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DESIGN OF THE COMPOSITION OF ALKALI ACTIVATED PORTLAND CEMENT USING MINERAL ADDITIVES OF TECHNOGENIC ORIGIN

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Робота охоплює результати розробки складів цементу і технології виробництва для поширених цементних систем «портландцементний клінкер – мінеральні добавки – лужний активатор – водоредикуюча добавка», що містять більше 60 % за масою мінеральних добавок. Добавки обрано з групи: доменний гранульований шлак, золи теплових електростанцій (зола виносу та відвальні золи) та червоний шлам (відходи глиноземного виробництва). Актуальність роботи пов'язана із необхідністю покращення цілої низки показників, що обмежують широке застосування традиційних високонаповнених відходами цементів (шлакопортландцементу, зокрема ранньої міцності та строків тужавлення).

Розроблено основні принципи конструкційної побудови цементних складів та показана технологія виробництва. Встановлено, що з точки зору вимог існуючих українських та європейських стандартів, а саме EN 197-1, розроблені цементні не тільки не поступаються цементам EN: CEM I, CEM II, CEM III за властивостями, але й перевершують за міцністю. Розроблені склади цементів, що містять портландцементний клінкер, не більше ніж 40 % за масою відповідають вимогам стандарту EN згідно класам за міцністю на стиск (у віці 28 діб) 32,5N – 32,5R; 42,5R – 52,5R. В деяких випадках вміст супутніх продуктів промисловості у складі цементу може сягати 95 % за масою.

Досліджено вплив лужних компонентів на процеси структуроутворення штучного каменю лужного цементу на різних рівнях. Встановлено, що підвищення лужності середовища цементу обумовлює зниження основності фазового складу новоутворень цементу на макрорівні. Використання лужного активатора сприяє збільшенню загальної пористості штучного каменю, яка здатна знижуватись протягом часу експлуатації

Ключові слова: лужний цемент, композиційний цемент, супутні продукти, утилізація відходів, червоний шлам, лужна активація

1. Introduction

An analysis of data given in [1] allows us to conclude that the modern trends in the production of cement have been focused on increasing the content of active mineral additives and pozzolanic materials in cement compositions. The aim was to reduce emissions and eliminate the environmental impact (CO₂ emissions, energy consumption, the exhaustion of natural resources).

The most common among ordinary cements are those that contain additional mineral supplements (granulated blast furnace slag, fly ash, pozzolana, etc.). The finer grinding of cements, the introduction of SAS and intensifiers [2], as well as changing the distribution of particles in the grinding products (increasing the content of fractions to 10 μm and

to 60 μm), would make it possible to produce cements with the content of industrial by-products up to 54 % by weight. Such materials meet the requirements for strength, which is defined by standards, namely: compressive strength during early terms of hardening (on day 7 to 20...24 MPa) [3]. However, compressive strength of the obtained cements on day 2 of hardening is very low.

Based on an analysis of studies into directed synthesis of the structure and properties of alkali activated cements [4], it is proposed to resolve the problem by introducing into cement (with a high content of related industrial products) the alkaline activator in a combination with SAS. That would ensure the required hydration rate of the portland cement clinker, as well as the setting terms, would reduce water consumption and stimulate high chemical activity of the clinker

free components. The application of such approaches will make it possible to reduce the content of clinker in a cement composition, to dispose of large volumes of industrial waste, and improve the operational properties of the examined cements. In turn, that would contribute to solving not the engineering issues alone, but to resolving the environmental problems as well.

2. Literature review and problem statement

The alkali activated slag portland cement deserves special attention as it could replace much of the valuable material, specifically the portland cement clinker, with mineral supplements. Recycling the industrial by-products in order to produce new materials is the principal driver of sustainable development. The alkaline activation could become an effective means to achieve this goal, especially when the carbon fly ash and granulated blast furnace slag replace the calcined natural clays, such as metakaolin, and are used as source materials [5].

