

UDK 666.948

G.M. Shabanova^a, *A.M. Korogodska*^a, *R.M. Vorozhbiyan*^a, *N.S. Tsapko*^b, *E.V. Khrystych*^c,
O.G. Shutynskyy^a

STUDYING THE SPECIFIC FEATURES OF THE HYDRATION PROCESSES OF ALUMINA CEMENTS BASED ON THE COMPOUNDS OF CaO–NiO–Al₂O₃ SYSTEM

^a National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine

^b Ukrainian Scientific Research Institute of Ecological Problems, Kharkiv, Ukraine

^c National University of Civil Defense of Ukraine, Kharkiv, Ukraine

The article gives the results of studying hydration processes occurring in cement synthesis using waste products of chemical industry. Cement clinker was synthesized with the relation of initial raw components, calcium-containing water treatment waste and rejected nickel-containing catalyst of AZOT Private Joint Stock Company (Severodonetsk, Luhansk Region, Ukraine), equal to 50/50. The obtained samples were studied by Strelkov minor method: normal density, setting time and mechanical strength were determined within 1, 3, 7 and 28 days. The results regarding the setting product were analyzed by differential thermal, X-ray phase analysis, microscopic analysis and electron microscopy; this enables to control the phase relation in the synthesis of a new class of aluminate cements using waste products of chemical industry. The obtained data showed the absence of cubic hydroaluminates which deteriorate the strength. The methods of physicochemical analysis revealed that the phase composition of hydrated alumina cement is represented by calcium hydroaluminate of different basicity, whereas cleavage structure consists of prismatic crystals which give dual coalescence, and this is favorable form to provide matrix self-reinforcement. The developed composition of aluminous nickel-containing cement referred to hydraulic binders. The results of physical-mechanical tests of the synthesized cements indicated that the obtained cements are quick-setting, fast-hardening and high-strength materials.

Keywords: nickel oxide, alumina cement, hydration, X-ray analysis, calcium hydroaluminates, structure.

Introduction

In conditions of swift development and industrialization, special attention is paid to the use of secondary raw materials or substandard materials that are amenable to recycling. The main fields of application of such materials are the industrial branches of construction materials, chemical and metallurgy industries. [1]. A great attention is also focused on the refractory cementing materials. A deficiency of raw materials and a high cost of pure raw materials encourage the development of the new types of binding materials of a special purpose that enable a more efficient use of the resources reducing thus the cost price of end products [2,3].

Experimental methods, results and discussion

For research purposes, we synthesized the cement clinker with the 50/50 ratio of initial raw materials, in particular the calcium-containing water preparation waste and the nickel catalyst carrier waste

from the Private Joint Stock Company «North-Donetsk Association AZOT» (K-905 D2) [1].

Using a number of physical and chemical methods of analysis, we studied the hydration products of alumina nickel-containing cement. The cements were manufactured and exposed to hardening under air-moist conditions during 1, 3, 7, 14 and 28 days. The hardening products were studied using the differential-thermal, X-ray phase analysis and microscopic methods of analysis [8]. Figure 1 gives the data of differential-thermal research of hydrated cement. It has been established that a specific stepwise dehydration of available calcium hydroaluminates of a different composition is observed with the temperature rise that results in the endothermic effect at the temperatures of 140 to 160°C [4].

The endothermic effect at the temperatures of 280 to 440°C is related to the stepwise character of

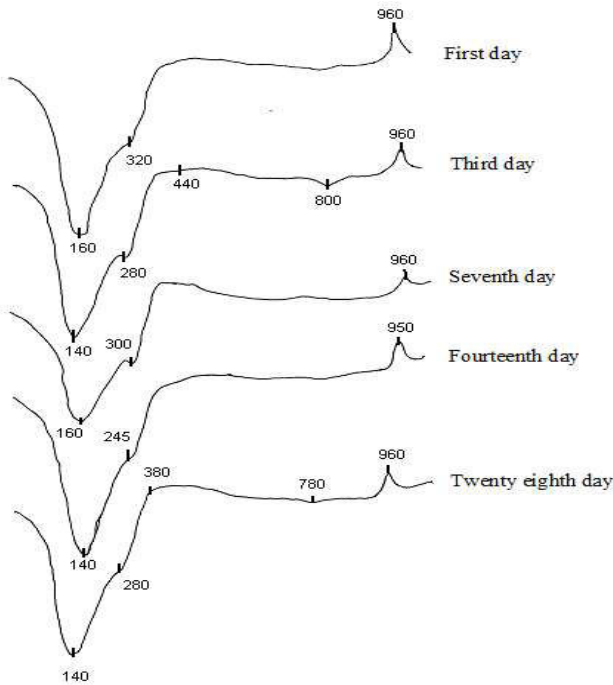


Fig. 1. DTA curves of hydrated alumina cement

water removal. The endothermic effect at 380°C corresponds to the removal of the constituent water from $Al(OH)_3$. The endothermic effects at the temperatures of 780°C and 960°C correspond to the

