

Cement hydration with zeolite-based additive

Danutė Vaičiukynienė^{1*},

Gintautas Skipkiūnas²,

Mindaugas Daukšys¹,

Vytautas Sasnauskas¹

¹*Kaunas University of Technology,
Studentų St. 48, LT-51367 Kaunas,
Lithuania*

²*Vilnius Gediminas
Technical University,
Saulėtekio Ave. 11,
LT-10223 Vilnius,
Lithuania*

This study has examined the effect of a zeolite-based additive on cement hydration processes. This additive and samples of hardened cement pastes have been examined using X-ray diffraction, thermoanalytical methods (TG and DSC) and FTIR spectroscopy analysis. The results show that a modified zeolite additive increases the compressive strength of hardened cement paste specimens. The increase in compressive strength may be related to active SiO₂ and Al₂O₃ present in the modified zeolite. The highest density was recorded in specimens containing 10% of the modified zeolite additive. Instrumental analysis has revealed that with the increase of this zeolite additive content the content of portlandite – Ca(OH)₂ – in the mineral composition of hardened cement paste reduces from 11.9 to 5.3% after 3 days of setting and from 15.0 to 7.6% after 28 days of setting. The highest amounts of C-S-H gel are observed when the modified zeolite additive is used.

Key words: zeolite, cement, cement hydration

INTRODUCTION

Recently many researchers have investigated into the effects of natural and synthetic zeolite-based additives on the structure of concrete and hydration processes in hardened cement paste [1–4]. Alkali-silica reactivity potential of modified zeolites was investigated [5], as well as the reaction of zeolites with separate groups of minerals present in ash and blast furnace slag. Resistance of Portland cement to aggressive acid and sulphate media was also researched [6, 7].

A number of tests with complex additives made of zeolite and alumina-rich substances are described in research papers. The use of zeolite as conversion preventing additives for inhibition of hydrogarnet formation in high alumina cement products is described in the research paper [8]. The compressive strength of cement pastes was determined. The effect of setting conditions, such as low initial and high final temperatures, on compressive strength was analyzed. The compressive strength of high alumina cement pastes did not drop when 12% of zeolite was added and the samples were

left to set at 38 °C temperature. Stratlingite phase prevailed in those samples. Little or no hydrogarnet phase in the paste was detected by XRD analysis.

Hydration and strength development characteristics of high alumina cement containing sodium sulphate and zeolite additives were investigated [9]. Many specimens made of high alumina cement with sodium sulphate and zeolite had the compressive strength of 60 MPa after 24 hours. Hydrogarnet formation was significantly inhibited. Zeolite alone was not able to prevent the hydrogarnet formation in high alumina cement paste. In the absence of sodium sulphate zeolites do not inhibit the formation of hydrogarnet in high alumina cement paste. Chabazite was the most effective zeolite in promoting stratlingite formation in the high alumina cement paste.

Alumina-rich materials are widely used all over the world for the manufacturing of high alumina cement [10]. High alumina cement is produced by fusion and sintering of bauxite and limestone. Such cements have several advantages, such as fast setting, durability, sulphate resistance. Among disadvantages high hydration heat should be mentioned [11, 12].

When Al(OH)₃ additive is mixed into gypsum-free Portland cement, a new material – hydrogarnet Ca₃Al₂(SiO₄) · (OH)₈ –

* Corresponding author. E-mail: danute.palubinskaite@ktu.lt

is formed [13]. Mathieu's article [14] presents the analysis of applying finely ground $\text{Al}(\text{OH})_3$ in Portland cement technology. In the research paper [15] fast setting of cement is related with more intensive formation of ettringite. Ettringite in the form of fibers is formed due to increased $\text{Al}_2\text{O}_3/\text{SO}_3$ ratio. Neither singenite nor gypsum is formed in cement paste during the first 24 hours.

Rapid hardening of cement was achieved by adding a mechanically activated $\text{Al}(\text{OH})_3$ - $\text{Ca}(\text{OH})_2$ mixture to the starting cement paste. Those hydration products increased the compressive strength of the cement paste at a very early stage of hardening [16].

Researchers Matusinovic and Vrbos investigated the effect of alkali metal salts on the setting time of high alumina cement. The results of the research indicate that alkali metal salts are set accelerators of high alumina cement [17].

It was observed that setting times were slightly shortened, whereas the flexural and compressive strengths were increased for cements pastes which were prepared by adding eloxal waste to Portland cement at various ratios up to 4% by weight [18].

The effect of alunite, a mineral of the jarosite group, mixed into Portland cement was investigated [19]. It was determined that the alunite blended cements developed higher strength, at 28 days, compared to the reference one. The higher the strength increase, the higher the alunite content was. The increase of compressive strengths was attributed to the ettringite formation after the reaction of the $\text{Ca}(\text{OH})_2$ with the SO_4^{2-} and Al^{3+} ions produced from the alunite dissolution at the high pH of the hydrated cement.