As shown in papers [6, 7], traditional portland cement cannot accommodate a significant portion of the waste in its composition, and, at a significant replacement, it loses certain performance characteristics. In this case, the content of industrial waste is 25...40 % by weight of cement. It is the imperfection of traditional systems that highlights the benefits of the alkali activated portland cement.

Papers [8–10] demonstrate the successful development of the alkali activated cements using red mud as a component in two areas: high early and late strength and excellent resistance to aggressive environments. However, the cited studies do not make it possible to utilize red mud in large quantities, as its content in the system is up to 30 % by weight of cement. According to research reported in [11, 12], the basic phase composition of red mud is represented by amorphous aluminosilicate and two calcium silicate (β -C₂S), hematite (α -Fe₂O₃), calcite and perovskite (CaTiO₃). Owing to the metastable modification β -C₂S, cements have binding properties. It was established that in the process of hydration the diffraction intensity of β -C₂S decreases with an increase in the time of cement stone hardening, and the use of a cement clinker admixture accelerates the rate of hydration at the expense of creating the crystallization centers. The cited studies require research into processes of structure-formation of the alkali activated cement when using different types of an alkaline activator. Scientific studies [13, 14] confirm the emergence of zeolite-like minerals in the artificial stone of the alkali activated cement. Thus, the use of red mud in the composition of the alkali activated cement confirms the possibility of forming such structures at a temperature of 80 °C with a decrease in intensity when approaching the standard conditions for hardening. The derived neo formations are represented by C–S–H gel with a low ratio of Ca/Si. However, the studies conducted require investigation into processes of structure formation of the cement matrix under conditions of exposure to normal temperatures, which would extend the scope of its application.

Research results [15, 16] prove that the use of related industrial products as a component of the alkali activated cement ensures not only the physical-mechanical characteristics of artificial stone, but also meet the requirements of normative documents to the environmental safety. The alkali activated cements and concretes could safely utilize

industrial waste [17, 18] that, in particular, contains heavy metal compounds, which was proven by research into immobilizing and radiological properties of the artificial stone [19]. The results of studying the ecological safety of the received materials make it possible to assume that the resulting alkali activated slag portland cement, which contains a significant amount of mineral additives (red mud, granulated blast furnace slag, and fly ash), will meet the requirements of regulations concerning the safety of the environment. It could be applied as a general building material.

Summarizing the results of an analysis, we can note that the use of traditional cements with a high degree of filling with technogenic waste and related products (for example, slag portland cement) does not make it possible to dispose of the large amounts of industrial wastes. The alkali activated cements open a promising way to dispose of a significant portion of the waste in the system; they, however, require additional research into their application under conditions of normal hardening. The studies conducted suggest that the employment of the alkaline activation in the slag portland cements should greatly increase the amount of mineral additives in the system (60–90 % by weight of cement) through combined grinding of components and applying the plasticizing admixtures while maintaining high performance efficiency.

3. The aim and objectives of the study

The aim of this study was the development of the composition of the alkali activated cements with a high content of clinker-free components and a content of the portland cement clinker not exceeding 40 % by weight. Such cements must have the high gain in strength at an early age (2...7 days), as well as strength at the age of 28 days not below 40 MPa.

To achieve the set aim, the following tasks have been solved:

- to investigate physical and mechanical characteristics in the systems – «portland cement clinker – granulated blast furnace slag», «portland cement clinker – fly ash», «portland cement clinker – granulated blast furnace slag – fly ash from TPP», and «portland cement clinker – granulated blast furnace slag – red mud»;
- to explore the role of an alkaline activator in the processes of structure formation of artificial stone in the alkali activated cements with a significant content of related industrial products.

4. Materials and methods of research

We have used, as the main calcium-aluminosilicate component, the granulated blast furnace slag – GBS (Kamianske, Ukraine). We applied, as aluminosilicate components, the fly ash from thermal power plants (Ladyzhyn, Ukraine) and red mud (produced in Ukraine using the Bayer technique) in quantities between 60 to 92 % by weight of cement.