complete dehydration of calcium hydroaluminates, recrystallization and growth of the crystals of calcium aluminates that form the reinforcing skeleton and increase the cement strength [5,6,7].

It should be noted that the peak typical of the stepwise dehydration of calcium hydroaluminates of a different composition deepens as the hydration time is increased, and the peak typical of the dehydration of aluminium hydrates of a different composition drops. However, a drop in the cement stone strength due to the crystallization of cubic hydroaluminates is not observed; it complies with the data of X-phase analysis.

The research performed by using the X-ray analysis data (Figs. 2–6) shows that the main crystal phases of hydrated nickel-containing alumina cement are the calcium aluminates that failed to react, in particular $CaAl_2O_4$ ($d \cdot 10^{-10} = 2.4; 2.519; 2.973; 3.719; 4.68$ m), $NiAl_2O_4$ ($d \cdot 10^{-10} = 4.68; 2.856; 2.438$ m), $CaAl_4O_7$ ($d \cdot 10^{-10} = 2.597; 3.089; 3.509$ m), gelenite $Ca_2Al_2SiO_7$ ($d \cdot 10^{-10} = 1.761; 2.4; 2.438; 2.856$ m), calcium hydroaluminate $CaAl_2O_4 \cdot 10H_2O$ ($d \cdot 10^{-10} = 4.446; 7.21; 14.19$ m), and also $(CaO, MgO) \cdot Al_2O_3 \cdot CO_3 \cdot 11H_2O$ ($d \cdot 10^{-10} = 2.519; 2.856; 3.719$ m).

The obtained data match well with the data of differential thermal analysis and show the absence of cubic calcium hydroaluminates that facilitate the

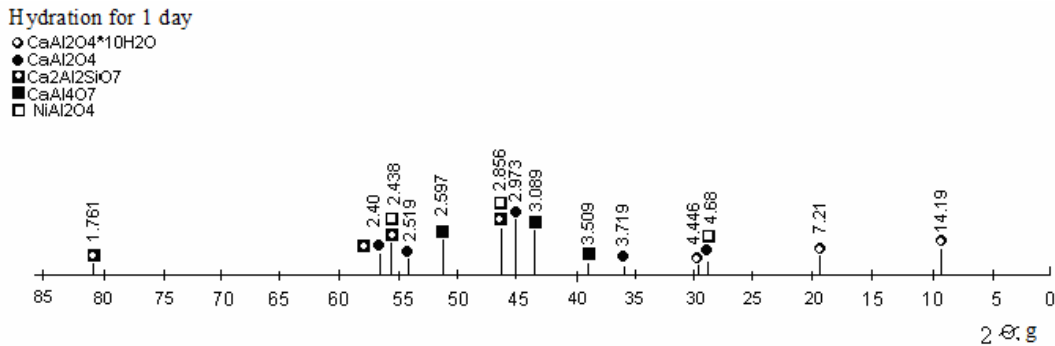


Fig. 2. Bar roentgenogram of hydrated alumina cement (1 day old)