Although zeolites are widely used in concrete technologies, the reviewed references did not contain any data of the use of zeolite-based additive in concrete technologies. The possibilities of using this material as a hydraulic admixture and its influence on cement paste hydration process were investigated.

The goal of this research paper is to determine the effect of zeolite-based additive as a hydraulic additive on hydration processes in cement paste.

EXPERIMENTAL

In this study the Portland cement CEM I 42.5R (specific surface – 378 m^2/kg , initial setting time – 105 min, compression strength – 29.1 MPa (after 2 days) and 54.3 MPa (after 28 days)) was used.

Zeolite was synthesized from NaOH, $\text{Al}(\text{OH})_3$, and AlF_3 production waste. In this production waste there are $\text{SiO}_2 = 51.28\%$; $\text{Al}_2\text{O}_3 = 12.67\%$. The molar ratio of the starting material $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$ is 2 : 1 : 2 : 10. Low-temperature (95 °C) zeolite synthesis was performed in the unstirred suspension at isothermal curing duration of 2 hours. The final product of synthesis was filtered, dried at 60 °C temperature and sieved through a 0.5 mm-mesh sieve. Ion exchange reactions were performed in the unstirred suspension: saturated CaCl_2

solution obtained from CaCl_2 was poured on the zeolite. Ion exchange investigations at the temperature of 85 °C lasted about 5 minutes. It was found that in the synthesized zeolite there were $\text{SiO}_2 = 28.63\%$; $\text{Al}_2\text{O}_3 = 37.65\%$; $\text{Na}_2\text{O} = 14.06\%$; $\text{CaO} = 0.8\%$. The modified zeolite composition was as follows: $\text{SiO}_2 = 29.31\%$; $\text{Al}_2\text{O}_3 = 36.47\%$; $\text{Na}_2\text{O} = 7.33\%$; $\text{CaO} = 7.49\%$.

In all test sample compositions the cement and water ratio (W/C) was stable (W/C = 0.55). The compositions differed by the contents of the modified zeolite addition – 0; 5; 10; 15 and 20%. The formed test samples, 2 × 2 × 2 cm sized cubes, were hardened for 28 days under conditions prescribed by the EN 12390-2 standard. The compressive strength of hardened cement paste was measured by EN 196-1.

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

Simultaneous thermal analysis (STA: 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. Thermal analysis of hardened cement paste was carried out using these sample amounts: after 3 days 16.70 mg without addition, 13.58 mg with 10% addition, 14.640 mg with 20% addition; after 28 days 15.68 mg without addition, 17.05 mg with 10% addition, and 14.97 mg with 20% addition.

IR spectra were recorded with a 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.

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. Chemical compositions of zeolite were investigated by an energy-dispersive X-ray spectrometer (EDS) with a silicon type drift droplet detector.

RESULTS AND DISCUSSIONS

X-ray curves of pure (1) and modified (2) zeolites (Fig. 1) show that the interplanar distances (d): 1.231; 0.870; 0.710; 0.410; 0.371; 0.328; 0.262 nm are common to zeolite A (Na). Next to the zeolite there are peaks common to $\text{Al}(\text{OH})_3$ with the interplanar distances (d): 0.485; 0.438; 0.433; 0.234. When this zeolite is modified by CaCl_2 , i. e. after the exchange of ions, calcium inserted zeolite (Ca, Na) · $\text{Al}_2\text{Si}_2\text{O}_9 \cdot 6.4\text{H}_2\text{O}$ is formed together with zeolite A ($\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384} \cdot 2164\text{H}_2\text{O}$) (Fig. 1a).

A wide absorption band in the IR spectrum of modified zeolite (Fig. 1b) at the wavelength of 3 434 cm^{-1} is common

to the hydroxyl group with hydrogen bonds. The absorption band at the wavelength of 1639 cm^{-1} indicates deformation vibrations of water molecules. The wavelengths most common in zeolite A are as follows: 998 cm^{-1} asymmetric valence, 660 cm^{-1} symmetric valence and $550, 464\text{ cm}^{-1}$

deformation vibrations. The absorption peaks in gibbsite are most probably covered by the absorption bands of zeolite.

The thermal analysis of modified zeolite has confirmed that this zeolite additive is made of zeolite A and $\text{Al}(\text{OH})_3$, Gibbsite, i. e. $\text{Al}(\text{OH})_3$, exhibits the characteristic endothermic