The mineralogical composition of portland cement clinker (hereinafter clinker) is represented by: C₃S – 67.34 %; C₂S – 11.15 %, C₃A – 7.29 %, C₄AF – 10.15 %. All components were exposed to combined grinding at a laboratory drum mill (MBL, made in the USSR) to attain the specific surface of 400...450 m²/kg (by Blane). Chemical composition of the raw materials is given in Table 1.

Table 1

Chemical composition of raw materials

Designation	Content of oxides, % by weight				
	Clinker	Fly ash	Disposed ash	Granulated blast furnace slag	Red mud
SiO ₂	21.82	55.50	48.20	39.00	9.77
Al ₂ O ₃	5.30	24.70	19.60	5.90	14.50
Fe ₂ O ₃	4.86	4.00	4.50	0.29	36.90
FeO	–	–	3.15	–	
TiO ₂	–	0.20	0.89	–	5.23
MnO	–	1.50	0.11	0.10	0.03
CaO	65.91	2.50	3.18	47.70	10.40
MgO	1.11	1.30	1.36	5.56	0.17
P ₂ O ₅	–	–	0.02	–	0.19
K ₂ O	0.22	2.70	–	–	0.12
Na ₂ O	–	–	1.04	–	5.58
SO ₃	0.99	0.80	0.11	1.48	0.30
Mass loses	0.20	–	16.00	0.50	16.79

In the work we used, as surface-active substances, technical sodium lignosulfonate (TSL) in line with DSTU B V.2.7-171:2008 (EN 934-2:2001).

The alkaline component was represented by soda ash, sodium metasilicate pentahydrate (Na₂SiO₃·5H₂O) and sodium sulfate.

We added the alkaline activator and a surface-active substance in liquid form (ρ=1,050...1,250 kg/m³) by agitating together with water. The amount of the supplement-plasticizer in all cases was 1 % by the weight of cement.

We determined the composition of raw materials using a chemical analysis.

Preparation of cement slurry and cement-sandy mortars was carried out in a standard mixer type «Hobart».

Duration of cement setting time was determined based on DSTU B V.2.7-185:2009 (similar to EN 196-3).

The consistency of cement-sandy mortars was determined based on the spread of a standard cone at a shaking table in line with DSTU B V.2.7-187.

The strength of cements was determined based on DSTU B V.2.7-187:2009, DSTU B EN-196-1 with respect to requirements of DSTU B V.2.7-181:2009. The heat release of cement slurry was determined using a modified method in accordance with the requirements of DSTU B V.2.7-289:2011.

Porosity of the samples was determined according to DSTU B V.2.7-170:2008.

To acquire images of the surface of the chip from an artificial stone, we employed the raster electron microscope REMMA-102-02.

The content of Na₂O in a dispersive environment was determined via lixiviate based on the static method using distilled water.

5. Results of research into properties of the highly-filled cements

5.1. Cement of composition «clinker – granulated blast furnace slag»

We designed and optimized cement compositions in the system «clinker – granulated blast furnace slag – alkaline

activator – plasticizer» by selecting the maximum content of the granulated blast furnace slag. Criteria for estimation were ensuring the compressive strength not less than 40 MPa and the content of a surface-active substance and an activator not less than 5 % by weight.

We have chosen, as variable magnitudes, the content of the clinker and the density of the alkaline component solution.

Strength characteristics on day 28 of hardening are shown in Fig. 1.

