37. Kurlov A. S., Gusev A. I., Rempel A. A. Morphology Of Ultrafine Cobalt And Nickel Powders // Reviews on Advanced Materials Science. 2012. Vol. 32, Issue 1. P. 52–60.
38. Kareem T. A., Kaliani A. A. Glow discharge plasma electrolysis for nanoparticles synthesis // Ionics. 2011. Vol. 18, Issue 3. P. 315–327. doi: 10.1007/s11581-011-0639-y
39. Tokushige M., Nishikiori T., Ito Y. Synthesis of Ni nanoparticles by plasma-induced cathodic discharge electrolysis // Journal of Applied Electrochemistry. 2009. Vol. 39, Issue 10. P. 1665–1670. doi: 10.1007/s10800-009-9856-8
40. Preparation of nanosized nickel powder by direct-current electrolysis combined with high-voltage spark discharge / Ibishev K. S., Malyshev V. P., Kim S. V., Sarsembaev B. S., Egorov N. B. // High Energy Chemistry. 2017. Vol. 51, Issue 3. P. 219–223. doi: 10.1134/s0018143917030055

UDC 691.5
DOI: 10.15587/1729-4061.2018.119624

A COMPARATIVE STUDY ON THE INFLUENCE OF METAKAOLIN AND KAOLIN ADDITIVES ON PROPERTIES AND STRUCTURE OF THE ALKALI-ACTIVATED SLAG CEMENT AND CONCRETE

P. Krivenko
Doctor of Technical Sciences, Professor*
E-mail: pavlo.kryvenko@gmail.com
O. Petropavlovskyi
PhD, Senior Researcher*
O. Kovalchuk
PhD, Senior Researcher*
E-mail: kovalchuk.oyu@gmail.com
*Scientific Research Institute for
Binders and Materials
Kyiv National University of
Construction and Architecture
Povitroflotskiy ave., 31, Kyiv, Ukraine, 03037

Встановлено вплив добавок метакаоліна і каоліна на формування мікро- макроструктури й властивостей лугоактивованих шлакових цементів і бетонів. Проведено порівняльне дослідження впливу цих добавок. Встановлено, що введення 2,5–5,0 % добавки каоліну має більш ефективний вплив на процеси структуроутворення і властивості, ніж добавка метакаоліну. Окрім того, заміна добавки метакаоліну каоліном спрощує технологічний процес виробництва й суттєво знижує вартість цементу и бетону

Ключові слова: бетон, каолін, лугоактивований цемент, метакаолін, міцність при стиску, морозостійкість

Исследовано влияние добавок метакаолина и каолина на формирование микро- макроструктуры и свойств щелочеактивированных шлаковых цементов и бетонов. Проведено сравнительное исследование влияния этих добавок. Установлено, что введение 2,5–5,0 % добавки каолина оказывает более эффективное влияние на процессы структурообразования и свойства, чем добавка метакаолина. Кроме того, замена добавки метакаолина каолином упрощает технологический процесс производства и существенно снижает стоимость цемента и бетона

Ключевые слова: бетон, каолин, щелочеактивированный цемент, метакаолин, прочность при сжатии, морозостойкость

1. Introduction

Environmental concerns arising from cement production due to CO_2 emissions and high energy consumption required for high-temperature firing can be eliminated by a wider use of blended and composite cements [1].

One of such cements is the alkali-activated cement [2] (further, the AAC) which attracted an interest of scientists and industry worldwide [3] and promoted its fast development in recent years [4].

The AACs vary in proportions of basic oxides in the system $N(K)_2O–CaO–Al_2O_3–SiO_2–H_2O$ and, according to this, can be divided into three types: high, low and medium-calcium alkali-activated cements [5]. This predetermines a phase composition of the hydration products, hence, properties of the cements and concretes on their basis [6].

The most widely used are the alkali-activated cements with metallurgical slags as an aluminosilicate component – the alkali-activated slag cements (further, the AASCs).

Since metallurgical slags vary in chemical composition [7], correcting additives are to be added in order to give the required (target) properties to a cement stone [8]. These additives can affect both properties of the alkali-activated cement paste and alkali-activated cement concrete due to more favorable conditions for the concrete when the concrete to reveal “adaptive” properties (self-healing) during service [9].

The novelty of the study – to establish a possibility to regulate the structure formation processes and properties of the AACs and concretes by the addition of the kaolin additive instead of the metakaolin one. The expected result is the simpler production process and absence of energy required for the production of metakaolin.

2. Literature review and problem statement

The most commonly used alkali-activated cements are the alkali-activated slag cements. One of the drawbacks of these cements is small contents of Al_2O_3 in their composition. The solution to this is the introduction of metakaolin as an aluminosilicate additive.

Since metakaolin reacts with portlandite to form insoluble low-basic calcium aluminosilicate hydrates, it is used successfully in traditional cements and concretes. Clay materials do not interact with hydration products of the cement stone and act as passive fillers reducing strength characteristics. For this reason, the use of clay materials is restricted in Portland cement systems [10].