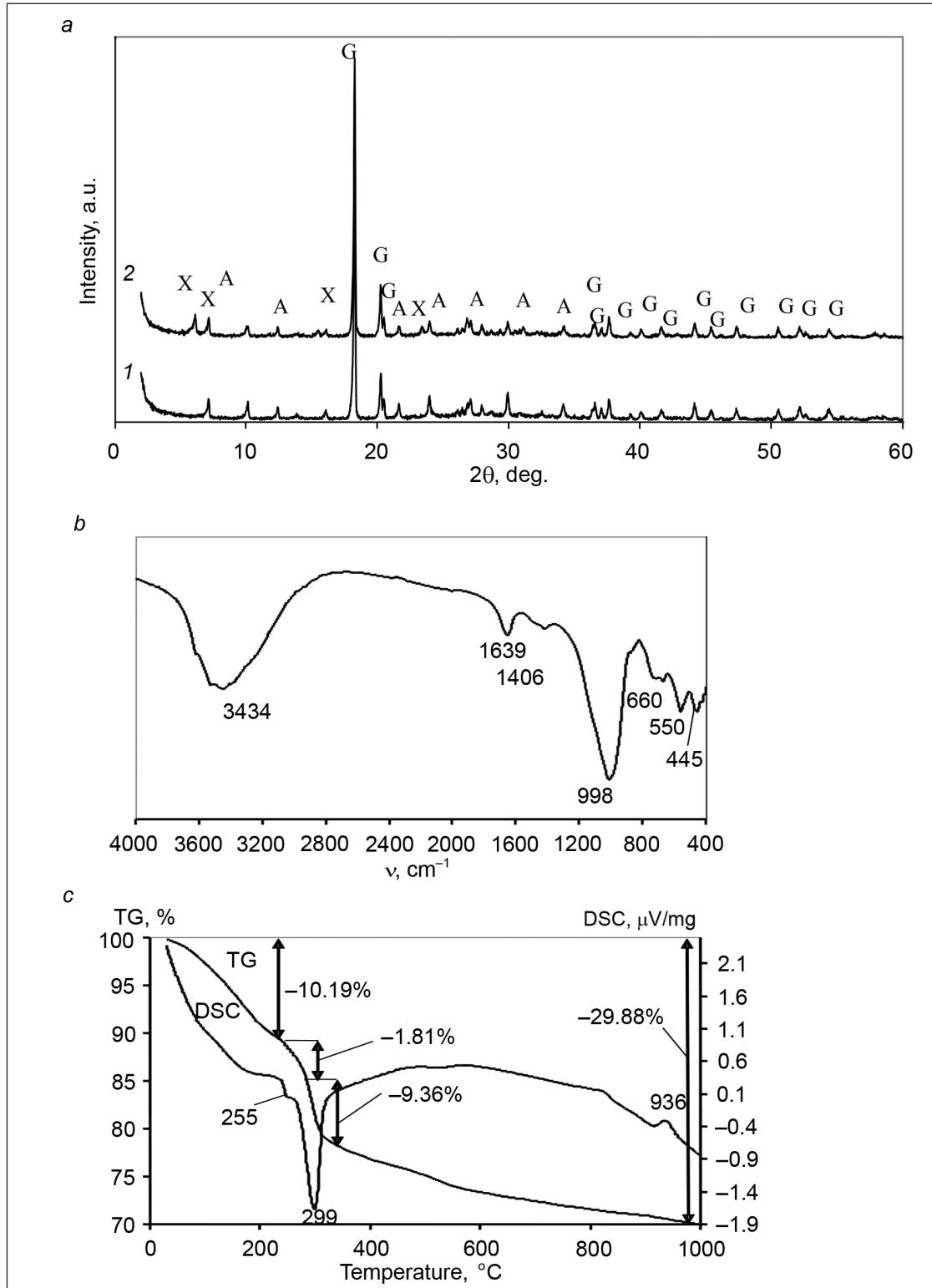


Fig. 1. X-ray diffraction patterns of modified zeolite (a), IR spectra (b), and DSC curves (c): 1 – pure; 2 – modified zeolite. Notes: X – zeolite $(\text{Ca}, \text{Na})\text{-Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.4\text{H}_2\text{O}$; A – zeolite $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384} \cdot 2164\text{H}_2\text{O}$; G – $\text{Al}(\text{OH})_3$

