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INFLUENCE OF ZEOLITIZED PERLITE ON BLENDED CEMENT PROPERTIES

Article Highlights

- The zeolitization of expanded perlite was carried out to improve its hydraulic properties
- During perlite zeolitization hydrosodalite form accelerating the hydration of cement
- It significantly improves cementitious binder adhesion with zeolitized perlite particles

Abstract

Perlite is a mineral of volcanic origin. Expanded perlite has good heat insulation and sound absorption properties. It is light, resistant to fire, moisture and micro-organisms, harmless to health. However, due to the presence of hyaline phase, its use in Portland cement mixture is problematic. In this paper, the zeolitization of expanded perlite was carried out to improve its hydraulic properties. The conversion of expanded perlite into zeolite material was carried out when $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}$ mole ratio was equal to 2:1:2:10 and the suspension of starting materials was treated for 3 h at 100 °C. Mechanical and physical properties of hardened cement paste containing 0, 5, 10 and 15% of pure perlite admixtures, zeolitized perlite, and perlite altered to calcium (Ca^{2+}) zeolite were researched. The results showed that zeolitization of expanded perlite activates its hydraulic properties; after 28 days of hydration under normal conditions, the compressive strength of the specimens modified with 5% of zeolitized perlite admixture was 49-50 MPa, whereas the compressive strength of the specimens containing 5% of pure perlite admixture was only 33 MPa.

Keywords: zeolitized perlite, blended cement, hydrosodalite.

Various pozzolanic admixtures are added to the mixture of composite cements. Expanded perlite is one such admixture. Previous studies [1-3] have shown that perlite powder has a significant pozzolanic effect. The research into the influence of natural pozzolans (perlite) on concrete systems showed that this material reacts with $\text{Ca}(\text{OH})_2$, and can be used in lightweight concrete production. The replacement of concrete aggregates by perlite increased water demand for the preparation of concrete mass and porosity of the specimens. The test results showed that perlite can reduce the porosity and hydration of the cement paste during curing.

During the gradual hydration process, small pores diminish in size until they disappear completely at the end of the hydration process. The total pore

volume of the hardened cement paste is thus reduced. The number of harmless pores (gel and micro-pores) increases, and the number of harmful (macro pores) decreases. Therefore, it can be concluded that perlite admixtures in porous concrete materials should improve their mechanical strength and durability over time.

Perlite is a siliceous volcanic glass with the volume expanding substantially under the effect of heat. It contains a large amount of SiO_2 and Al_2O_3 . Perlite is an active hydraulic admixture in concrete mixture. The use of perlite substantially improves thermal conductivity of concrete products but their strength characteristics are significantly reduced [4-7]. Low mechanical strength of the mixture with perlite can be increased by using high mechanical strength cements and superplasticizers [8-10].

Natural diatomite and perlite admixture in concrete can improve its durability. However, a large amount of diatomite and perlite reduced concrete compressive strength; therefore it is necessary to select the optimum admixture amount. To obtain the lightweight concrete of the maximum compressive

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strength, the optimum amount of diatomite and perlite is 10% by weight of the mixture [11].

The main reason for poor mechanical properties of composite perlite-cement materials is the lack of strong interfacial adhesion between the cement binder and perlite particles. The addition of nanosilicate particles into the mix increases the elasticity of cementitious materials and reduces the size and quantity of defects [8]. Due to this the mechanical properties of concrete products improve.

Therefore, low mechanical strength of the mix with perlite can be increased by using integrated concretes of high mechanical strength and by adding short polypropylene (PP) fibres for reinforcement [12]. However, test results have shown that high content of perlite reduces the mechanical strength and adhesion of concrete regardless of the addition of polymeric admixtures; water permeability also increases.

Morsy *et al.* investigated the effect of perlite on the thermal resistivity, solar reflectance and indirect tensile strength of nanostructured cementitious binder. In this composition, white Portland cement was partially substituted by nano-clay. As expected, the addition of perlite has reduced the indirect tensile strength but increased the thermal resistivity of the compound by 250%. The addition of perlite had not affected the solar reflectivity of the compound [8].

The literature review suggests that the use of pure perlite in composite cement is limited, so the aim of this research work is to determine the impact of modified zeolitized perlite admixture on the main properties of cement specimens.