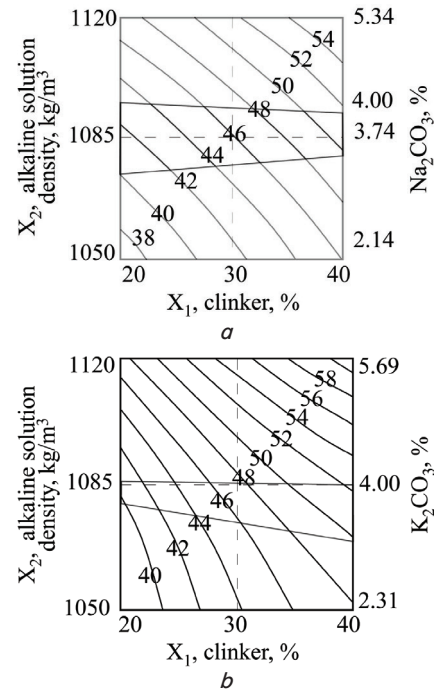


Fig. 1. Isolines of standard strength (aged 28 days) of the cement system «clinker – granulated blast furnace slag» with mobility (a standard cone) of 180–185 mm. Alkaline activator (solution): a – soda ash; b – potassium carbonate (potash)

An analysis of results revealed that in the region of the examined compositions and at a water/cement ratio of 0.40...0.42, standard flow of the cement-sand mortar (cement:sand ratio=1:3) varies in the range of 180...185 mm. In this case, compressive strength on day 28 of hardening is 38...60 MPa.

The effective action of the alkaline additive and SAS allowed us to establish the plasticizing effect, which made it possible to explore compositions with a smaller W/C ratio meeting the requirements of Ukrainian standards. For such compositions, the spread of a standard cone was no less than 135 mm. Strength characteristics of the examined cements at the values of mobility from 135...140 mm with the respective water/cement ratio from 0.35 to 0.38 are shown in Fig. 2.

Based on the obtained results, it was established that the required amount of the alkaline activator in order to achieve the strength of cement from 40 to 50 MPa is 2.13...2.35 % by weight.

Research into strength characteristics of the optimal compositions for the alkali activated cement was carried out at early (day 2, 7, 28) and later terms (day 90 and 180) of hardening (tested using the samples of a cement-sand mortar with the cement:sand ratio=1:3). The research results are given in Table 2 and Table 3.

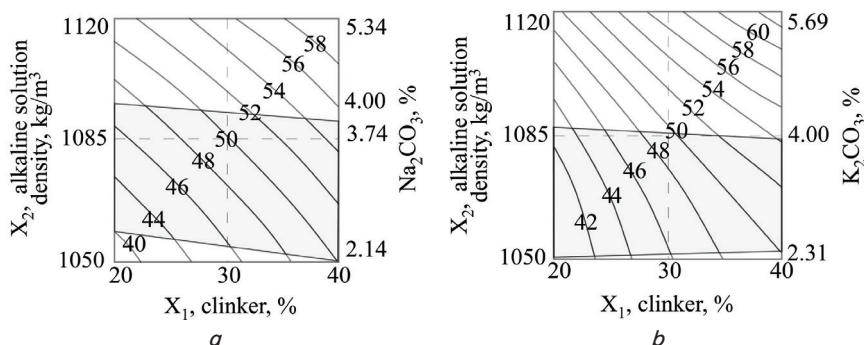


Fig. 2. Isolines for compressive strength (aged 28 days) of the system «clinker – granulated blast furnace slag» at the flow of cement-sand mortar of 135...140 mm. Alkaline activator (solution): a – soda ash; b – potash

Table 2

Strength characteristics of alkali activated cements at a mobility of the cement-sand mortar of 135...140 mm

No. of entry	Clinker by weight	GBS	Alkaline activator		Solution/Solid ratio	Compressive strength, MPa, days				
			Mean density, ρ, kg/m ³	Content of salts, % by weight		2	7	28	90	180
Alkali activated cement, class M400										
1	40	60	Na ₂ CO ₃ , 1,060	2.0	0.35	18.6	30.0	42.2	48.0	51.1
2	30	70	Na ₂ CO ₃ , 1,080	2.7	0.34	19.4	28.6	44.5	46.4	52.8
3	20	80	K ₂ CO ₃ , 1,080	3.9	0.35	15.2	27.4	41.2	44.1	45.6
Alkali activated cement, class M500										
4	40	60	Na ₂ CO ₃ , 1100	3.5	0.34	24.4	35.8	54.4	58.6	62.1
5	40	60	K ₂ CO ₃ , 1090	4.0	0.33	26.0	38.0	56.4	58.2	60.0
6	30	70	Na ₂ CO ₃ , 1120	4.2	0.33	21.8	32.4	51.4	57.2	58.8