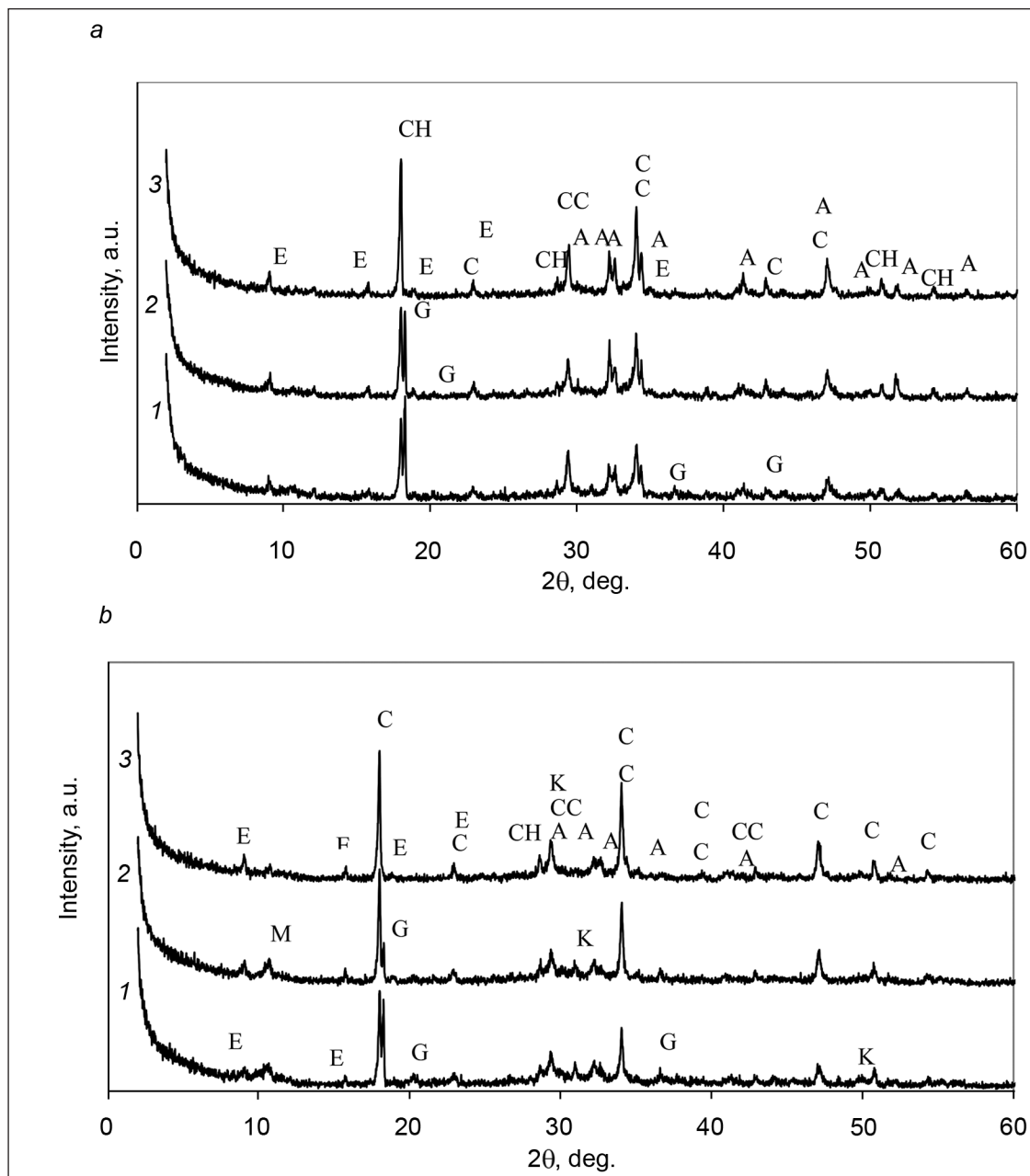


Fig. 2. X-ray diffraction patterns of hardened cement paste after 3 days (a) and 28 days (b). Modified zeolite addition content accounts for 20% (1); 10% (2); 0% (3). Notes: CH – $\text{Ca}(\text{OH})_2$; A – $\text{Ca}_{54}\text{MgAl}_2\text{Si}_{16}\text{O}_{90}$; K – C-S-H; G – $\text{Al}(\text{OH})_3$; D – $2\text{CaO} \cdot \text{SiO}_2$; M – $\text{Ca}(\text{Al}_2\text{Si}_7\text{O}_{18}) \cdot 7\text{H}_2\text{O}$; E – $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$; CC – $\text{Ca}(\text{CO}_3)_3$

peaks at 250–300 °C temperature. Partial dehydration of gibbsite occurs at this temperature and bemitte is formed (Fig. 1c). Zeolite A loses part of water at 25–300 °C temperature and has an endothermic peak in the DSC curve; however, it may also have an exothermic peak at 936 °C temperature. At 900 °C temperature this zeolite transforms to β crystallite.

X-ray curves of hardened cement paste with modified zeolite additive clearly show that with the increase of the said additive from 0 to 20% the content of $\text{Ca}(\text{OH})_2$ in hardened cement paste goes down (Fig. 2). The X-ray diffraction patterns presented in Fig. 2 show that the highest peak of

$\text{Ca}(\text{OH})_2$ with interplanar distance of 0.493 nm is the most intensive in the absence of modified zeolite additive. When the content of this additive in the cement paste is 10 or 20% the $\text{Ca}(\text{OH})_2$ peak becomes less intensive.

The research into the effect of specimen hydration time has revealed that with longer hydration time bigger amounts of alite and belite hydrate by forming calcium hydro-silicates and calcium hydroxide. Therefore, with longer hydration time the peaks of $\text{Ca}(\text{OH})_2$ become more intensive, whereas the peaks of alite and belite decrease. This zeolite additive accelerates cement hydration process because X-ray shows more intensive peaks of calcium silicate hydrates and less

intensive peaks of the main cement minerals. Ettringite peaks are less intensive when the zeolite additive is used (Fig. 2).