The alkali-activated cements, in contrast to portland cements, can contain the increased quantities of clay materials without any negative effect on physico-mechanical properties of the alkali-activated cement concretes [11].

The metakaolin additive in quantities up to 20 % by mass helps to form a structure, which is basically composed of alkaline aluminosilicate and Al-substituted calcium silicate hydrates (C–A–S–H) in the form of gel [12]. A conclusion was made that the metakaolin added to the AASC in quantities up to 20 % by mass did not affect its (cement) strength characteristics. However, in case of highly reactive ground granulated blast-furnace slags (ggbs) helps to keep setting under control [13]. In case of the higher quantities of the alkaline activator (>5 % Na_2O by mass of the ggbs + metakaolin), a gel of the C-A-S-H type was formed as a main cementing phase [14]. The alkali-activated cements and concretes produced using the following cement system “ggbs + metakaolin + alkaline activator” are characterized by the increased compressive strength compared to the cement system without metakaolin (“ggbs + alkaline activator”) [15].

However, the increased quantities of metakaolin in the alkali-activated cement composition can affect negatively macro- and microstructure of the resulted cement stone [16]. In this case, the cost of the alkali-activated cement will be higher and concrete technology more complicated [17]. Moreover, high quantities of reactive metakaolin promote the formation of large quantities of gel phases of mixed composition like CASH, NASH, CNASH along with the CSH phase at the initial stages of hardening [18]. This may result in danger associated with the lower deformative properties and “deteriorated” pore structure of the formed cement stone. Optimal structure of the AASC can be formed when main phases of the CSH type are formed at the initial stage, and the other phases are formed at the later stages, predominantly in a pore space and in cracks [19]. This mechanism provides self-healing of the cement stone macrostructure.

In order to keep these processes under control, the use of the less reactive additive, compared to metakaolin, for example, of kaolin can be a solution. Various clays can also interact with alkali metal compounds to form alkaline aluminosilicate hydrates that are analogues to natural zeolites [20]. However, these processes flow very slowly. Presence of clays in the composition of cements and concretes was always undesirable. That is why no any studies on the influence of quantities of clay additives on alkali-activated slag cements were carried out. Taking the above into account, as well as the fact that production of metakaolin is a very energy extensive process and its (metakaolin) cost is very high, a necessity occurred to study whether metakaolin could be substituted by kaolin.

3. The aim and objectives of the study

The aim of the study is to analyze the influence of the metakaolin and kaolin additives on physico-mechanical properties, as well as macro- and microstructure of the alkali-activated slag cements and concretes based on them. This will allow establishing a possibility to substitute expensive metakaolin by kaolin. To achieve this aim, it was necessary to the following tasks:

– to compare regularities of the influence of the correcting additives of metakaolin and kaolin on the formation of technological and physico-mechanical properties of the AASC and concretes;

– to compare regularities of the influence of the metakaolin and kaolin additives on the formation of micro- and macrostructure of the AASC and concretes;

– based on the results of comparison of the influence of the additives to establish a possibility to substitute expensive metakaolin by kaolin as a correcting additive to the AASC.

4. Constituent materials and testing techniques

Type I alkali-activated slag cement as per national standard of Ukraine was used in the study. $Na_2SiO_3{\cdot}5H_2O$ in a liquid form (density =1,160 kg/m^3) was used as an alkaline component and sodium lignosulphonate (further, LST) with pH=8.5 was used as a plasticizer. Ground granulated blast-furnace slag (ggbs) (modulus of basicity =1.1, content of glass phase =84 %, fineness measured as a specific surface by Blaine =4,500 cm^2/g) was used as an aluminosilicate component. Chemical composition of the slag is shown in Table 1. Kaolin and metakaolin of the Ukrainian origin, the chemical composition of which is given in Table 1, were used as mineral additives.

River sand (fineness modulus =1.2) was used as fine aggregate in the alkali-activated slag cement mortars. Crushed granite (fractions 5/10 mm and 10/20 mm) was used as coarse aggregate in the alkali-activated slag cement concretes.

Table 1

Chemical composition of constituent materials

Cement components	Oxides (% by mass)							
	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	R_2O	TiO_2
Slag (ggbs)	37.90	6.85	0.31	0.11	5.21	44.60	1.13	0.35
Kaolin	58.50	39.50	0.50	–	–	0.80	–	0.70
Metakaolin	57.33	36.80	0.58	–	–	0.21		0.79

Preparation of the alkali-activated slag cement pastes was done in accordance with the European Standard EN 196-3.

Compressive strength of the alkali-activated slag cements was determined as per EN 196-1 with an account of the requirements of the national standard of Ukraine DSTU B V.2.7-181:2009, namely: the ratio between an alkaline solution and slag (ggbs) (A/S) in the alkali-activated slag cement mortars was determined after the flow value of the mortar of 106–115 mm was achieved. Strength of the alkali-activated slag cement concretes was determined as specified in DSTU B V.2.7-25:2011. The class of the concrete in compressive strength was determined on cube specimens (100 mm) at an age of 28 days after hardening in normal conditions (t=20±2 °C, R.H.=95±5 %).