EXPERIMENTAL

Commercial Portland cement of type CEM I 52.5R (specific surface 470 m²/kg, paste of normal consistency 27.3%, the initial setting time is 130 min, the final setting time is 215 min) for the tests was used. Chemical and mineral composition of Portland cement and expanded perlite is shown in Table 1.

The following reagent materials for zeolitization of expanded perlite were used: perlite, Al(OH)₃ (Lach-Ner, Czech Republic), NaOH (Chempur, Poland) and CaCl₂.

The water to cement ratio (*W/C*) was stable (*W/C* = 0.45) in all test specimen compositions. The compositions differed by the contents of the zeolitized perlite: 0, 5, 10 and 15%. The test specimens (20 mm×20 mm×20 mm-size cubes) were cured for 28 days. The compressive strength of hardened cement paste was determined by EN 196-1. An automated and computerized ToniTechnik 2020 press was used

to evaluate the compression strength of hardened cement paste.

Table 1. Chemical and mineral composition of Portland cement clinker and perlite

Chemical and mineral composition	Quantity, %	
	CEM I 52.5 R	Perlite
SiO ₂	20.61	74.1
TiO ₂	-	0.3
Al ₂ O ₃	5.45	13
Fe ₂ O ₃	3.36	0.7
MnO	-	-
MgO	3.84	0.2
CaO	63.42	0.9
SO ₃	0.80	-
Na ₂ O	0.20	3.8
K ₂ O	1.00	6.1
P ₂ O ₅	-	-
Na ₂ O _{eq.}	0.86	0.8
Loss of ignition	1.00	-
C ₃ S	60.7	-
C ₂ S	13.5	-
C ₃ A	9.7	-
C ₄ AF	10.2	-

The X-ray powder diffraction data was collected by a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered CuK α radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range of 2-70° in steps of 0.02°.

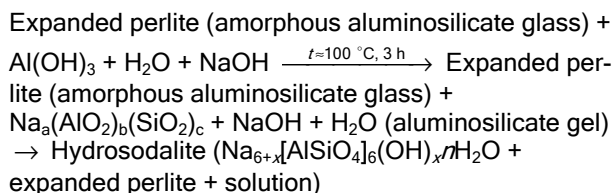
Simultaneous thermal analysis, differential scanning calorimetry and thermogravimetry were also used to measure the thermal stability and phase transformation of the products at the heating rate of 15 °C/min, the temperature ranged from 30 °C up to 1000 °C under the atmospheric pressure. The test was carried out on a simultaneous thermal analyzer 409 PC Luxx (Netzsch STA instruments). The ceramic specimen handlers and Pt-Rh crucibles were used.

The microstructure of hardened cement paste was studied using a high resolution scanning electron microscope FEI Quanta 200 FEG with a Schottky field emission gun (FEG). Chemical compositions of perlite and perlite with hydrosadolite were investigated using an energy-dispersive X-ray spectrometer (EDS) with a silicon type drift droplet detector.

RESULTS AND DISCUSSION

Expanded perlite is an amorphous (Figure 1, 1 cr.) volcanic rock of spongy structure (Figure 1a).

Zeolites may be obtained by heating some aluminosilicate materials in the presence of alkaline solutions. So, in this test hydrosodalite was synthesized from expanded perlite (glass). By zeolitization process the amorphous perlite structure changes into crystalline structure and zeolite forms on the perlite framework. The water rich form of the hydrosodalite is $\text{Na}_{6+x}[\text{AlSiO}_4]_6(\text{OH})_x \cdot n\text{H}_2\text{O}$ with $0 \leq x \leq 2$ and $0 \leq n \leq 8$. The zeolitization of perlite was performed under the following scheme:



The optimum composition, often used for the synthesis of zeolites, $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}$ of mole ratio of 2:1:2:10 was selected for perlite zeolitization [13]. Additionally, NaOH, Al(OH)₃ and water were added to expanded perlite. The zeolitization process continued by heat treatment of the initial mixture for 3 h at 100 °C. The surplus NaOH obtained after the synthesis reaction in the products was washed with water. The obtained dry material particles were used as an admixture in Portland cement hydration studies. All the peaks in the X-ray image of the product (Figure 1, cr. 2) are attributed to zeolite hydrosodalite ($\text{Na}_{6+x}(\text{SiAlO}_4)_6(\text{OH})_x \cdot n\text{H}_2\text{O}$) with crystal size of 1.5 μm. The crystals are glassy, porous structures, grown on expanded perlite (Figure 2b).