The endothermic peaks below 200 °C are mainly due to the dehydration of CSH (tobermorite-like phase) as well as ettringite. Calcium silicate hydrate is identified in thermographs by loss of water (i. e. endothermic peak) in the temperature range 120–150 °C. In hardened cement paste without addition, the C-S-H endothermic peak may

be overlapped by the ettringite dehydration peak. In the XRD patterns of samples ettringite was identified. Thus, the endothermic peak in the temperature 158 °C in the curve of this sample may be attributed exactly to the high content of C-S-H. From Fig. 3 it can be seen that the amount of C-S-H gel is the greatest when modified zeolite addition is used.

In the case of pastes with the additive, one can find an additional peak on the DSC curve at temperature about

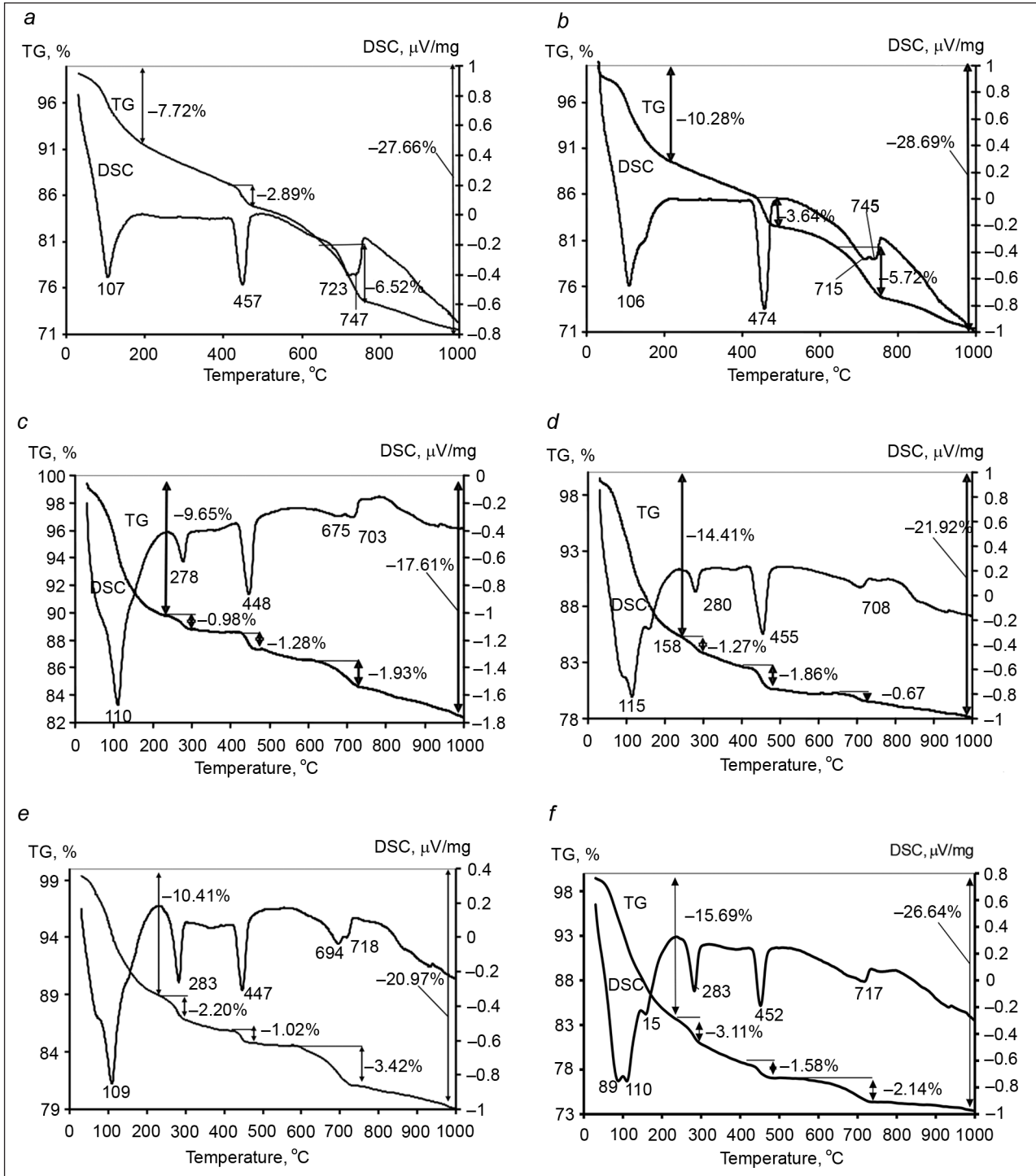


Fig. 3. DSC curves of hardened cement paste after 3 days (a, c, e) and 28 days (b, d, f). Modified zeolite addition content accounts for 0% (a, b); 10% (c, d); 20% (e, f)