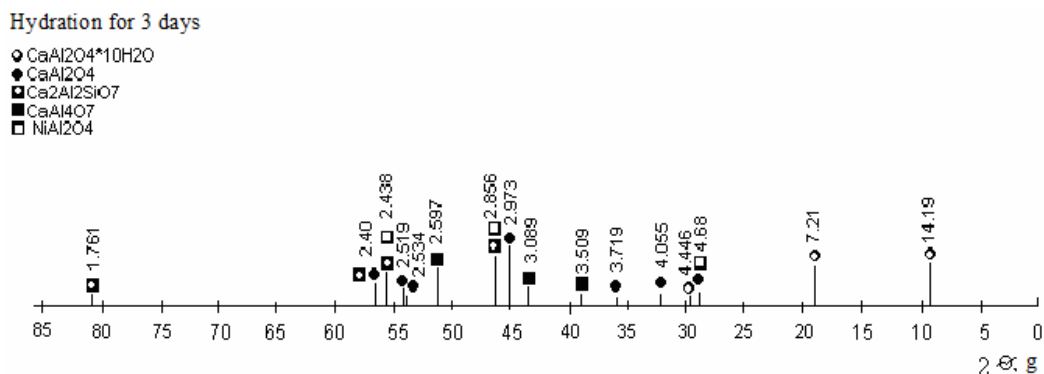


Fig. 3. Bar roentgenogram of hydrated alumina cement (3 days old)

Hydration for 7 days

- $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$
- CaAl_2O_4
- $\text{Ca}_2\text{Al}_2\text{SiO}_7$
- CaAl_4O_7
- NiAl_2O_4

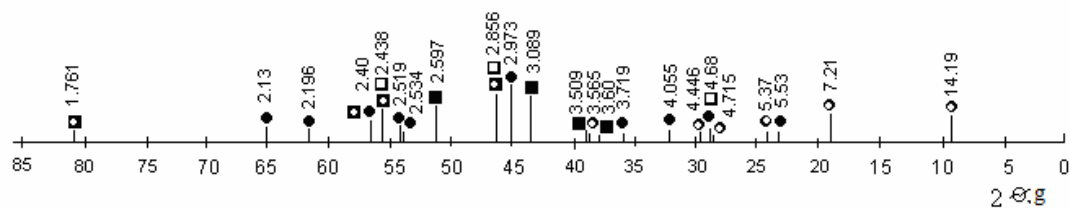


Fig. 4. Bar roentgenogram of hydrated alumina cement (7 days old)

Hydration for 14 days

- $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$
- CaAl_2O_4
- $\text{Ca}_2\text{Al}_2\text{SiO}_7$
- CaAl_4O_7
- NiAl_2O_4

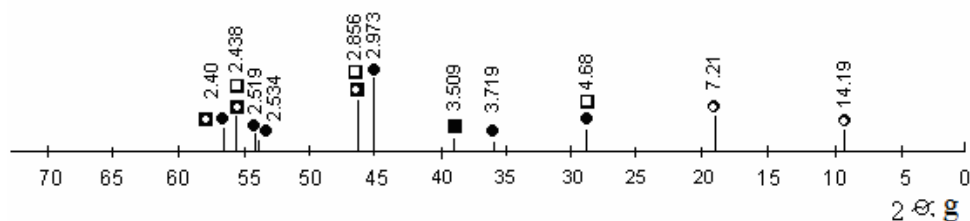


Fig. 5. Bar roentgenogram of hydrated alumina cement (14 days old)

Hydration for 28 days

- ▲ $(\text{CaO}, \text{MgO}) \cdot \text{Al}_2\text{O}_3 \cdot \text{CO}_3 \cdot 11\text{H}_2\text{O}$
- $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$
- CaAl_2O_4
- CaAl_4O_7
- NiAl_2O_4

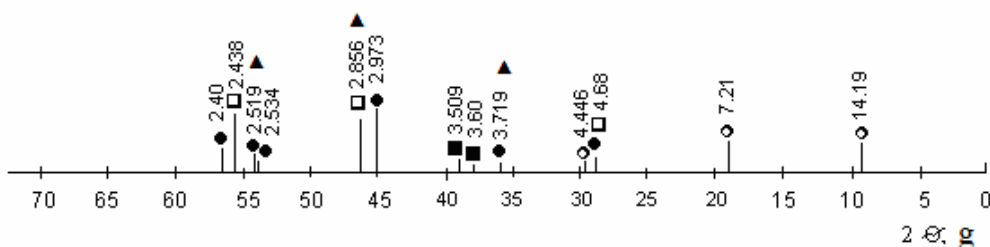


Fig. 6. Bar roentgenogram of hydrated alumina cement (28 days old)

strength drop.

Microscopic investigations showed that the cleavage structure of hydrated nickel-containing alumina cement is mainly represented by uniformly distributed colorless needle crystals and grayish-brown crystals with hexagonal outlines and a weak double-refraction (Fig. 7). The grains are identified as calcium hydroaluminate, apparently containing Ca (to 35 vol.%) [8,9]. Some pores are fine, they are of a closed type and are not communicating with each other.

