 1 INTRODUCTION

Various minerals are often incorporated in Portland cement composition including zeolites [1–3], additives improving the characteristics of the resulting product manufacturing composite building materials. Scientists C. Karakurt and I. B. Topcu [4] found that the natural zeolite pozzolanic activity is higher than amorphous, natural pozzolanic materials pozzolanic activity. Concrete strength increased, while the zeolite reduced chloride penetration and corrosion of concrete having used only 15 % of natural zeolite. The samples with zeolite shrinkage deformations were lower in comparison with control samples.

Studying the pozzolanic additives (natural zeolite, fly ash, blast furnace slag) influence on the concrete properties (its alkali corrosion, resistance to high temperatures and sulphates) the researchers [5, 6] found that at high temperatures, ash additive reduces sample tension strength loss and cracks appearance. Concrete strength increases due to the pozzolanic reactions with portlandite. Length variations and micro-structure research, compared with the usual CEM I 42.5 showed that the building blends with different additives reduce the alkaline corrosion probability and increases the resistance to sulphates.

Also, natural zeolite (clinoptolite) was used as filling and bubble-generating additive in the manufacturing aerated concrete [7]. Test results showed that the burnt zeolite can perform both the function of filling and bubble-

generating agent. Also, it is not necessary to use aluminum powder in the cement production, and its compressive strength reaches up to 4.6 MPa and density – 930 kg/m<sup>3</sup>.

Modified zeolite additive can increase the strength and durability of concrete at its optimal amount is between 0.6 % and 1.0 % [8]. Concrete absorption improves regardless of the cement and mixture ratio in the mixture, and concrete water permeability improves having added 30 % of fly ash. It was concluded that the most effective to use the composite mixtures of fly ash and zeolite.

The ultrasonic transmission rate also increases increasing the amount of zeolite in mixture, but the Young's modulus, compressive and bending strength decreases [9]. The research results showed that the zeolite can be used as a filling, but not as a substitute for cement, as during the tests on the fresh concrete paste replacing up to 30 % of cement by zeolite it was found that it improves the dough resistance to delamination. Rapid chloride penetration test (RCPT) curves at solid state, replacing up to 30 % of the cement, showed lower values and higher surface resistance [10].

The research of natural zeolite rocks and Ca(OH)<sub>2</sub> solution pozzolanic activity by conductometry power method [11] stated that the zeolite rock has a large pozzolanic activity. These results have also described the direct zeolite dispersivity dependence on mechanical and pozzolanic properties.

Although natural zeolite with silica fume and ash is pozzolanic material, however it more influences the strength of the mixture in compound cement dough with a lower water and cement ratio. However in the cement dough with a bigger water/cement ratio and the lower

\*Corresponding author. Tel.: +370-37-300465; fax.: +370-37-300454.  
E-mail address: [danpal@ktu.lt](mailto:danpal@ktu.lt) (D. Vaičiukynienė)

replaced part of the zeolite by cement, hydration reaction takes place better [12].

The calculation of composite zeolite cement hydration rate solidification for 360 days and their hydration products, it was concluded that zeolite additive in mixture during hydration reacted with  $\text{Ca}(\text{OH})_2$  and made cement hydration products [13]. Pozzolanic reaction of zeolite in the first days was slow, but it became much faster after 28 days of hydration.

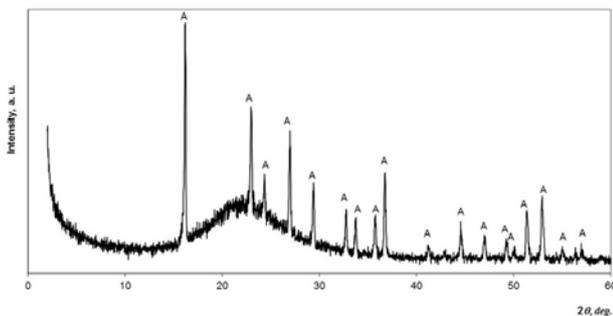
Th. Perraki investigated the influence of natural zeolite to cement hydration. Tested zeolite from “II type of heulandite” had a considerable pozzolanic activity of 0.555 g  $\text{Ca}(\text{OH})_2$  per gram of zeolite (according to Chappelle methodology). During hydration time a larger quantities of  $\text{Ca}(\text{OH})_2$  are bounded having inserted this zeolite into dough and the compounds similar to cement hydration compounds are produced [14].