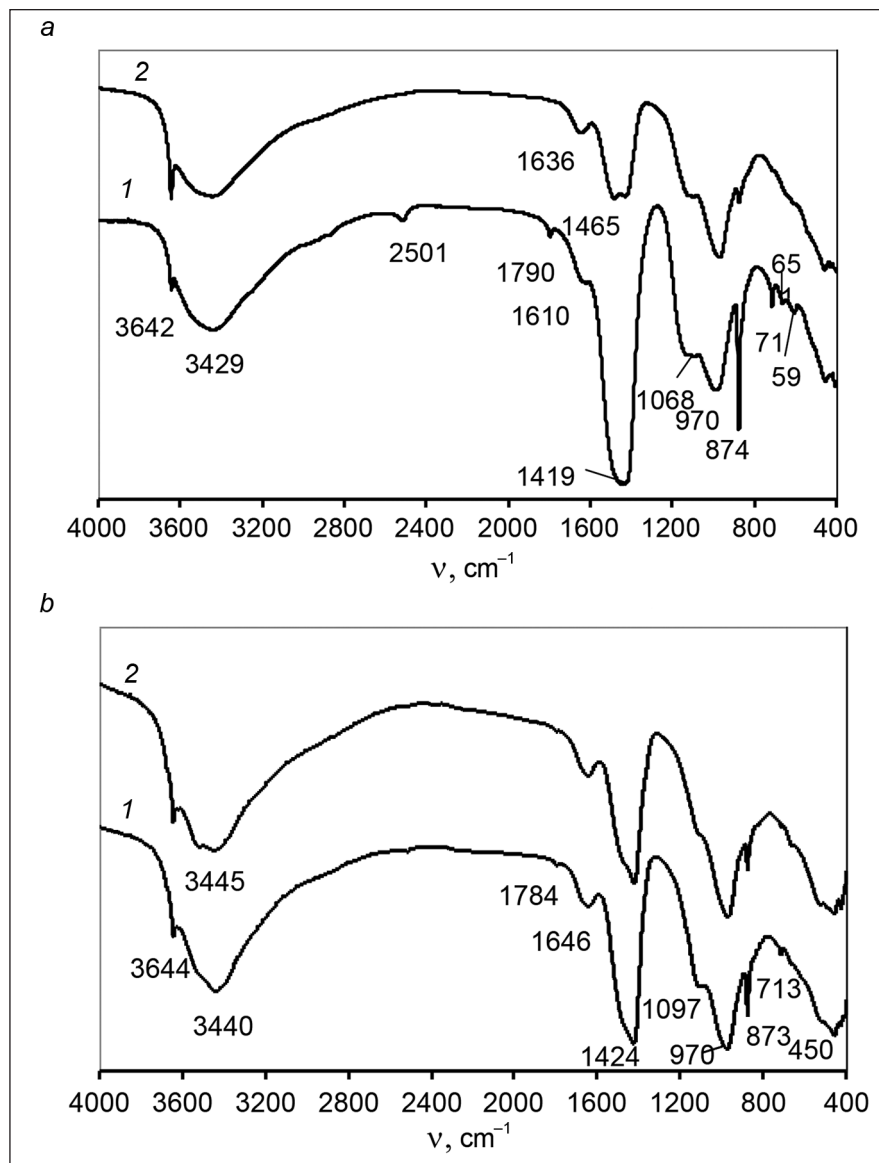


Fig. 4. FT-IR spectra of hardened cement paste after 3 days (1) and 28 days (2). Modified zeolite addition content accounts for 0% (a) and 10% (b)

278–282 °C. This endothermic peak becomes stronger with the percentage of admixture and hydration time. This could possibly be explained by the decomposition of the $\text{Al}(\text{OH})_3$ and hydrated aluminate phase formed.

DSC curves of hardened cement paste show decomposition of $\text{Ca}(\text{OH})_2$ in the temperature range 490–505 °C. However, in samples containing 10 or 20% modified zeolite addition after 3 and 28 days of hardening, the $\text{Ca}(\text{OH})_2$ decomposition peak was weaker (Fig. 4).

The endotherms at 708–747 °C indicate CaCO_3 decomposition. The endothermic peak at 674–723 °C can be attributed both to CaCO_3 decomposition and a full dehydration of C-S-H.

On the TG curve for cement pastes, the three steps of weight loss, together with corresponding endothermic DSC peaks, are observed (Fig. 3). In the range up to about 450 °C, the complex dehydration of C-S-H, sulphoaluminates and aluminates is observed. In the range from 447 to about 474 °C, dehydration of $\text{Ca}(\text{OH})_2$ takes place, and close to 708–747 °C

decomposition of carbonates is observed. The amount of hydrates of all binders could be assessed from the positions of their respective weight loss curves; the greater this weight loss, the greater the amount of hydration products in the paste.