Table 3

Strength characteristics of alkali activated cements at a mobility of the cement-sand mortar of 180...185 mm

No. of entry	Clinker by weight	GBS	Alkaline activator		Solution/Solid ratio	Compressive strength, MPa, days				
			Mean density, ρ, kg/m ³	Content of salts, % by weight		2	7	28	90	180
Alkali activated cement, class M400										
1	40	60	Na ₂ CO ₃ , 1,060	2.3	0.42	17.4	30.4	45.5	46.0	48.6
2	30	70	Na ₂ CO ₃ , 1,080	3.2	0.41	18.2	28.0	43.2	45.1	49.2
3	20	80	K ₂ CO ₃ , 1,080	4.4	0.40	14.5	23.1	43.4	46.0	46.6
Alkali activated cement, class M500										
4	40	60	Na ₂ CO ₃ , 1,100	4.1	0.40	22.4	31.8	52.5	54.6	58.2
5	30	70	K ₂ CO ₃ , 1,080	4.4	0.40	20.8	28.5	53.0	53.0	56.1
6	30	70	Na ₂ CO ₃ , 1,100	4.1	0.40	20.6	28.2	50.8	52.6	56.8

It is established that the developed cements are characterized by compressive strength (on day 28 of hardening) from 40.4 to 58.8 MPa. The early strength of cements is: on day 2 – 14.1...26 MPa, on day 7 – 20.8...38 MPa.

It was established that a change in the water/cement ratio from 0.33...0.35 to 0.4...0.42 leads to that the alkali activated cements increase mobility of the cement-sand mortar without loss of strength characteristics.

5. 2. Cement of composition «clinker – ash from thermal power plants»

Based on the results from our study, it was found that the introduction of surface-active substances (TSL in the

amount of 1 % by weight of cement) in a combination with the alkaline activator makes it possible to decrease the amount of the required water to 23...35 % and to achieve the increased strength, by 37...58 %. Research results are given in Table 4.

The replacement of soda ash with sodium metasilicate in a combination with TSL revealed the absence of the plasticizing effect, though that made it possible to maintain the terms for setting the system.

Thus, the introduction of 1 % TSL to the system «clinker – fly ash – sodium metasilicate» slows down the initial setting duration from 19 to 51 minutes without reducing the strength.

Table 4

Strength characteristics of cements containing fly ash at a mobility of the cement-sand mortar of 110...140 mm

No. of entry	Basic components, % by weight		TSL, % by weight	Alkaline activator		Solution/Solid ratio flow, mm	Compressive strength, MPa, days			
	Clinker	Ash		Mean density, ρ, kg/m ³	Content of salt, % by weight		7	28	90	t, °C
Cement containing disposed ash										
1	40	60	–	Na ₂ CO ₃ , 1,060	2.12	0.44 110	13.8	28.5	50.0	41.7
2	40	60	1		1.72	0.38 135	21.0	43.8	68.5	57.4
3	40	60	–	K ₂ CO ₃ , 1,060	2.50	0.43 112	17.8	30.5	57.8	48.0
4	40	60	1		2.00	0.37 140	26.5	46.2	70.9	66.0
5	40	60	–	water	–	0.43 108	7.1	17.8	33.9	30.4
Cements containing fly ash										
6	40	60	–	Na ₂ CO ₃ , 1,120	4.20	0.43 112	17.5	31.5	53.9	47.9
7	40	60	1		2.73	0.36 136	23.7	42.8	70.5	65.9
8	40	60	–	Na ₂ SiO ₃ , 1,120	3.50	0.34 116	16.0	34.2	62.9	56.2
9	40	60	1		3.42	0.33 138	25.5	55.9	63.8	58.9
10	40	60	–	water	–	0.40 114	7.2	19.0	40.6	37.3

5. 3. Cement of composition «clinker – granulated blast furnace slag – fly ash»

The content of clinker in the examined systems varies within 10–30 % by weight, of slag – 10–40 % by weight, of fly ash – 45–60 % by weight. We used, as an alkaline activator, soda ash (Na₂CO₃) in the amount of 3.8 % by weight (exceeding 100 % of the total system).