The literature data show that natural zeolites are promising pozzolanic additive. Therefore, this work investigates artificial zeolites derived from highly contaminated with fluorine compounds amorphous  $\text{SiO}_2$  the use capabilities in cement systems.

## 2. MATERIALS AND METHODS

### 2.1. Raw materials

The Portland cement CEM I 52.5 R (specific surface is  $370 \text{ m}^2/\text{kg}$ , paste of normal thickness 27.3 %, the initial setting time is 130 min, final setting is 215 min) was used in this study.



**Fig. 1.** X-ray diffraction pattern of  $\text{AlF}_3$  production waste. Notes: A –  $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$

**Table 1.** The element composition of  $\text{AlF}_3$  production waste

Element	Wt, %	At, %
Oxygen	41.98	52.09
Aluminum	2.98	2.19
Silicon	33.43	23.64
Fluorine	20.84	21.79
Calcium	0.30	0.15
Iron	0.46	0.16
Total	100	100

Reagents  $\text{NaOH}$  (DeltaChem, Czech Republic),  $\text{Al}(\text{OH})_3$  (Lachema, Czech Republic), industrial by-product, i. e., amorphous  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  (Lifosa, Lithuania), as silica and alumina source were used in the synthesis of

zeolites. According to the X-ray diffraction curves (Fig. 1) there are amorphous  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$  (rise from 10 up to 30°) and crystalline  $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$ .

Very high fluoride concentrations were obtained after the amorphous silica elemental analysis (Table 1). It is believed that fully unreacted  $\text{H}_2\text{SiF}_6$  in investigated silica should be left in addition to these compounds. The determination of  $\text{H}_2\text{SiF}_6$  in heterogeneous systems is problematic.

### 2.2. Experimental techniques

The X-ray powder diffraction data were collected with DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered  $\text{Cu K}\alpha$  radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range  $2^\circ - 70^\circ$  ( $2\theta$ ) in steps of  $2\theta = 0.02^\circ$ .

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) was used. The quantitative analysis was carried out with the energy-dispersive X-ray adapted to the SEM for microanalysis. An energy-dispersive X-ray spectrometer (EDS) has a 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  $-270^\circ\text{C}$  to  $+1820^\circ\text{C}$ ).

The pH was determined by a Premium Aquatics Supplies Hanna HI-98129 tester, which simultaneously measures aqueous pH and temperature. Range pH is from 0.00 to 14.00 pH.

IR spectra were recorded with Perkin Elmer FT-IR System spectrometer. For the IR analysis, 1 mg of the substance was mixed with 200 mg of KBr and compressed in a forming press under vacuum.

Zeolites have been produced by using mechanical treatment, by grinding in the laboratory ball mill (grinding bodies – steel balls), or by heating a suspension in kiln SNOL 200/200.