When the modified zeolite combination was used, there was a decrease in the amount of portlandite (447–455 °C interval) in all cases. It can be observed that the consumption of portlandite was due to the pozzolanic reaction occurring when the modified zeolite was incorporated. Portland cement paste reduces the content of non-carbonated $\text{Ca}(\text{OH})_2$ from 11.9 to 5.3% after 3 days of hydration and from 15.0 to 7.6% after 28 days.

In Fig. 4, the FT-IR spectra of hardened cement pastes are compared after 3 and 28 days of hydration. The wide band that is observed in the region 3100–3700 cm^{-1} is caused by the symmetric and asymmetric stretching of the O-H vibrator of the water molecules. The absorption band at 3642 cm^{-1} is characteristic of portlandite. The band at approximately

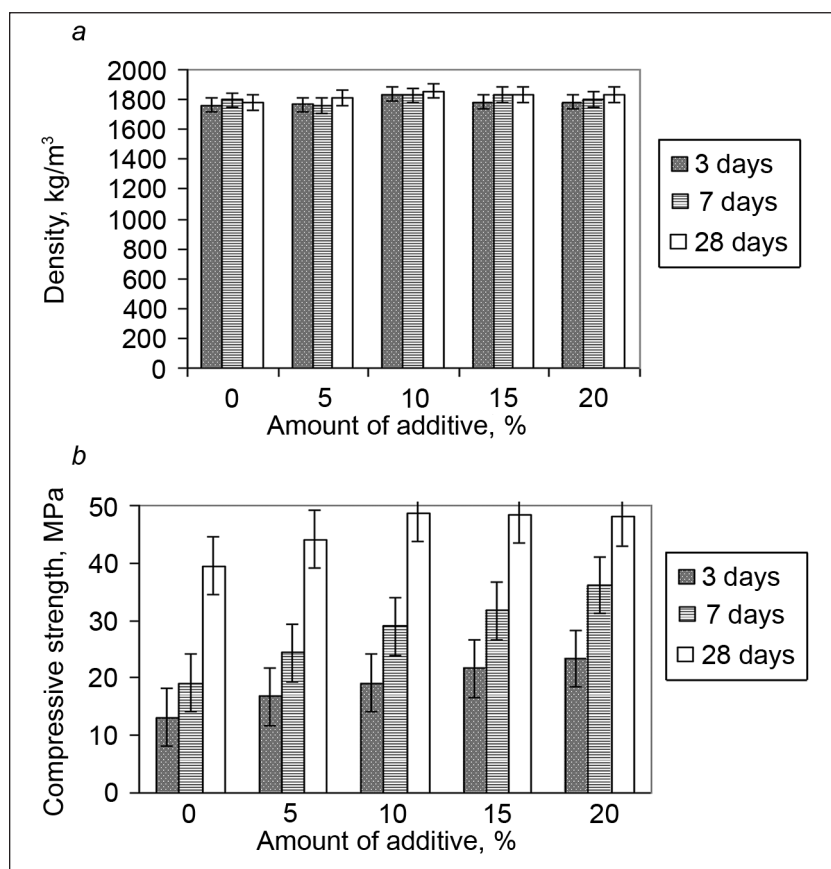


Fig. 5. Dependence of the compressive strength of hardened cement paste on the additive amount after 3 days (1), 7 days (2), and 28 days (3)

1610–1646 cm^{-1} is the deformation mode H-O-H of the molecular water absorbed.

The bands in the range 2501, 1416–1419, 874 and 713 cm^{-1} are attributed to CO_3^{2-} . The presence of CaCO_3 is attributed to the atmospheric CO_2 absorbed during the air hydration sample. The peaks of cement paste samples without additives (Fig. 4) are much more intense than peaks with the modified zeolite additive, especially after 3 days of hydration.

Shoulders at 1068 and 1091 cm^{-1} present SO_4^{2-} ions account for the acute peaks and characteristic of ettringite monosulphoaluminate are observed. Peaks at ~ 1068 and 1091 cm^{-1} are detected after 3 days of hydration, pointing to the early formation of ettringite. Intensity of this band decreases with hydration time increasing.

Absorption bands with the peaks of 970 cm^{-1} in spectrum curves are seen in all spectrograms. These absorption bands are attributed to valence fluctuations of Si-O bond in tetrahedron along the line linking the oxygen atom of $[(\text{Si})\text{O}_4]$ – tetrahedron with the central Si atom and characterize calcium silicate hydrates.

It is well known that calcium silicate hydrate (C-S-H) is a mechanically strong phase, more resistant than hydrated calcium aluminate or silica aluminate and portlandite which have a low strength because of the lamellar structure.

5–20% of the modified zeolite additive increase the compressive strength of hardened cement paste specimens (Fig. 5). The growth in compressive strength is observed after

3, 7 and 28 days of setting. The highest compressive strength was recorded in specimens with 10% of the modified zeolite additive. The increase in compressive strength may be related with active SiO_2 and Al_2O_3 , present in the modified zeolite.