The SEM microphotograph (Fig. 8) shows the pore in the nonisotropic heterophase material at a

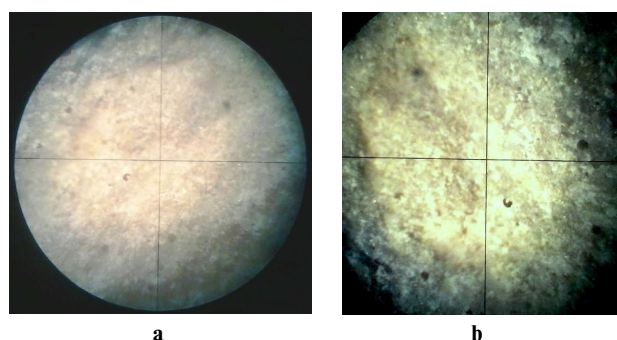


Fig. 7. Microscopic structure of the cleavage of hydrated nickel-containing alumina cement: a – magnification $\times 40$; b – magnification $\times 64$

magnification of $\times 6000$. The pore structure is represented by disperse particles with an almost spherical shape (a diameter of ca. 10 nm), short prismatic and cubic crystallites (with the ribs of 1×2 nm and 1 nm, respectively) and also multiple finer microcrystals with fuzzy outlines that cover the entire internal pore surface [9].

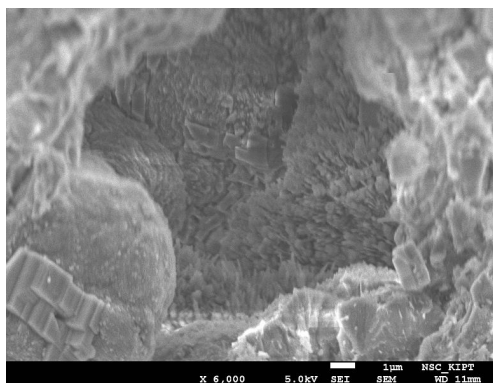


Fig. 8. Microscopic structure of the cleavage of hydrated nickel-containing alumina cement (magnification: $\times 6000$)

The surface of specimen (Fig. 9) shows the matrix fine-disperse phase. The media were not identified morphologically due to fine particles; however, long prismatic crystals (up to 0.5 μm) and thin-needle crystals of up to 7 μm long were identified.

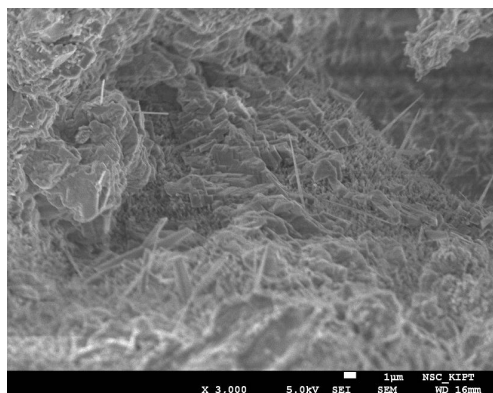


Fig. 9. Microscopic structure of the cleavage of hydrated nickel-containing alumina cement (magnification: $\times 3000$)

Prismatic crystals are interlaced and give double concretions (below and to the left of the center of the photo) that cause the effect of mechanical meshing. Needle crystals penetrate into the fine-disperse matrix phase and sometimes their sharp portion protrudes into the pore space that provides the effect of self-reinforcement and disperse

reinforcement [1].

The synthesized cements were subjected to physical and mechanical tests. The specimens were made of the paste of a normal density and were tested using the methods of small-size specimens. The specimens have been hardened for 1, 3, 7, 14 and 28 days in air-moist conditions. The results of the test are given in Table.

Physical and mechanical test data for the alumina nickel-containing cement obtained using standard raw materials*

Age, days	Compression strength margin, MPa
1	19
3	56
7	63
14	68
28	74

Note: * – Initial material: alumina nickel-containing cement (50–50); water/cement=0.27; hardening conditions: air-moist.

The obtained data show that the developed composition of alumina nickel-containing cement refers to hydraulic binding materials with a normal water-to-cement ratio and it is fast-setting (it starts to set after 60 min to 1 hour 30 min and the setting process ends after 1 hour 50 min to 2 hours 30 min), fast hardening (the compression strength margin is 56 MPa at the age of 3 days of the hardening) and it is a high strength material (the compression strength margin is 74 MPa at the age of 28 days of the hardening).