Density, water absorption and porosity of the alkali-activated slag cement concretes were studied in accordance with the procedure as specified in DSTU B V.2.7-170:2008. According to this procedure, the concrete cubes (100 mm) after 28 days were dried up to a constant weight at t=105±10 °C. Then, the specimens were saturated with water until a constant weight would be obtained at t=20±2 °C. The values of porosity were calculated from the values of average density and water absorption of the concrete specimens.

Freeze/thaw resistance was studied in accordance with the third (accelerated) test method prescribed by the national standard of Ukraine DSTU B V.2.7-47-96. According to this method, concrete cubes (100 mm) were saturated in a 5 % solution of NaCl at t=18±2 °C and then were subjected to freezing at t=–50 °C. Thawing was performed in a 5 % solution of NaCl. A class of the alkali-activated slag cement concrete in freeze/thaw resistance was designated as a number of alternate freezing and thawing cycles, after which a mean compressive strength has decreased by no more than 5 %.

The phase composition of the hydration products of alkaline aluminosilicate hydrates was studied by X-ray diffraction (XRD), differential thermal analysis (DTA) and scanning electron microscope (SEM) (Ukraine).

The X-ray diffraction analysis was carried out at the diffractometer DRON 4-07 (USSR) with a copper tube at a voltage of 30 kV, current 10...20 mA and the range of angles 2θ=10...60°. Identification of the hydration products was carried out using the database PDF-2 Data Base (Sets 1–50 plus 70–88) with the software module JCPDFWIN 2.1 (JCPDS-ICDD 2000). Comprehensive differential thermal analysis was carried out at the derivatograph (Paulik-Paulik-Erdey, MOM (Hungary)). The data of [21, 22] were used for identification.

5. The influence of the additives on setting time of the cements

The influence of the kaolin (a) and metakaolin (b) additives (Fig. 1) showed that the kaolin additive in quantities of 2.5 %, 5.0 % and 10.0 % affected setting times and normal consistency of the AASC paste (further, NCP). So, the initial setting time was shorter (from 45 min to 40 min) and the value of NCP increased from 23.0 % to 24.0 %. Contents of the plasticizer (LST) were higher (from 0.75 % (without the kaolin additive) to 1.20 % (with the kaolin additive – 10 %), thus allowing to maintain the initial setting time between 40 and 45 min.

The same effect on initial setting time and value of paste of normal consistency NCP was observed in case of the metakaolin additive added in quantities of 2.5 %, 5 % and 10 %. A conclusion was made that the values of NCP tended to even greater increase: from 24.0 to 27.5 % (against 23.5 % in the composition without the metakaolin additive). In this case, the initial setting time was between 43 min and 47 min, LST=1.0...1.2 % by cement mass.

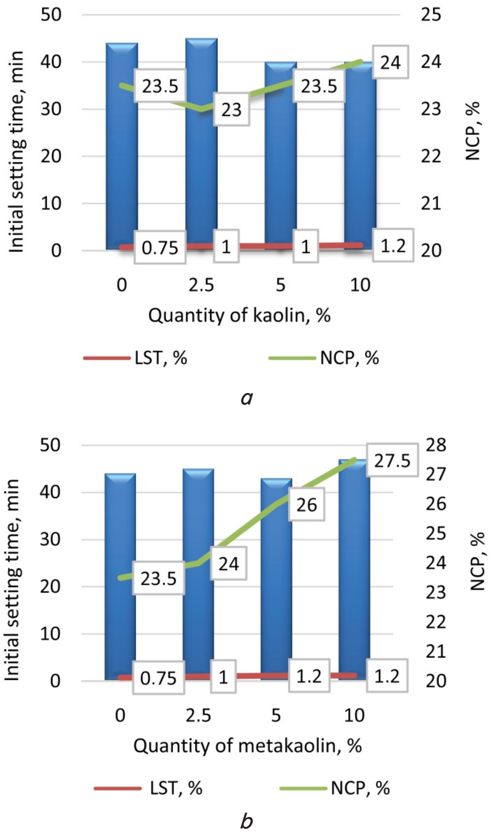


Fig. 1. Initial setting time of the alkali-activated slag cement and value of NCP vs. quantity and type of the additive: *a* — kaolin; *b* — metakaolin

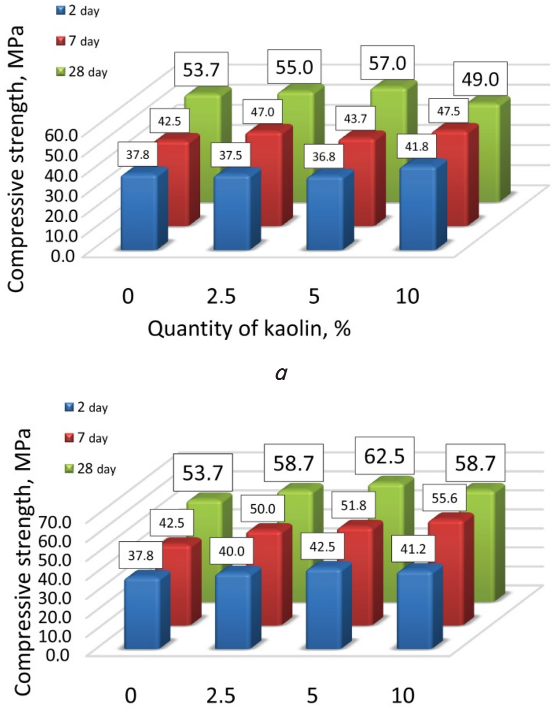
6. The influence of the additives on compressive strength of the cements and concretes