Density characteristics of the specimens are similar to the characteristics of strength. The highest density was recorded in the specimens containing 10% of the modified zeolite additive.

CONCLUSIONS

Instrumental analysis has revealed that with the increase of modified zeolite additive content the content of portlandite – $\text{Ca}(\text{OH})_2$ – in the mineral composition of hardened cement paste reduces from 11.9 to 5.3% after 3 days of setting and from 15.0 to 7.6% after 28 days of setting. The highest amounts of C-S-H gel are observed when the modified zeolite additive is used.

The modified zeolite additive increases the compressive strength of hardened cement paste specimens. The compressive strength of specimens with a 10% zeolite-based additive increases about 23% compared with the control hardened cement paste samples. The increase in compressive strength may be related to active SiO_2 and Al_2O_3 present in the modified zeolite. The highest density 1858 kg/m^3 was recorded in specimens containing 10% of the modified zeolite additive while the density of the samples without additives was 1832 kg/m^3 after 28 days of setting.

ACKNOWLEDGEMENTS

This work was supported by the Lithuanian Science and Study Foundation Research Work Program "Particularities of Nano-Structures Formation in the Cementations Building Materials" (Reg. No. B-08009).

Received 10 June 2013

Accepted 30 July 2013

References

1. Th. Perraki, G. Kakali, F. Kontoleon, *Microporous Mesoporous Mater.*, **61**, 205 (2003).
2. M. Uehara, T. Sasaki, *Chem. Lett.*, **30**, 1040 (2001).
3. F. Canpolat, K. Yilmaz, M. M. Kose, M. Sumer, M. A. Yurdusev, *Cem. Concr. Res.*, **35**, 1020 (2005).
4. M. Grutzeck, S. Kwan, M. Dicola, *Cem. Concr. Res.*, **34**, 949 (2004).
5. Q. Niu, N. Feng, *Cem. Concr. Res.*, **35**, 1784 (2005).
6. I. Janotka, L. Kraj, M. Dživák, *Clays Clay Miner.*, **51**, 616 (2003).
7. I. Janotka, L. Krajci, *Ceramics*, **39**, 105 (1995).
8. Y. Fu, J. Ding, J. J. Beaudoin, *Adv. Cem. Based Mater.*, **3**, 37 (1996).
9. J. Ding, Y. Fu, J. J. Beaudoin, *ACI Mater. J.*, **94**, 220 (1997).
10. E. Erdem, M. E. Günay, R. Donat, *J. Mater. Process. Tech.*, **136**, 35 (2003).
11. J. Piasta, Z. Sawicz, W. G. Piasta, *Cem. Concr. Res.*, **19**, 103 (1989).
12. A. N. Scian, J. M. Porto Lopez, E. Pereira, *Cem. Concr. Res.*, **21**, 51 (1991).
13. V. Sevcík, F. Skvára, *Ceram.-Silik.*, **46**, 104 (2002).
14. A. Mathieu, Patent GB 2 063 240 A 1981.
15. Q. Xu, J. Stark, *Zkg Int.*, **61**, 82 (2008).
16. M. Kitamura, M. Kamitani, M. Senna, *J. Am. Ceram. Soc.*, **83**, 523 (2000).
17. T. Matusinovic, N. Vrbos, *Cem. Conc. Res.*, **23**, 177 (1993).
18. E. Erdem, M. E. Günay, R. Donat, *J. Mater. Process. Tech.*, **35**, 136, (2003).
19. M. Katsioti, D. Giannikos, P. E. Tsakiridis, Z. Tsibouki, *Constr. Build. Mater.*, **23**, 1011 (2009).

Danutė Vaičiukynienė, Gintautas Skipkiūnas,
Mindaugas Daukšys, Vytautas Sasnauskas

CEMENTO SU CEOLITINIŲ PRIEDU HIDRATACIJA

Santrauka

Darbe tirta ceolitinio priedo įtaka cemento hidratacijai. Minėtas priedas ir cementinio akmens bandiniai buvo tiriami naudojant rentgeno spindulių difrakciją, terminės analizės metodus (TG ir DSC) ir FTIR spektroskopijos analizę. Modifikuoto ceolito priedas gniuždamas padidina cementinio akmens bandinių stiprį. Šis gniuždomojo stiprio padidėjimas gali būti susijęs su ceolito sudėtimi, t. y. su aktyviu SiO₂ ir Al₂O₃. Didžiausias cementinio akmens bandinių tankis buvo su 10 % modifikuoto ceolito priedu. Remiantis instrumentinės analizės metodais teigiama, kad didinant ceolitinį priedą cementiniuose bandiniuose portlandito (Ca(OH)₂) kiekis sumažėjo beveik du kartus: nuo 11,9 iki 5,3 % po 3 parų hidratacijos ir nuo 15,0 iki 7,6 % po 28 parų kietėjimo. Modifikuotas ceolitinis priedas turėjo įtakos C-S-H gelio kiekiui cementinio akmens bandinyje.