Conclusions

Using a variety of the physical and chemical methods of analysis, we studied the hydration products of nickel-containing alumina cement. It was established that high cement strength is provided by the presence of calcium hydroaluminates of $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ type, aluminium hydroxide and the unhydrated grains of calcium aluminates that contribute to a further durable gain in strength. The coexistence of the phases both in crystal and colloidal states provides a high strength of the cement stone. It was established that the cleavage structure of hydrated alumina cement is mainly represented by uniformly distributed colorless needle crystals that facilitate the reinforcement of the cement stone and also by the grayish-brown crystals with hexagonal outlines and weak double refraction that are identified as calcium hydroaluminate, apparently of a $\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$ (up to 35 vol.%) composition.

REFERENCES

1. Vorozhbiian R.M., Shabanova G.N., Ryshchenko T.D. Alumina cement on chemical industry wastes // FIB – Sammlung von Beiträgen. – Weimar, Bundesrepublik Deutschland. – 2015. – Band 2. – P.743-749.
2. Modified alumina cement with high service properties / G.N. Shabanova, A.N. Korogodskaya, S.M. Logvinkov, E.V. Khrystych // China's Refractories. – 2016. – Vol.25. – No. 4. – P.1-5.
3. Shabanova G.N., Korogodskaya A.N. Alkali-earth element aluminates and chromites cement bonded refractory castables // China's Refractories. – 2016. – Vol.25. – No. 1. – P.26-31
4. Ukrainczyk N. Kinetic modeling of calcium aluminate cement hydration // Chemical Engineering Science. – 2010. – Vol.65. – P.5605-5614.
5. Constantinides G., Ulm F., Vliet K. On the use of nanoindentation for cementitious materials // Materials and Structures. – 2003. – Vol.36. – No. 257. – P.191-196.
6. Bensted J., Barnes P. Calcium aluminate cements in structure and performance of cements. – London: Spon Press. – 2002. – P.114-138.
7. Ukrainczyk N., Matusinovic T. Thermal properties of hydrating calcium aluminate cement pastes // Cement and Concrete Research. – 2010. – Vol.40. – P.128-136.
8. Microstructure development in mixes of calcium aluminate cement with silica fume or fly ash / A. Hidalgo, J. Garcia, M. Cruz Alonso, L. Fernandez, C. Andrade // Journal of Thermal Analysis and Calorimetry. – 2009. – Vol.96. – No. 2. – P.335-345.
9. Mechanical properties and microstructures of calcium aluminate based ultra high strength cement / E. Sakai, T. Sugiyama, T. Saito, M. Daimon // Cement and Concrete Research. – 2010. – Vol.40. – P.966-970.

Received 26.03.2018

ДОСЛІДЖЕННЯ ОСОБЛИВОСТЕЙ ПРОЦЕСІВ ГІДРОТАЦІЇ ГЛІНОЗЕМІСТИХ ЦЕМЕНТІВ НА ОСНОВІ СПОЛІК СИСТЕМИ $\text{CaO-NiO-Al}_2\text{O}_3$

Г.М. Шабанова, А.М. Корогодська, Р.М. Ворожбіян, Н.С. Цапко, О.В. Христюч, О.Г. Шутинський

В даній статті наведені результати дослідження процесів гідратації, що відбуваються при синтезі цементу на основі відходів хімічної промисловості. Для здійснення досліджень синтезовано цементний клінкер з співвідношенням вихідних сировинних матеріалів 50/50: кальцієвмісні відходи водопідготовки і відбраковані (відпрацьований) нікель-вмісний каталізатор ПрАТ «Азот» м. Северодонецька (Луганська область, Україна). Виготовлені зразки досліджувалися з залученням малої методики Стрелкова: нормальна густина, терміни схоплювання і механічна міцність у віці 1, 3, 7 і 28 діб. Надані результати продуктів твердіння аналізувалися за допомогою диференційно-термічного, рентгенофазового, мікроскопічного методів аналізу, а також електронної мікроскопії, що дає можливість технологічного регулювання співвідношення фаз при синтезі нового класу алюмінатних цементів з використанням відходів хімічної промисловості. Отримані дані показують відсутність кубічних гідроалюмінатів кальцію, сприяють скидання міцності. Фізико-хімічними методами аналізу встановлено, що фазовий склад гідратованого глиноземистого цементу наданий гідроалюмінатами кальцію різної основності, а структура відколу – призматичними кристалами, які дають подвійні зрощення, що сприяє самоармуванню матриці. Розроблений склад глиноземистого нікель цементу відноситься до гідравлічних в'язких матеріалів, здійснені фізико-механічні випробування синтезованих цементів свідчать про те, що одержані цементи є швидкотужавними, швидкотвердними і високоміцними матеріалами.