Analysis of the data given in Fig.2 a showed that with an increase in quantities of the kaolin in the alkali-activated slag cement composition, the A/S increased from 0.32 to 0.36, the flowability being unchanged. Regardless of quantities of the kaolin (varying from 0 to 10 %), the early strength (2 days) of the AASCs did not change (36–40 MPa). Standard (28 days) strength of 57.0 MPa was achieved with 5 % of the kaolin additive. A further increase in quantities of the additives up to 10 % deteriorated strength characteristics (from 57.0 MPa down to 49.0 MPa).

Similar dependences and regularities of the influence of quantities of the additive were observed in case of substitution of the metakaolin by the kaolin (Fig. 2, *b*). The only difference was the compressive strength of the specimens in case of the metakaolin additive at the early stages of hardening which was somewhat higher compared to the compressive strength of the specimens containing the kaolin additive. In both cases, the optimal quantities of the additive were 2.5–5.0 % by mass. The decrease of the compressive strength with an increase in the additive content up to 10 %, especially at the age of 28 days, coincide well with the known data on a role played by the gel phases on structure formation and properties of the resulted cement stone [23].

The addition of the kaolin and metakaolin additives to the alkali-activated slag cement composition was found to accelerate the structure formation consisting mainly of the alkaline aluminosilicate and Al-substituted calcium silicate hydrates in the form of a gel [17, 18]. The addition of the kaolin and metakaolin additives had no significant effect on strength characteristics, but in case of highly reactive slag (ggbs) helped to control the initial setting [19].

In contrast to the kaolin additive, the metakaolin additive interacted more actively with the alkaline activator solution [20]. The addition of it in quantities of 2.5–10.0 % resulted in high early strength: early strength of 42.5 MPa and standard age (28 days) strength of 62.5 MPa could be achieved by the alkali-activated slag cement with 5 % of the metakaolin additive. The decrease and increase in quantities of the metakaolin additive from the optimal content of 5 % down to 2.5 % and up to 10 % reduced a class of cement in compressive strength (from M600P to M500P).



a

b

Fig. 2. Compressive strength of the alkali-activated slag cements vs. quantity and type of the additive: *a* – kaolin; *b* – metakaolin

Analysis of the above data led to the conclusion that the addition of the metakaolin and kaolin additives in optimal quantities (5 % by cement mass) allowed obtaining the cements of standard consistency and with improved strength characteristics.

The obtained results were tried in the production of concretes from these cements.

Mix design of the alkali-activated slag cement concrete was: slag (ggbs) – 425 kg/m^3; sand – 650 kg/m^3; crushed granite (5/10) – 350 kg/m^3; crushed granite (10/20) – 800 kg/m^3. Consistency of the fresh alkali-activated slag cement concrete corresponded to S4 class in consistency (160–200 mm).

The obtained data showed that the addition of the kaolin or metakaolin additives to substitute the slag (ggbs) leads to a directly proportional increase in the A/S without any significant loss in strength characteristics.

Since some of the alkali are bound by the metakaolin and kaolin, the standard (28 days) strength of the alkali-activated slag cement concretes was somewhat lower (by 8 to 10 %) compared to that of the concretes made from the cements without the additives. After 6 to 9 months, this difference has disappeared and the higher strength has been reached due to the deepening of the hydration processes, synthesis of low-basic calcium silicate hydrates, synthesis of analogues to zeolite and feldspathoid minerals and absence of destructive processes.

7. The influence of the additives on macrostructure of the concrete

Characteristics of pore structure of the alkali-activated slag cements and concretes depending on quantity (0 %; 2.5 %; 5.0 %) and type of the additive (kaolin and metakaolin) are shown in Table 3 and Fig. 3.

Table 3

Characteristics of porosity and strength of the alkali-activated slag cement stone