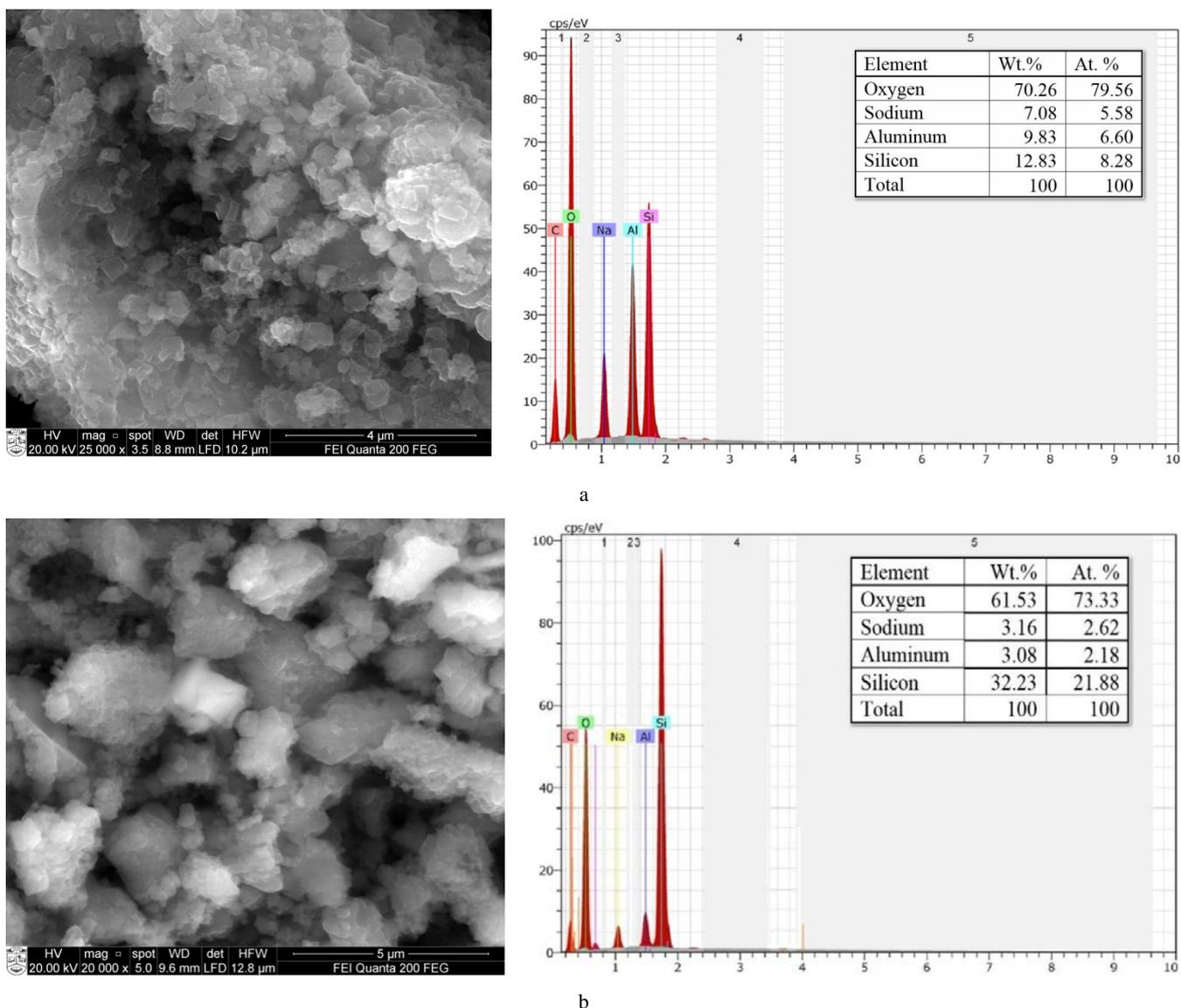
Constant flow was stable and the content of the modified zeolite addition was 0; 5; 10 and 15 % mass in all test samples. Water and cement ratio ( $V/C = 0.40$ ) was constant in all samples. The formed test samples ( $2 \times 2 \times 2$  cm size cubes) were hardened for 3, 28, and 60 days. The compressive strength of hardened cement paste was measured by EN 196-1.

## 3. RESULTS AND DISCUSSION

### 3.1. Zeolitization of $\text{AlF}_3$ production waste

$\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$  molar ratio equal to 1.5–2 : 1 : 2 : 10 was taken for  $\text{AlF}_3$  production waste zeolitization. This ratio is the most optimal to get the synthetic zeolite A, which is widely used [15, 16].

The initial dry matter was thoroughly mixed until homogenous; then pouring the required amount of water it was stirred until a homogeneous liquid suspension. In the first case, it was heat-treated by heating a suspension for four hours at  $110^\circ\text{C}$  (hereinafter referred to as 1-zeolite),



**Fig. 2.** SEM images and element of composition of synthetic zeolites. Notes: a – 1-zeolite; b – 2-zeolite

and in the second case, mechanically grinding it for 15 minutes in vibro mill (hereinafter referred to as 2-zeolite). 15 min duration is optimal based on previous work [17]. The excess amount of sodium hydroxide in the obtained zeolites was washed with water to neutral pH medium. The product was dried at 80 °C in 24 hours.