EDS analysis of zeolitized perlite (perlite with hydrosodalite) showed that the material mainly consists of Al₂O₃ (31.36%), SiO₂ (31.41%) and Na₂O (19.56%), Figure 3a.

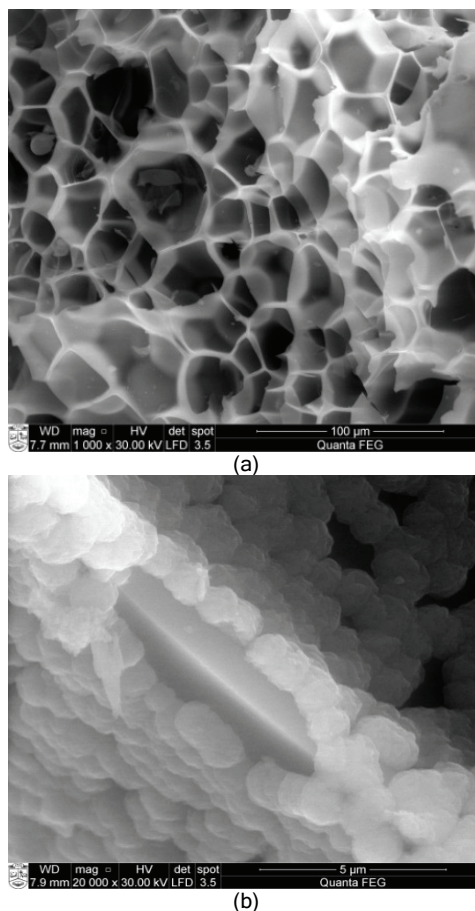


Figure 2. SEM pictures of expanded perlite; a) expanded perlite, b) zeolitized perlite.

In order to reduce the probability of concrete alkaline corrosion, zeolitized perlite with inserted Ca^{2+} was produced. Ion-exchange reaction was carried out in CaCl_2 aqueous solution. This solution was poured onto hydrosodalite at 85 °C and the suspension was