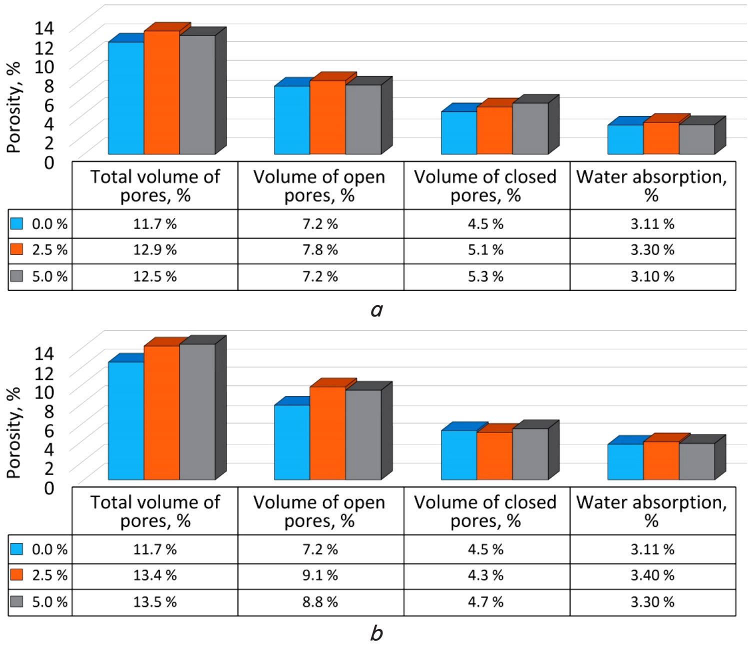
No.	Kaolin, %	Metakaolin, %	Water absorption, %	Characteristics of porosity, %			Compressive strength, MPa, 28 days
				Total volume of pores	Volume of open pores	Volume of closed pores	
1	–	–	8.0	22.7	15.4	7.3	**86.0**
2	2.5	–	7.8	24.9	14.9	9.0	**90.2**
3	5.0	–	7.6	21.8	14.9	6.9	**85.4**
4	10.0	–	7.0	22.8	13.6	9.2	**72.1**
5	–	2.5	9.1	27.7	16.5	11.2	**81.0**
6	–	5.0	10.8	26.5	19.9	6.6	**86.5**
7	–	10.0	12.2	30.5	21.3	9.2	**62.5**

Table 2

Cement composition (concrete mix design) and characteristics of the alkali-activated slag cements and concretes

No.	Cement composition, % by mass*				Aggregates, kg/m^3			A/S**	Slump, mm	Class in consistency	Compressive strength, MPa		
	Slag (ggbs)	Kaolin	Metakaolin	LST	Sand	Crushed granite, fr.					3 days	7 days	28 days
						5/10	10/20						
1	100.0	–	–	0.75	650	350	800	0.35	170	S-4	41.7	49.3	56.8
2	97.5	2.5	–	1.00	650	350	800	0.36	170	S-4	33.4	39.4	50.5
3	95.0	5.0	–	1.00	650	350	800	0.37	165	S-4	34.2	43.1	53.2
4	97.5	–	2.5	1.00	650	350	800	0.37	180	S-4	35.8	41.5	51.5
5	95.0	–	5.0	1.20	650	350	800	0.39	175	S-4	37.3	43.9	55.0

*Note: * – $Na_2SiO_3 \cdot 5H_2O$ in a liquid form (density =1160 kg/m^3) was used as an alkaline component (taken in quantity over 100 % of the cement mass), ** – A/S – an alkaline activator solution to slag ratio*



	Total volume of pores, %	Volume of open pores, %	Volume of closed pores, %	Water absorption, %
🟦 0.0 %	11.7 %	7.2 %	4.5 %	3.11 %
🟧 2.5 %	12.9 %	7.8 %	5.1 %	3.30 %
▨ 5.0 %	12.5 %	7.2 %	5.3 %	3.10 %

a

	Total volume of pores, %	Volume of open pores, %	Volume of closed pores, %	Water absorption, %
🟦 0.0 %	11.7 %	7.2 %	4.5 %	3.11 %
🟧 2.5 %	13.4 %	9.1 %	4.3 %	3.40 %
▨ 5.0 %	13.5 %	8.8 %	4.7 %	3.30 %

b

Fig. 3. Porosity of the alkali-activated slag cement concretes vs. quantities and type of the additive: *a* — kaolin; *b* — metakaolin

The results of the study showed the increase in volumes of ''conditionally'' closed pores, which was directly proportional to the quantities of the additives.

When analyzing the obtained data, a conclusion was made that the addition of the kaolin additive in quantity of 5 % allowed increasing the volume of "conditionally" closed pores (by 17.7 %) compared to the concrete made from the AASC without the kaolin additive, while maintaining the same volume of open pores.

In case of the metakaolin additive (5 % by mass), the alkali-activated slag cement concrete was characterized by a slight increase in volume of the closed pores (4.4 %) due to the increased (by 22.2 %) quantities of open pores compared to the concrete mix design made from the AASC without the metakaolin additive.

Testing of freeze/thaw resistance of the concretes made from the alkali-activated slag cement with the kaolin additive instead of the metakaolin additive showed the higher freeze/thaw resistance (F500 against F400) due to the formation of the larger quantities of closed pores.

8. The influence of the additives on the formation of microstructure of the cement stone

The AASC compositions 1, 3 and 6 (Table 3) have been chosen to study the effect of the metakaolin and kaolin additives on structure formation processes.