The content of the supplement-plasticizer was used 0.8 % by weight (exceeding 100 % of the total system).

All components were put in a mixer in a dry form followed by the addition of water and standard sand. Test results are given in Table 5.

Table 5

Physical-mechanical characteristics of the designed cements, the system «clinker – granulated blast furnace slag – fly ash»

No. of entry	Cement composition, % by weight			W/C	Compression/bend strength, MPa, aged, days		
	Clinker	GBS	Fly ash		3	7	28
1	30	30	40	0.38	26.4/6.8	45.0/8.1	52.5/8.7
2	30	10	60	0.39	25.1/6.8	29.2/7.1	40.2/7.8
3	18	20	62	0.40	25.5/6.8	29.1/7.0	41.0/7.9
4	8	30	62	0.40	21.0/5.8	26.3/5.9	39.2/6.1
5	30	20	50	0.40	26.0/6.9	31.5/7.1	41.5/7.5
6	20	30	50	0.39	25.4/6.9	29.4/6.9	40.2/7.3
7	10	40	50	0.39	22.7/6.1	27.3/6.2	39.7/6.5

Based on an analysis of the results, it was revealed that the decisive role for the strength characteristics on day 28 day of hardening belongs to the content of ash in cement.

At a constant content of ash, special attention is to be paid to the content of clinker and granulated blast furnace slag in cement, which affects the early high strength.

5. 4. Cement of composition «clinker – granulated blast furnace slag – red mud»

We investigated the possibility of obtaining the cements that would contain red mud as one of the main components (up to 60 % by weight) using liquid glass with a silicate module of 2.8 and the meant density of 1,250 to 1,400 kg/m³. The obtained cements are characterized by high brand strength (aged 28 days) at compression to 47.5 MPa. It should be noted that in the absence of granulated blast furnace slag in the system and at the content of red mud to 70 % by weight, the strength of cements is up to 29 MPa. That makes it possible to reduce the consumption of granulated blast furnace slag and to decrease the clinker content in the system. The results obtained are given in Table 6.

Table 6

Strength characteristics of the alkali activated cement containing red mud

No. of entry	Cement composition, % by weight			Liquid glass, Mb=2.8	Solution/Solid ratio	Compressive strength, MPa, aged, days		
	Red mud	GBS	Clinker			3	7	28
1	60	30	10	ρ=1,400 kg/m ³	0.33	17.5	27.5	47.5
2	60	30	10	ρ=1,350 kg/m ³	0.35	11.2	17.5	36.2
3	60	30	10	ρ=1,300 kg/m ³	0.35	7.5	8.75	25.0
4	60	30	10	ρ=1,250 kg/m ³	0.37	2.5	22.5	40.0
5	70	–	30	ρ=1,300 kg/m ³	0.45	3.1	14.3	29.0

A change in the density of liquid glass makes it possible not only to adjust the duration of cement setting, but also change viscosity of the system, which improves the workability of the mixture.

5. 5. Patterns of hydration of the alkali activated cement

In the course of this work we examined the processes of heat release that occur during hydration of cement and depend on the rate of the structure formation processes (Fig. 3–6). The heat evolution during hydration of the system «clinker – granulated blast furnace slag – soda ash» is illustrated in Fig. 3.

Since the maximum value of heat release is measured during early terms of the systems hardening (over the first 3 days), it is possible then in this period to determine the orientation of the initial hydration process and characteristics of the basic component of cement. In this case, it is important to highlight the processes, dominated by reactions of slag hydration at a temperature peak after 27 hours, which are characteristic of a given system. The peak in 47 hours indicates the onset of processes of structure formation of hydrated clinker and the structure formation of the stone.