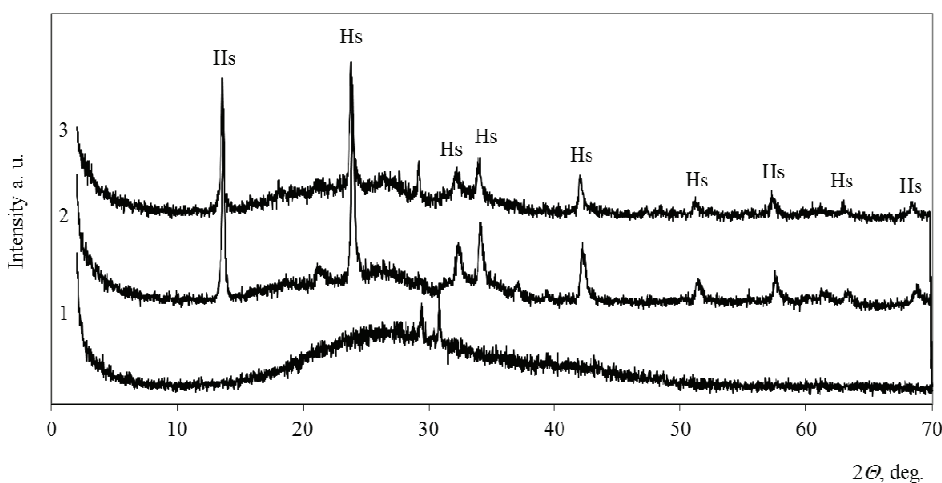
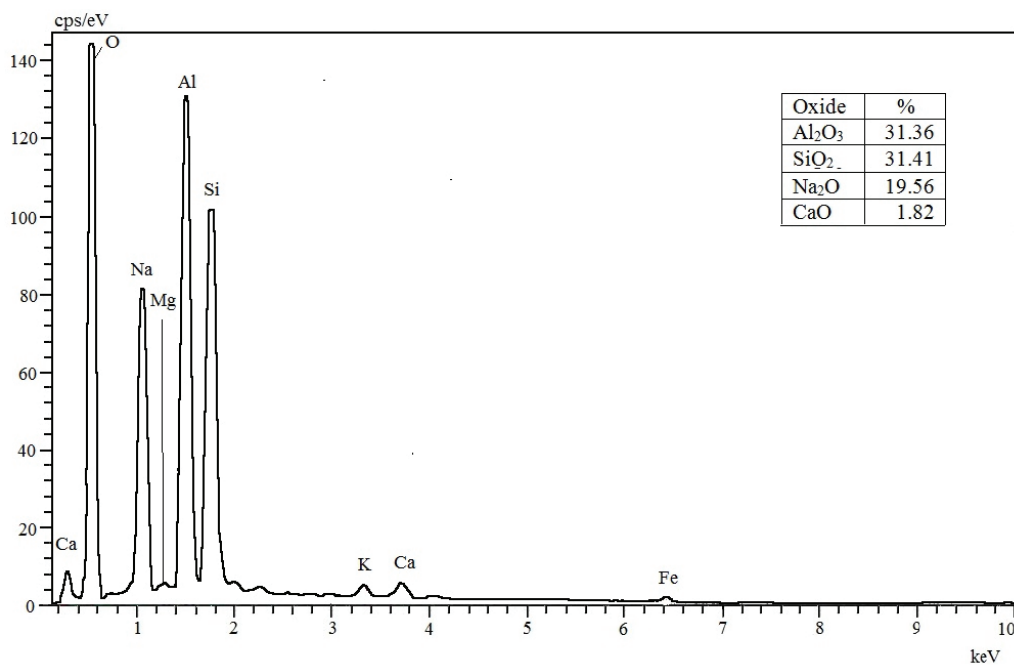
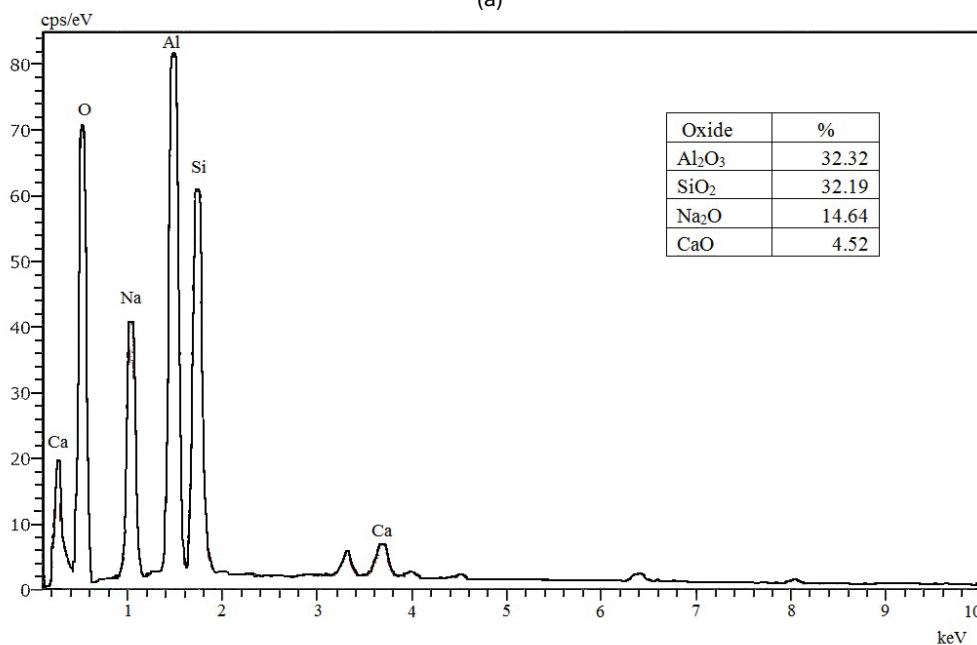


Figure 1. X-Ray diffraction pattern of expanded perlite (1 cr.), zeolitized perlite (2 cr.) and zeolitized perlite with inserted Ca^{2+} (3 cr.). Hs is hydrosodalite.



(a)



(b)

Figure 3. EDS analysis of zeolitized perlite (a) and zeolitized perlite with inserted Ca²⁺ (b).

stirred for 5 min; afterwards the mixture was filtered and the solids were dried. The X-ray diffraction analysis (Figure 1, 3 cr.) shows that hydrosodalite prevails in the exploratory material. The peaks before and after the ion-exchange reaction are very similar. The curves show that the diffraction peaks with diffraction angles at 13.8, 24.1, 32.4, 34.3, 42.3 and 57.6° are characteristic of hydrosodalite. The structure of hydrosodalite crystals was observed to be stable because the shape of the X-ray diffraction patterns (Figure 1,

cr. 2 and cr. 3) did not change. Similar results were obtained in previous investigations [14].