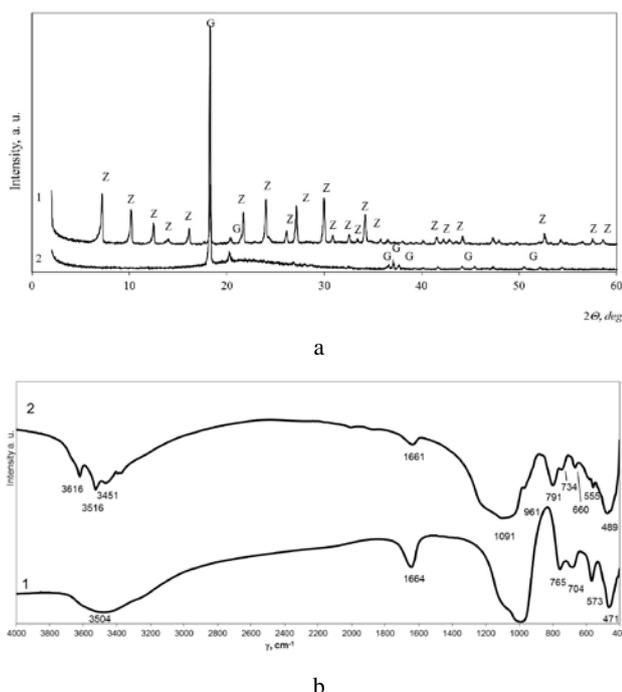
Both zeolite samples were examined by scanning electron microscopy (Fig. 2). SEM images show that 1-zeolite obtained during the process of  $\text{AlF}_3$  production waste zeolitization for four hours at the temperature of 110 °C (Fig. 2, a) crystals have a cubic character, and zeolitizing  $\text{AlF}_3$  waste mechano-chemically (grinding in vibro mill 15 min) (Fig. 2, b) besides to cubic crystals, characteristic to zeolite A there are particles of not defined form, which yet have not fully recrystallize to crystalline zeolite.

EDS analysis showed that silicon, aluminum, and sodium dominated in both synthetic zeolites. Sodium concentration was managed to reduce up to 2.62 % by washing 2-zeolite with water, while 5.58 % sodium remained in 1-zeolite.

According to the X-ray diffraction curves of synthetic zeolites (Figure 3), zeolite A (Na) ( $d$ : 1.231, 0.870, 0.710, 0.410, 0.371, 0.328, 0.262 nm) dominate and there are also not completely unreacted  $\text{Al}(\text{OH})_3$  ( $d$ : 0.485, 0.438, 0.433, 0.234 nm).

Infrared IR spectra can provide valuable information in study of the material structure difference. IR curves (Fig. 3, b) of analyzed zeolites had a large number of absorption bands in  $(400-4000) \text{ cm}^{-1}$  range. Zeolites structure peculiarities are determined according to  $(1100-400) \text{ cm}^{-1}$  zone. The characteristic absorption bands for Zeolite A [18] are:  $(1000-1091) \text{ cm}^{-1}$  in the range of asymmetric valence fluctuations, 765, 791, and 704,  $660 \text{ cm}^{-1}$  in the range of symmetric valence fluctuations, 573,  $555 \text{ cm}^{-1}$  in the range of double shell rings fluctuation and 471,  $489 \text{ cm}^{-1}$  in the range of  $\text{Si}(\text{Al})-\text{O}$  deformation vibration.

The absorption bands in 2-zeolite spectrum 3616, 3516, 3451, 961, 734,  $660 \text{ cm}^{-1}$  are assigned to gibbsite ( $\text{Al}(\text{OH})_3$ ), i.e., to initial material, which remained unreacted. The received FT-IR analysis results agree well with the research results of other scientists [19–21].

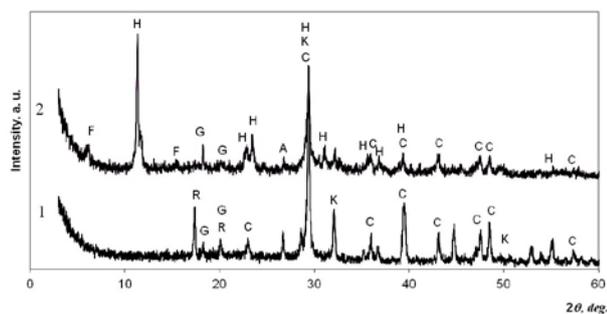


**Fig. 3.** X-ray diffraction patterns (a) and FT-IR spectra (b) of synthetic zeolites: 1 – 1-zeolite; 2 – 2-zeolite; G – gibbsite  $\text{Al}(\text{OH})_3$ ; Z – zeolite A  $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384} \cdot 16\text{H}_2\text{O}$

### 3.2. Pozzolanic activity of 1-zeolite and 2-zeolite

Zeolites can be used as a pozzolanic material according to ENV 197-1 directive. Mixed with water, zeolites do not harden like most other pozzolanic materials, but zeolites begin to react with soluble calcium hydroxide (in the water), if they are very finely granulated at normal i.e., at room temperature; calcium silicates and calcium aluminates, determining the strength of the concrete [22] is the result of this process.