Heat evolution during hydration processes in the system «clinker – fly ash – soda ash» is illustrated in Fig. 2.

Further research into processes of heat evolution was carried out at the content of clinker up to 15 % by weight of cement in the system «clinker – granulated blast furnace slag – fly ash – soda ash». It was established that the obtained cements are represented by a rather low exothermia. Research results are shown in Fig. 5.

It was determined by thermodynamic calculations [20] that the main characteristics of initial phases define the basicity of hydration products and the values of heat evolution during hydration. Thus, reducing the number of Ca²⁺ ions and the ratio of CaO/SiO₂ and CaO/Al₂O₃ in the groups of silicates and calcium aluminate reduces the value of heat evolution, which is also confirmed by the results from practical studies (Fig. 6). The high basicity of the cements containing clinker is due to the formation of Ca(OH)₂, the high-base hydro calcium hydro silicates and calcium hydro aluminates at the initial stages of hardening the systems. The formation of such compounds predetermines the high heat evolution, which can reach 750.850 kJ/kg [26].

In the cements containing active silica and Al-containing mineral additives, owing to the reduced basicity of the disperse phase during alkaline activation, there is an acceleration in the formation of low-base compounds and alkaline hydro aluminosilicates. The heat required for their formation is

lower compared to the heat needed for the formation of high-base hydrates. Therefore, the values of heat release for alkali activated cements containing mineral additives are less than those for the heat release of portland cement. These values vary about 350.600 kJ/kg.

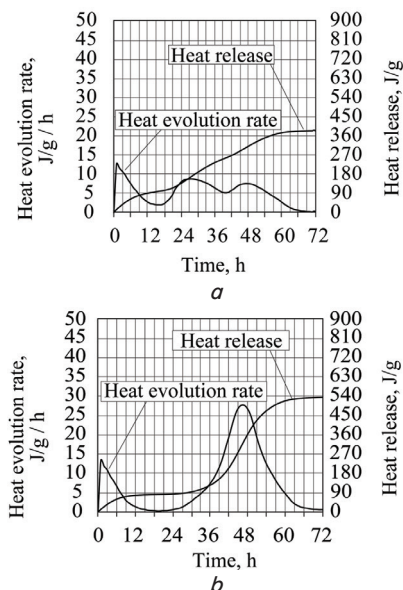


Fig. 3. Heat evolution during hydration of cement (the system «clinker – granulated blast furnace slag – soda ash»). The content of slag in the system: a – 90 % by weight, b – 60 % by weight

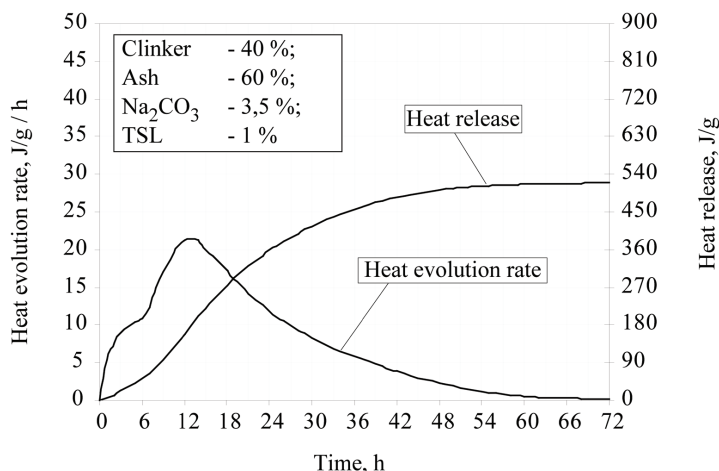


Fig. 4. Heat evolution during hydration of the system «clinker – fly ash – soda ash»