Al₂O₃ (32.32%), SiO₂ (32.19%), Na₂O (14.64%), and CaO (4.54%) dominated in this material (Figure 3b).

Hardened cement paste specimens were formed by changing part of Portland cement by perlite admixtures. It was found that the highest 58 °C temperature was achieved in the specimens of zeolitized perlite with inserted Ca²⁺ (Figure 4). Cement paste with zeolitized perlite at 57 °C temperature was close to the

hydration peak temperature. Temperatures of the control specimen and the specimen with perlite were 55 and 53 °C, respectively. A similar tendency is also observed comparing the duration of temperature maxima. The earliest peak was reached in the control specimen, then in the specimens with zeolitized perlite with inserted Ca^{2+} and zeolitized perlite, during 608 and 601 min, respectively, and the maximum temperature of the specimen with expanded perlite was reached the latest, after 646 min. The obtained test results show that the hydration time increases almost by 65 min when Portland cement is replaced by perlite. Zeolitized perlites accelerate hydration and hydration time becomes shorter. Pure perlite reduces hydration temperature and zeolitized perlite increases hydration temperatures in comparison with the control specimen.

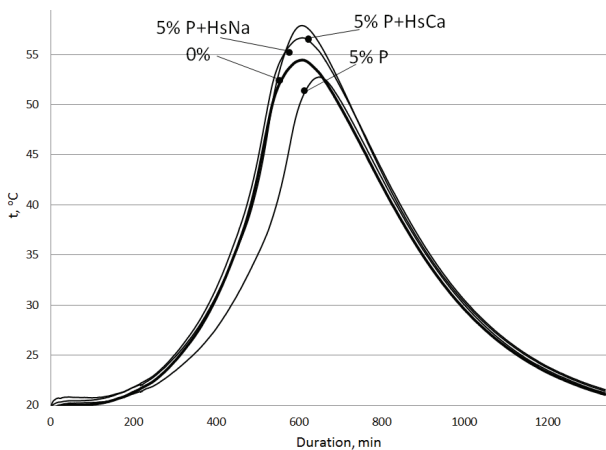


Figure 4. Used cement substitutes (expanded perlite, zeolitized perlite and zeolitized perlite with inserted Ca^{2+}) influence on cement paste hydration curves, where P is expanded perlite, P + HsNa is zeolitized perlite, P + HsCa is zeolitized perlite with inserted Ca^{2+} .

Cement paste specimens hydrated for 28 days were investigated by X-ray method. The specimens without perlite and specimens in which part of the cement was replaced with perlite, with zeolitized perlite, and with zeolitized perlite with inserted Ca^{2+} were compared interdependently. The specific for hardened cement paste compounds, such as: portlandite, alite, belite, calcite, CSH, ettringite and vaterite were present in these specimens.

X-ray curves of hardened cement paste with zeolitized perlite admixtures show that the amount of $\text{Ca}(\text{OH})_2$ in hardened cement paste decreases (Figure 5, 4 cr.), *i.e.*, significantly reduces the maximum $\text{Ca}(\text{OH})_2$ characteristic peak with 18.0° diffraction angles. The mentioned peak had the highest intensity in the control specimen and in the specimen with perlite. The amount of calcium carbonate increases besides the decrease of portlandite amount, as the peaks characteristic of this compound increase in intensity.

It can be maintained that the investigated zeolitized perlite behaves as pozzolanic material; a part of portlandite is bounded to secondary calcium hydrosilicate and also promotes carbonization process in the specimen.

Thermal analysis was carried out for the specimens of pure hardened cement paste after 28 days of hydration and of hardened cement paste with 5% expanded perlite admixtures after 28 days of hydration (Figure 6).

The endothermic effect at $101\text{--}113^\circ\text{C}$ and at 149°C temperatures observed in DSC curves of the investigated thermal images characterizes dehydration of calcium silicate hydrates. Endothermic peaks of cement specimens with zeolitized perlite or zeolitized perlite with inserted Ca^{2+} after 28 days of hydration (Figure 6b and 6c) at 110 and 113°C , respectively, showed higher intensities than in the specimen without the admixture (Figure 6a).