Ключові слова: оксид нікелю, глиноземистий цемент, гідратація, рентгенофазовий аналіз, гідроалюмінати кальцію, структура.

STUDYING THE SPECIFIC FEATURES OF THE HYDRATION PROCESSES OF ALUMINA CEMENTS BASED ON THE COMPOUNDS OF CaO–NiO–Al₂O₃ SYSTEM

G.M. Shabanova ^a, A.M. Korogodska ^a, R.M. Vorozhbiyan ^a, N.S. Tsapko ^b, E.V. Khrystych ^c, O.G. Shutynskyy ^a

^a National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine

^b Ukrainian Scientific Research Institute of Ecological Problems, Kharkiv, Ukraine

^c National University of Civil Defense of Ukraine, Kharkiv, Ukraine

The article gives the results of studying hydration processes occurring in cement synthesis using waste products of chemical industry. Cement clinker was synthesized with the relation of initial raw components, calcium-containing water treatment waste and rejected nickel-containing catalyst of AZOT Private Joint Stock Company (Severodonetsk, Luhansk Region, Ukraine), equal to 50/50. The obtained samples were studied by Strelkov minor method: normal density, setting time and mechanical strength were determined within 1, 3, 7 and 28 days. The results regarding the setting product were analyzed by differential thermal, X-ray phase analysis, microscopic analysis and electron microscopy; this enables to control the phase relation in the synthesis of a new class of aluminate cements using waste products of chemical industry. The obtained data showed the absence of cubic hydroaluminates which deteriorate the strength. The methods of physicochemical analysis revealed that the phase composition of hydrated alumina cement is represented by calcium hydroaluminate of different basicity, whereas cleavage structure consists of prismatic crystals which give dual coalescence, and this is favorable form to provide matrix self-reinforcement. The developed composition of aluminous nickel-containing cement referred to hydraulic binders. The results of physical-mechanical tests of the synthesized cements indicated that the obtained cements are quick-setting, fast-hardening and high-strength materials.

Keywords: nickel oxide; alumina cement; hydration; X-ray analysis; calcium hydroaluminates; structure.

REFERENCES

1. Vorozhbiyan R.M., Shabanova G.N., Ryshchenko T.D. Alumina cement on chemical industry wastes. *FIB – Sammlung von Beiträgen*, 2015, vol. 2, pp. 743-749.
2. Shabanova G.N., Korogodskaya A.N., Logvinkov S.M., Khrystych E.V. Modified alumina cement with high service properties. *China's Refractories*, 2016, no. 4, pp. 1-5.
3. Shabanova G.N., Korogodskaya A.N. Alkali-earth element aluminates and chromites cement bonded refractory castables. *China's Refractories*, 2016, no. 1, pp. 26-31.
4. Ukrainczyk N. Kinetic modeling of calcium aluminate cement hydration. *Chemical Engineering Science*, 2010, vol. 65, pp. 5605-5614.
5. Constantinides G., Ulm F.-J., Van Vliet K. On the use of nanoindentation for cementitious materials. *Materials and Structures*, 2003, vol. 36, pp. 191-196.
6. Bensted J., Barnes P., *Structure and performance of cements*. Spon Press, London and New York, 2002.
7. Ukrainczyk N., Matusinovic T. Thermal properties of hydrating calcium aluminate cement pastes. *Cement and Concrete Research*, 2010, vol. 40, pp. 128-136.
8. Hidalgo A., Garcia J.L., Cruz Alonso M., Fernandez L., Andrade C. Microstructure development in mixes of calcium aluminate cement with silica fume or fly ash. *Journal of Thermal Analysis and Calorimetry*, 2009, vol. 96, no. 2, pp. 335-345.
9. Sakai E., Sugiyama T., Saito T., Daimon M. Mechanical properties and micro-structures of calcium aluminate based ultra high strength cement. *Cement and Concrete Research*, 2010, vol. 40, pp. 966-970.