After Chepelle test [23] it was found that 2-zeolite bound almost the same amount of calcium hydroxide ( $0.9751 \text{ g} \pm 0.01 \text{ g Ca}(\text{OH})_2/\text{g zeolite}$ ) as well as 1-zeolite ( $0.9633 \text{ g} \pm 0.01 \text{ g Ca}(\text{OH})_2/\text{g zeolite}$ ), so both zeolites can be attributed to pozzolanic materials group.



**Fig. 4.** X-ray diffraction patterns of pozzolanic reaction product. Notes: 1 – 1-zeolite; 2 – 2-zeolite. F –  $(\text{Na}_2\text{Ca})_{0.075}(\text{Al}_{0.3}\text{Si}_{0.7})\text{O}_2(\text{H}_2\text{O})_{0.22}$ ; H – hydrocalumite –  $\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$ ; R – hydrogranate –  $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$ ; G – gibbsite  $\text{Al}(\text{OH})_3$ ; C – calcite  $\text{CaCO}_3$ ; K – calcium silicate hydrate  $\text{Ca}_{1.5}\text{SiO}_{3.5}\text{H}_2\text{O}$

X-ray analysis of pozzolanic reaction products (solids) showed that sodium calcium alumohydrosilicates  $(\text{Na}_2\text{Ca})_{0.075}(\text{Al}_{0.3}\text{Si}_{0.7})\text{O}_2(\text{H}_2\text{O})_{0.22}$ , calcium aluminate

hydrate (hydrocalumite)  $\text{Ca}_2\text{Al}(\text{OH})_7 \cdot 3\text{H}_2\text{O}$ ; gibbsite  $\text{Al}(\text{OH})_3$  and calcium silicate hydrate  $\text{Ca}_{1.5}\text{SiO}_{3.5}\text{H}_2\text{O}$  in 1-zeolite (Fig. 4, curve 2) formed after the pozzolanic reaction. 2-zeolite in reaction with calcium hydroxide formed calcium aluminate hydrates (hydrogranates)  $\text{Ca}_3\text{Al}_2(\text{O}_4\text{H}_4)_3$ ; gibbsite  $\text{Al}(\text{OH})_3$ , calcite  $\text{CaCO}_3$  and calcium silicate hydrate  $\text{Ca}_{1.5}\text{SiO}_{3.5}\text{H}_2\text{O}$ .

### 3.3. Synthetic zeolites in cement systems

Portland cement clinker mineral hydration reactions are relatively slow. Their rate depends on many factors, including nature and quantity of the cement additives. It is convenient to follow the progress of these reactions according to solidifying samples temperature change kinetic curves (Fig. 5). Hydration maximum temperature of cement sample when 5 % of 1-zeolite is modified Portland cement (Fig. 5, a) increases by 3 degrees (up to  $58^\circ\text{C}$ ) compared with the control – free of zeolite – sample hydration temperature ( $55^\circ\text{C}$ ). Hydration temperature drops to  $50^\circ\text{C}$  and  $48^\circ\text{C}$  C taking its larger quantities (10 % and 15 %).

Analogous tendencies are observed using 2-zeolite (Fig. 5, b) also. Hydration maximum temperature of cement sample with 5 % of 2-zeolite amount is higher than the control sample, and the temperature of these samples was similar to controls inserting into the cement increased by 10 % and 15 % 2-zeolite amount. However, any investigated amount of 1-zeolite and 2-zeolite decreases the initial setting of cement paste (the maximum of temperature moves to longer duration area).