Examination with the help of XRD (Fig. 4), DTA (Fig. 5) and SEM (Fig.6) showed that a phase composition of the cement under study without additives (Fig. 4, curve 1) was represented, predominantly, by $CaCO_3$ and calcium aluminosilicate hydrates of various basicity such as tobermorite $C_5S_6H_5$, CSH(I), CSH(II) and okenite ($Ca_3C_2S_6O_{15}H_6$). This conclusion was supported by the endothermic effects (peaks) (Fig. 5, DTA curve 1) at temperatures 160, 760, and 850 °C, as well as by an exothermic peak at t=830 °C, testifying to decomposition and crystallization. Moreover, the formation of sodium aluminosilicate hydrates of the nepheline-hydrate ($Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) type, as well as calcium aluminosilicate hydrates of gismondite ($Ca_4[Al_8Si_8O_{32}]{\cdot}16H_2O$) type could be observed.

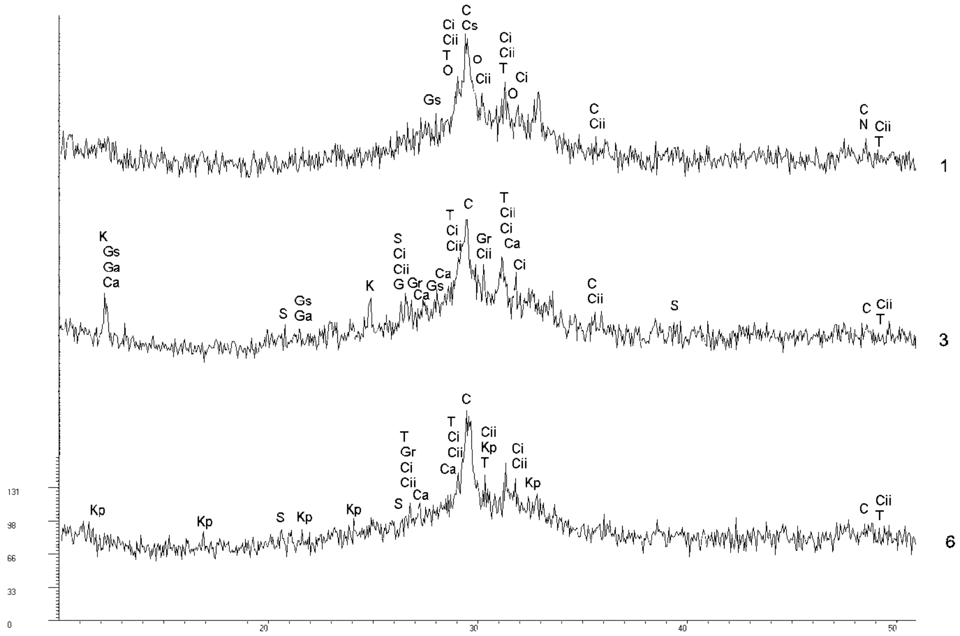


Fig. 4. X-ray phase diffraction patterns of the cement stone, compositions 1, 3, 6 (Table 3) after 28 days of hardening in normal conditions: C — $CaCO_3$; K — kaolinite; Ci — C-S-H(I); Cii — C-S-H(II); Ca — CAH_{10}; S — SiO_2; Gs — gismondite; Ga — garronite; T — tobermorite; Gr — gyrolite; N — nepheline-hydrate; O — okenite; Kp — clinoptilolite

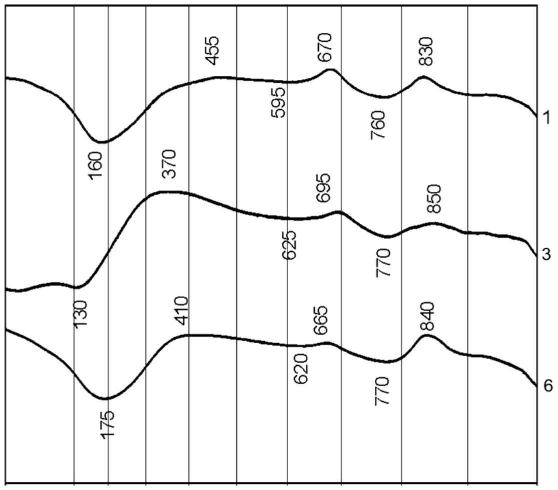
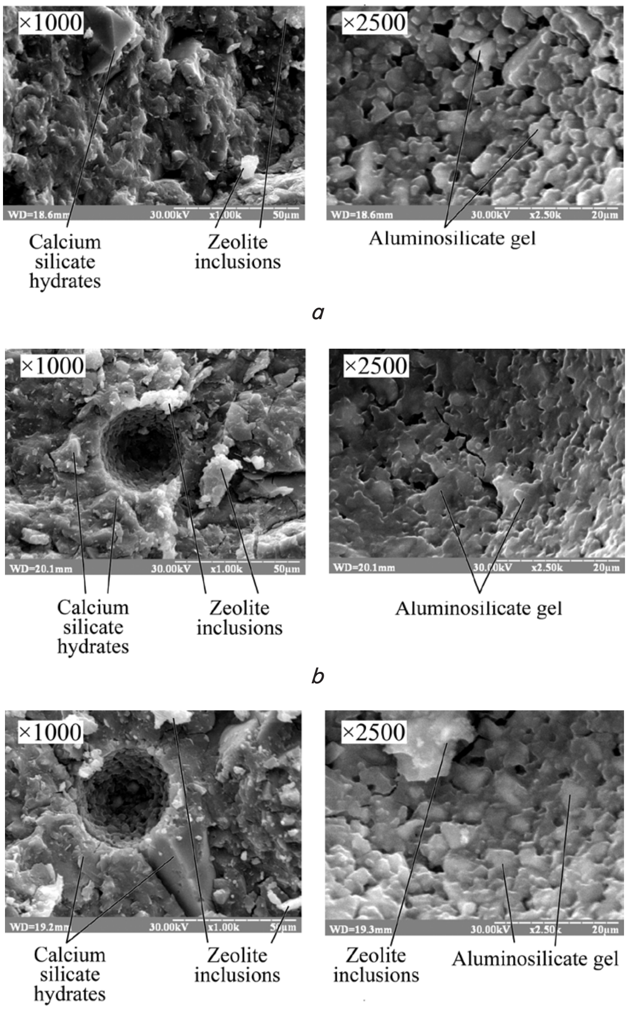