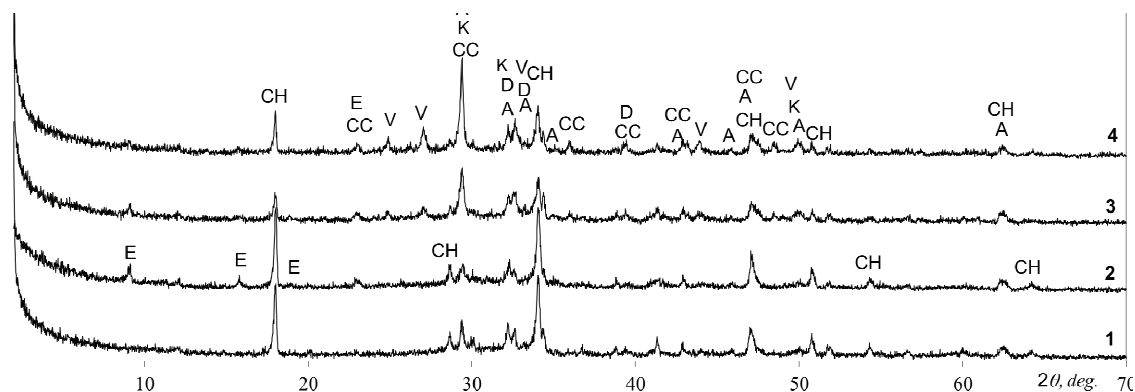


Figure 5. Pure hardened cement paste (1), the specimen with expanded perlite (2), with zeolitized perlite (3) and zeolitized perlite with inserted Ca^{2+} (4), X-ray after 28 days of hydration. Admixture amount in hardened cement paste contains 5%. CH is portlandite, A is alite, K is calcium silicate hydrate, D is belite, E is ettringite and CC is calcite.

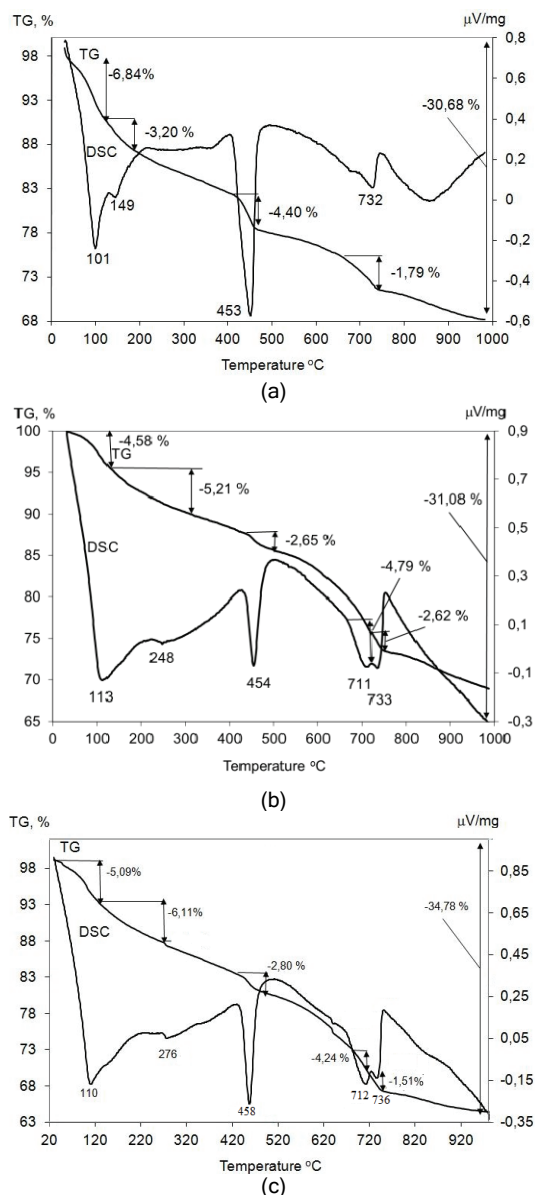


Figure 6. Thermograms of hardened cement paste specimens after 28 days of hydration; a) reference specimen without admixtures; b) specimen with 5% of zeolitized perlite (P+HsNa), c) zeolitized perlite with inserted Ca^{2+} (P+HsCa).