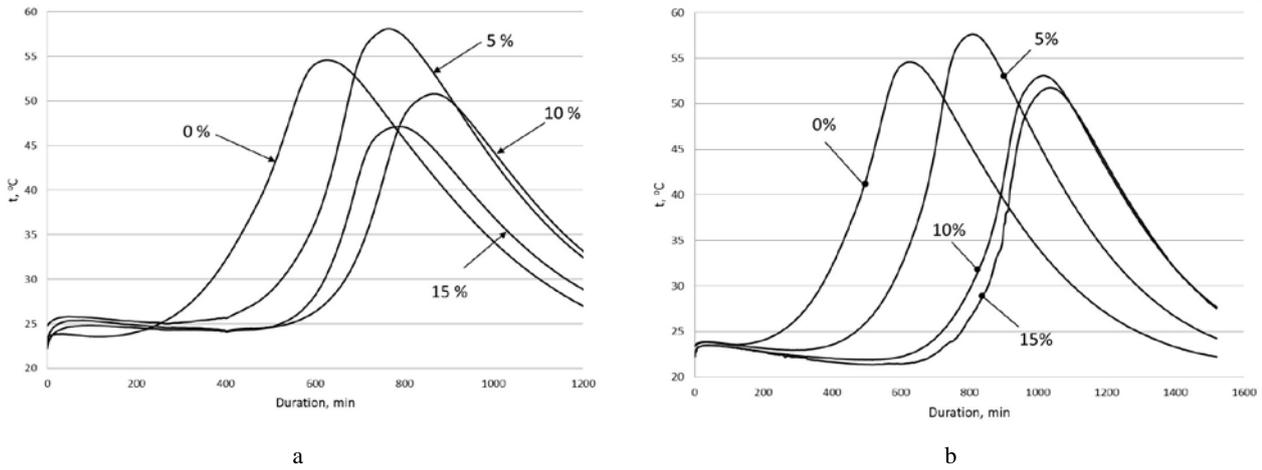
The compressive strength of the samples after three days of hydration remained close to the control samples strength (Fig. 6). The highest compressive strength in tested conditions after 28 days had the samples containing 5 % of 1-zeolite, changing Portland cement to 1-zeolite in different quantities. So, the zeolite of pozzolanic properties displays not immediately; they become apparent after longer hydration time, i.e., only after 28 days. Zeolite reacting with calcium hydroxide composes secondary hydration products, the pores and capillaries in cement stone as hydraulic additives.

After 60 days, the best compressive strength had the samples, which were formed replacing Portland cement by 2-zeolite. Taking 5 % of this zeolite, the samples compressive strength increased by about 9 % compared with the control (Fig. 6, b).

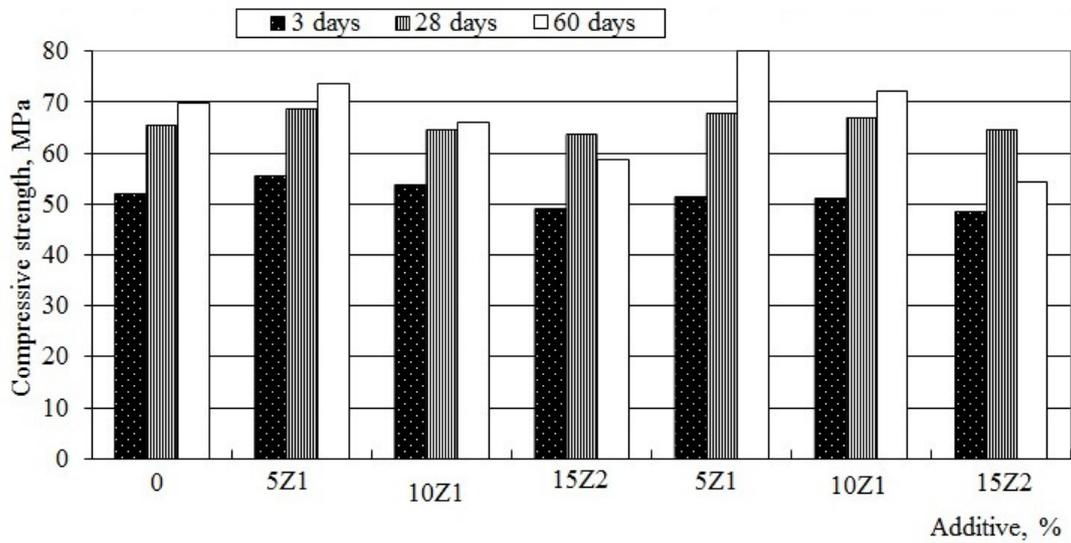
X-ray diffraction analysis results of the hydrated samples (Fig. 7) show that calcium hydrosilicate, alite, belite, portlandite and calcite, as well as small amount of vaterite and gibbsite dominated in the cement stone with 1-zeolite. Calcium silicate hydrates, alite, and belite also prevail in the samples with 2-zeolite.

In both cases portlandite peak in the X-rays diffraction patterns decreases increasing the amount of zeolite. It can be concluded that the replacement of Portland cement binds portlandite to secondary calcium silicate hydrates during the hydration.