Fig. 5. DTA curves of the cement stone, compositions 1, 3, 6 (Table 3)



a

b

c

Fig. 6. Electron microphotos of cleavage surface of the cement stone: *a* — composition 1; *b* — composition 3; *c* — composition 6 (Table 3)

Electron microscopy examination (Fig. 6, composition 1 *a*, *b*) showed inhomogeneity of the resulted cement stone microstructure. Poorly hydrated particles of the ggbs are frequently met. The products of crystallization of calcium aluminosilicate hydrates that are being formed are clearly seen in pores and in the intergranular space.

In case of the metakaolin additive (Fig. 6, composition 6 *a*, *b*), mixed sodium- calcium silicate hydrates of the garronite ($NaCa_{2.5}[Al_3Si_5O_{16}]_2 \cdot 13.5H_2O$), as well as of the gyrolite $Na_2Ca[Si_4O_{10}] \cdot 4H_2O$) types are formed in addition to the above-mentioned phases. The endothermic and exothermic effects are shifted to the field of the increased temperatures (Fig. 5, DTA curve 6), being an evidence of the increase in degree of crystallization of the phases that are being formed. The SEM pictures showed needle-like crystals of calcium silicate hydrates, plates of carbonate formations, as well as sphere-like crystals characteristic of the alkaline aluminosilicate hydrates (Fig. 6, *b*). The resulted cement stone microstructure is homogeneous.

The substitution of the metakaolin by the kaolin was found to result in deceleration of the phase formation processes (Fig. 6, *b*). At the same time, quantities of the gel phases tended to increase, according to the DTA (Fig. 6, *b*) and SEM (Fig. 6, *b*) data.

The obtained data support conclusions on similar influence of the metakaolin and kaolin additives on the formation of strength properties of the alkali-activated slag cement stone and its macrostructure.

9. Conclusions

1. The addition of the kaolin instead of the metakaolin was found to act as follows: 2.5–10 % by mass reduced the value of NCP by 9.5–8.7 %, respectively; 2.5–5 % by mass did not affect setting times, but with increase up to 10 % by mass the setting times were shorter (from 48 to 40 minutes); 2.5–5 % by mass did not affect compressive strength at all stages of hardening, but with increase up to 10 % by mass reduced strength characteristics of the cement-sand specimens (from 57.0 MPa to 49.0 MPa).

2. The processes of microstructure formation of the cement stone with the kaolin and metakaolin additives were found to flow with the formation of similar phases, however, these processes were found taking place with higher intensity in case of the metakaolin additive. In case of the kaolin, an optimal macrostructure of the concrete was formed, providing the higher freeze-thaw resistance. So, in case of the 5 % kaolin by mass, the quantities of conditionally closed pores has increased by 17.7 % as compared to the concretes containing the same quantities of the metakaolin. This resulted in the higher freeze-thaw resistance of the concrete (from F400 up to F500).

3. Based on the comparison of properties and structure of the cement and concrete with the kaolin and metakaolin additives, a possibility to substitute the metakaolin by the kaolin as a correcting additive was established.

References

1. Shi C., Jiménez A. F., Palomo A. New cements for the 21st century: The pursuit of an alternative to Portland cement // Cement and Concrete Research. 2011. Vol. 41, Issue 7. P. 750–763. doi: 10.1016/j.cemconres.2011.03.016
2. Gluhovskiy V. D. Gruntosilikaty. Kyiv: Gosstroyizdat, 1959. 127 p.