On the other hand, the endothermic peak at 453–458 °C characterizes portlandite decay. The comparison of hardened for 28 days specimens with and without zeolitized perlite admixture revealed that portlandite amount in the specimens with the admixture was significantly lower; the weight loss associated with $\text{Ca}(\text{OH})_2$ fragmentation in the specimens with the admixture was almost twice as low compared to the specimens without the admixture, 2.65 and 2.80%, respectively. The weight loss in control specimen was equal to 4.40%. The thermal analysis revealed that when the amount of zeolitized perlite is increased from 5 to 15% the amount of portlandite -

$\text{Ca}(\text{OH})_2$ - decreases; after 28 days of hydration $\text{Ca}(\text{OH})_2$ amount in specimens with zeolitized perlite admixture changed from 10.9 to 7.3%, and in specimens containing zeolitized perlite with inserted Ca^{2+} ions it changed from 11.5 to 9.8%.

Endothermic peaks at 711 and 712 °C temperature can be attributed both to CaCO_3 decomposition and indicate the dehydration of calcium hydrosilicate, which is similar to tobermorite at C-S-H phase. The endothermic peaks for the temperature range between 732 and 736 °C are attributed to CaCO_3 decomposition [15,16].

The new endothermic effect occurring at 711 and 712 °C shows the increased content of calcium silicate hydrates in the specimens with zeolitized perlite admixture; it can be attributed to higher basicity of calcium silicate gel for complete dehydration when C_2S is formed.

The reduction of portlandite amount can be attributed to the outcome of pozzolanic reaction because, as discussed above, higher amount of calcium hydrosilicates is observed in the specimen with admixtures.

In order to determine the influence of zeolitized perlite in concrete systems the obtained data of compressive strength after 28 days of hydration are compared. Specimens with zeolitized perlite and zeolitized and Ca^{2+} inserted perlite admixture had considerably better strength properties than the specimens containing perlite admixture (Figure 7).

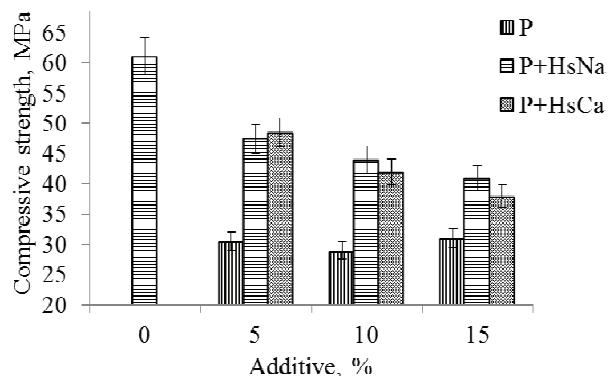


Figure 7. The dependence of hardened cement paste compressive strength on the type and quantity of admixture after 28 days of hydration. P is expanded perlite, P+HsNa is zeolitized perlite, P+HsCa is zeolitized perlite with inserted Ca^{2+} .

It was observed that porosity has an important effect on the mechanical properties of concrete [17]. The porosity of expanded perlite and zeolitized expanded perlites is different and it reflects in the properties of hardened cement paste. The expanded perlite has pore structure consisting of mesopores and

macropores [18]. These expanded perlite pores are shown in SEM picture (Figure 2a). Zeolites are microporous crystalline aluminosilicates. Hydrosodalite is a type of zeolite having micropores [19]. It is believed that large mesopores and macropores of expanded perlite have stronger influence on the strength characteristics of hardened cement paste specimens than smaller micropores of zeolite. It was concluded that zeolitization process makes perlite pores smaller which less negatively affect the mechanical strength of hardened cementitious systems. The fineness of expanded perlite and zeolitized expanded perlite powder materials affect the strength test results too. The investigated expanded perlite has a bulk density of 120 kg/m^3 and zeolitized perlites bulk density was about 153 kg/m^3 .

Fibrous structure of calcium silicate in the junction between perlite and hardened cement paste is visible in the images of cement specimens with zeolitized perlite admixture (Figure 8) obtained by scanning electron microscopy.