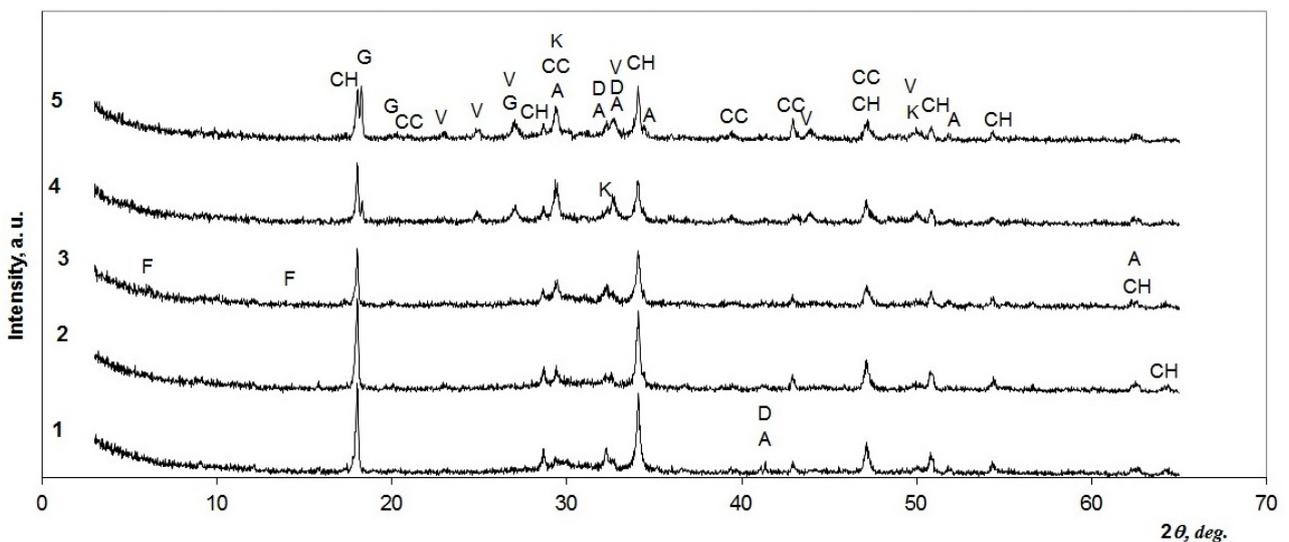
Microstructure of cement stone is given in SEM pictures (Fig. 8). Hexagonal calcium (sodium) silica alumina hydrate (Fig. 8, a) are formed in cement stone when Portland cement is replaced by 15 % of 1-zeolite. The EDS



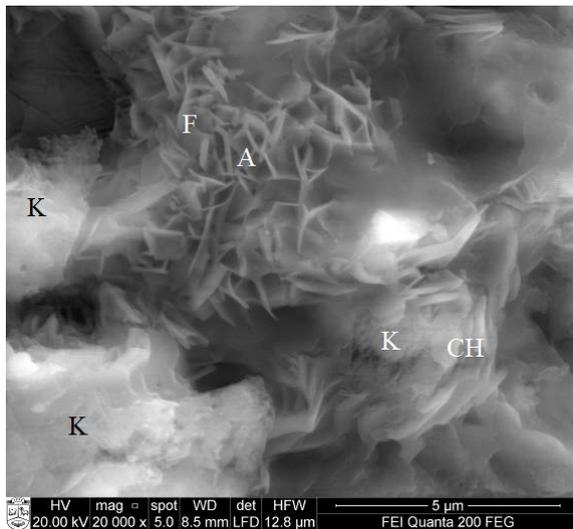
**Fig. 5.** Cement paste hydration process temperature dependence on the quantity of portlandcement supplementary material: a – 1-zeolite; b – 2-zeolite