3. Historical Aspects and Overview / Provis J. L., Duxson P., Kavalerova E., Krivenko P. V., Pan Z., Puertas F., van Deventer J. S. J. // RILEM State-of-the-Art Reports. 2013. P. 11–57. doi: 10.1007/978-94-007-7672-2_2
4. Demonstration Projects and Applications in Building and Civil Infrastructure / Provis J. L., Brice D. G., Buchwald A., Duxson P., Kavalerova E., Krivenko P. V. et. al. // RILEM State-of-the-Art Reports. 2013. P. 309–338. doi: 10.1007/978-94-007-7672-2_11
5. A review on alkaline activation: new analytical perspectives / Palomo A., Krivenko P., Garcia-Lodeiro I., Kavalerova E., Maltseva O., Fernández-Jiménez A. // Materiales de Construcción. 2014. Vol. 64, Issue 315. P. e022. doi: 10.3989/mc.2014.00314
6. Garcia-Lodeiro I., Palomo A., Fernández-Jiménez A. An overview of the chemistry of alkali-activated cement-based binders // Handbook of Alkali-Activated Cements, Mortars and Concretes. 2015. P. 19–47. doi: 10.1533/9781782422884.1.19
7. Gluhovskiy V. D., Pahomov V. A. Shlakoshchelochnye tsementy i betony. Kyiv: Budivel'nik, 1978. 184 p.
8. A review on mineral waste for chemical-activated binders: mineralogical and chemical characteristics / Sedira N., Castro-Gomes J., Kastiukas G., Zhou X., Vargas A. // Mining Science. 2017. Vol. 24. P. 29–58.
9. Chernyavskiy V. L. Adaptatsiya abioticheskih sistem: beton i zhelezobeton. Dnipropetrovsk: Dnepropetr. nats. un-t zh.-d. transp., 2008. 415 p.
10. Metakaolin v budivelnykh rozchynakh i betonakh / Dvorkin L. Y., Lushnikova N. V., Runova R. F., Troian V. V. Kyiv: KNUBiA, 2007. 215 p.
11. Yip C. K., Lukey G. C., van Deventer J. S. J. The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation // Cement and Concrete Research. 2005. Vol. 35, Issue 9. P. 1688–1697. doi: 10.1016/j.cemconres.2004.10.042
12. Puertas F., Palacios M., Provis J. L. Admixtures // RILEM State-of-the-Art Reports. 2013. P. 145–156. doi: 10.1007/978-94-007-7672-2_6
13. Role of metakaolin additive on structure formation in the contact zone "cement-alkali-susceptible aggregate" / Krivenko P. V., Gelevera A. G., Petropavlovsky O. N., Kavalerova O. N. // 2nd International Conference on Non-Traditional Cement & Concrete. Brno, Czech Republic: Brno University of Technology & ZPSV AS, 2005.
14. Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na2O–CaO–Al2O3–SiO2–H2O / Garcia-Lodeiro I., Palomo A., Fernández-Jiménez A., Macphee D. E. // Cement and Concrete Research. 2011. Vol. 41, Issue 9. P. 923–931. doi: 10.1016/j.cemconres.2011.05.006
15. Li C., Sun H., Li L. A review: The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements // Cement and Concrete Research. 2010. Vol. 40, Issue 9. P. 1341–1349. doi: 10.1016/j.cemconres.2010.03.020
16. Puertas F., Fernández-Jiménez A., Blanco-Varela M. T. Pore solution in alkali-activated slag cement pastes. Relation to the composition and structure of calcium silicate hydrate // Cement and Concrete Research. 2004. Vol. 34, Issue 1. P. 139–148. doi: 10.1016/s0008-8846(03)00254-0
17. Bernal S. A., Mejía de Gutiérrez R., Provis J. L. Engineering and durability properties of concretes based on alkali-activated granulated blast furnace slag/metakaolin blends // Construction and Building Materials. 2012. Vol. 33. P. 99–108. doi: 10.1016/j.conbuildmat.2012.01.017
18. Generalized Structural Description of Calcium–Sodium Aluminosilicate Hydrate Gels: The Cross-Linked Substituted Tobermorite Model / Myers R. J., Bernal S. A., San Nicolas R., Provis J. L. // Langmuir. 2013. Vol. 29, Issue 17. P. 5294–5306. doi: 10.1021/la4000473
19. Krivenko P. V. Zakonomernosti formirovaniya struktury i svoystv tsementnogo kamnya shlakoshchelochnyh vyazhushchih // Tezisy dokladov P Vsesoyuznoy nauchno-prakticheskoy konferentsii. Kyiv, 1984.
20. Gluhovskiy V. D., Zhukova R. S., Kruglitskiy N. N. Issledovanie produktov vzaimodeystviya glinistyh mineralov s gidroksidom kaliya // Neorganicheskie materialy. 1972. Vol. 8, Issue 11.
21. Lothenbach B., Durdziñski P., De Weerdt K. Thermogravimetric analysis // A Practical Guide to Microstructural Analysis of Cementitious Materials. 2015. P. 177–212. doi: 10.1201/b19074-6
22. Zhdanov S. P. Synthetic zeolites. CRC Press, 1990. 679 p.
23. Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation / Bernal S. A., Provis J. L., Walkley B., San Nicolas R., Gehman J. D., Brice D. G. et. al. // Cement and Concrete Research. 2013. Vol. 53, Issue 127–144. doi: 10.1016/j.cemconres.2013.06.007