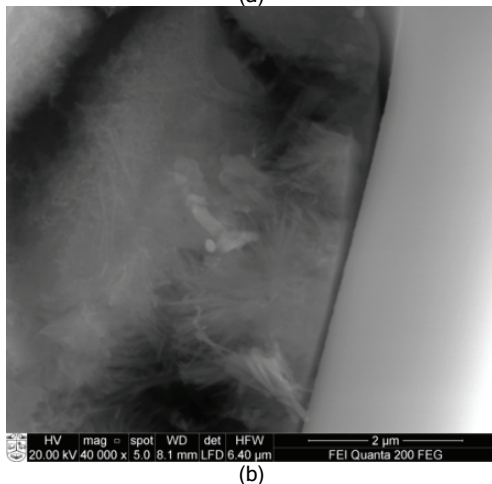
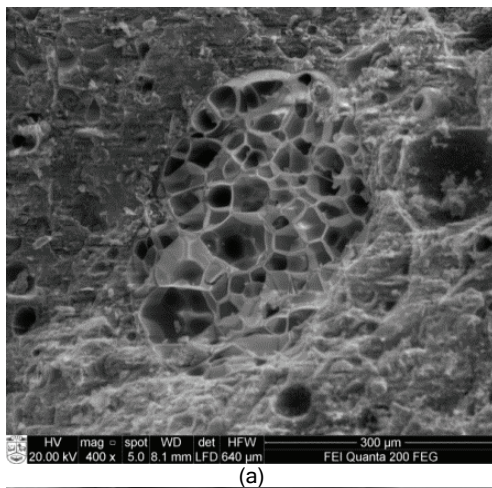


Figure 8. Hardened cement paste photos with zeolitized perlite admixture magnified: a) 400 and b) 40000 times.

Therefore, it can be said that hydrosodalite reacted with the portlandite and secondary calcium silicate hydrates were formed. The adhesion of cement binder with filler particles significantly improved using 5% of zeolitized perlite admixture in cementitious specimens.

CONCLUSIONS

1. Under the investigated conditions, it was determined that during perlite zeolitization $1.5 \mu\text{m}$ hydrosodalite crystals are formed on the surface of perlite. They accelerate the hydration of cement and significantly improve the adhesion of cementitious binder with the filler particles.

2. It was found that with the increase of zeolitized perlite admixture content from 5 to 15% in the concrete mixture the amount of $\text{Ca}(\text{OH})_2$ (portlandite) in hardened cement paste reduces after 28 days of hydration from 10.9 to 7.3% in specimens with zeolitized admixture, and from 11.5 to 9.8% in specimens containing zeolitized perlite with inserted Ca^{2+} .

3. The tests showed that after 28 days of curing the specimens without the admixture have the maximum compressive strength of 60 MPa; in specimens with 5% of zeolitized perlite admixture the compressive strength was 49 MPa, in specimens with zeolitized perlite with inserted Ca^{2+} the compressive strength was 50 MPa and in specimens with pure perlite admixture the compressive strength was 33 MPa.

It was proved that it is not feasible to process zeolitized expanded perlite additionally by $\text{Na}^+ \leftrightarrow \text{Ca}^{2+}$ exchange reaction as there is no appreciable difference between the strength of hardened cement paste under the analysed conditions.

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NAUČNI RAD

UTICAJ PERLITA PREINAČENOG U ZEOLIT NA SVOJSTVA KOMPOZITNOG CEMENTA

Perlit je mineral vulkanskog porekla. Ekspandovani perlit ima dobre toplotne karakteristike i pokazuje dobru zvučnu izolaciju. On je lak, otporan na vatru, vlagu i mikroorganizme i bezopasan po zdravlje. Međutim, zbog hilanditne strukture, njegova upotreba u portland cementnim kompozitima je problematična. U ovom radu je izvršena zeolitizacija ekspandiranog perlita da bi se poboljšala njegova hidraulična svojstva. Konverzija ekspandiranog perlita u zeolitni materijal je obavljena pri molskom odnosu $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}$ od 2:1:2:10 tretiranjem suspenzije polaznih materijala tokom 3 h na 100 °C. Istraživana su mehanička i fizička svojstva očvrsljih cementnih pasti koje su sadržale 0, 5, 10 i 15% čistog perlita, perlita sa zeolitom i perlita preinačenog u (Ca^{2+}) zeolit. Rezultati su pokazali da zeolitizacija ekspandiranog perlita aktivira njegova hidraulična svojstva; posle 28 dana hidratacije pod normalnim uslovima, čvrstoća uzoraka modifikovanih sa 5% preinačenog perlita u zeolit je 49-50 MPa, dok je čvrstoća uzoraka sa 5% čistog perlita samo 33 MPa.

Ključne reči: perlit zeolitne structure, kompozitni cement, hidrosodalit.