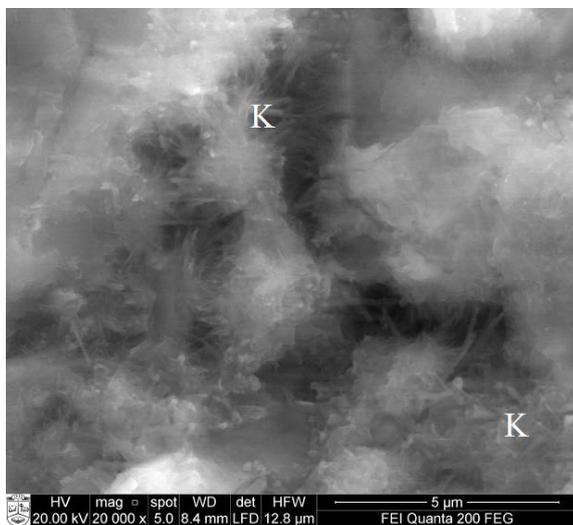
**Fig. 6.** Compressive strength of hardened cement paste after 3, 28 and 60 days with 0, 5, 10 and 15% of portlandcement supplementary material : Z1 – 1-zeolite; Z2 – 2-zeolite



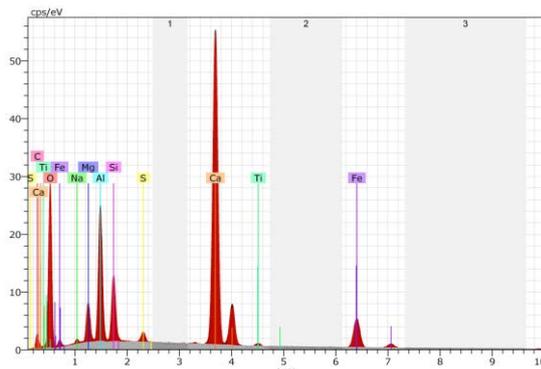
**Fig. 7.** X-ray diffraction patterns of hardened cement paste after 28 days hydration with 0 % (1); 5 % 1-zeolite (2); 10 % 1-zeolite (3); 5 % 2-zeolite (4) and 10 % 2-zeolite (5) of portlandcement supplementary material. Notes: CC – calcite; G – gibbsite; CH – portlandite; K – calcium hydrosilicate; V – vaterite; A – alite; D – belite



a



b



c

**Fig. 8.** The SEM images of hardened cement paste: with 15 % 1-zeolite (a) and with 15 % 2-zeolite (b). The elemental composition of point A (c). Notes: CH – portlandite; K – calcium hydrosilicate; F – calcium silica alumina hydrate

results reveal that those crystals are calcium aluminosilicate hydrate and its elemental composition is shown in (Fig. 8, c). Similar crystals are reported in studies [22, 23]. Hexagonal tabular  $\text{Ca}(\text{OH})_2$  crystals and small,

semi-amorphous calcium silicate hydrates needle crystals can also be identified in these pictures. Very detailed semi-amorphous microstructure can be seen in the SEM photos of the samples with 2-zeolite. The newly formed calcium silicate hydrates of CSH (I) type form small needle crystals (Fig. 8, b).

The obtained results shows that the most purposeful is to replace 5 % of Portland cement with 2-zeolite in cement mixture.

#### 4. CONCLUSIONS

The instrumental analysis (X-ray diffraction, IR spectroscopy, SEM) showed that zeolite A(Na) dominates and unreacted  $\text{Al}(\text{OH})_3$  remains in the investigated synthetics zeolites, made from thermal and mechanical treated  $\text{AlF}_3$  production waste. 1-zeolite crystals have a cubic shape and there are particles of smaller and uncertain form in 2-zeolite near the cubic crystals, characteristic to zeolite A. The Chapelle test showed that both 1-zeolite and 2-zeolite have good pozzolanic properties.

By using 5 % of investigated zeolites the hydration temperature maximum of cement pastes, increases by 3 degrees (up to  $58^\circ\text{C}$ ) compared with the hydration temperature ( $55^\circ\text{C}$ ) of reference sample. Hydration temperature drops down to  $50^\circ\text{C}$  and  $48^\circ\text{C}$  taking 1-zeolite larger quantities (10 % and 15 %). By using the larger quantities (10 % to 15 %) of 2-zeolite hydration temperature was close to the reference sample temperature. However, any investigated amount of 1-zeolite and 2-zeolite decreases the initial setting of cement paste (the maximum of temperature moves to longer duration area).

The samples compressive strength remained close to the control samples compressive strength, reducing the amount of Portland cement, i.e., changing it by zeolite. After 60 days, the compressive strength was the best in the samples where 5 % of Portland cement was replaced by the 2-zeolite. The compressive strength of the samples increased by 9 % compared with control samples. The increase of sample strength can be explained by the fact that enclosed zeolite during hydration binds portlandite to the secondary calcium silicate hydrates. This research provides a real opportunity to save cement thus disposing the waste.

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