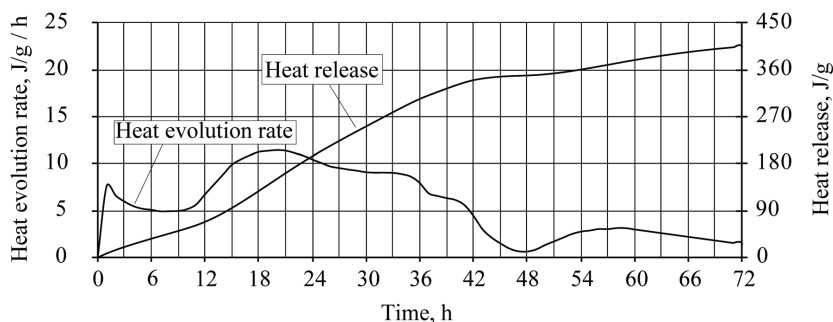


Fig. 5. Heat evolution during hydration of the system «clinker – granulated blast furnace slag – fly ash – soda ash»

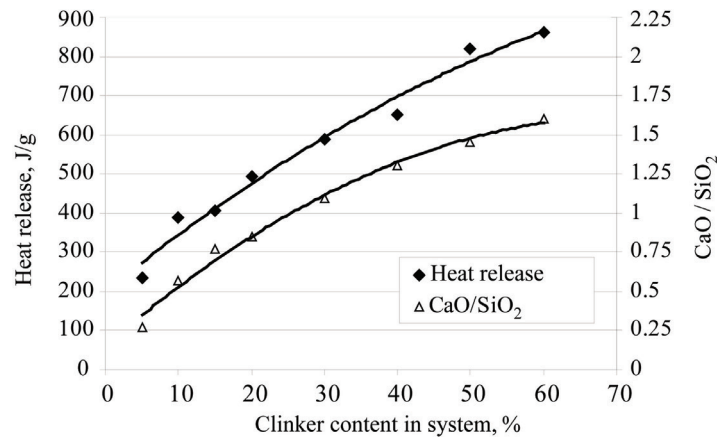


Fig. 6. Relationship between the content of clinker in a cement system, heat evolution of alkali portland cement and the basicity of hydration products

The low-base hydro silicates and alkaline hydro aluminosilicates are mostly formed in the alkali activated cements during hardening. The values of heat evolution are lower than 200.250 kJ/kg.

The intensity and completeness of heat release during hydration process is typically decreased with a decrease in basicity. The values of heat evolution after the first exothermal peak, caused by the wetting of cement powder with a mixing liquid, varies within 50...60 J/g for the cement systems containing 60 % of clinker. This indicator is reduced to 18...20 J/g for the cements containing 10...15 % of clinker. The duration of induction period increased from 6.9 hours for the cement compositions containing 50...60 % of clinker to 30...35 hours for the cements containing 5...15 % of clinker. The logical relationship between the basicity of cement and the value of the second exothermal peak is explained by the formation of hydration products of the crystalline structure. A reduction in basicity is accompanied by a decrease in the value of the second exothermal peak at 360...410 J/g for the cement compositions containing 40...60 % of clinker to 170...280 J/g for the cements containing 10...15 % of clinker. Therefore, the completeness of the process of heat evolution over 72 hours typically reduces governed by the following sequence: portland cement – slag portland cement – alkali activated cement.

Next, we carried out comparative tests of the fine-grain concretes based on the alkali activated slag portland cement (AASOPC) with a clinker content of 40, 30 and 15 %, and conventional slag portland cement (SOPC) in terms of porosity and strength. Research results are shown in Fig. 7, Fig. 8.

It was established that the capillary saturation of samples of the alkali activated slag portland cement containing 15, 30, and 40 % of clinker after 4.5 hours is 4.2 %, 5.4 %, and 6.04 %, respectively; while the slag portland cement containing 40 % of clinker corresponds to 6.32 %. In this case, important is not only the resulting value for saturation in water, but the character (that is, rate) of water saturation. Rapid water saturation of samples of traditional slag portland cement is explained by the large number of open macropores, while the character of saturation for the alkali activated slag portland cement samples showed that the ratio of macro- and micropores shifted towards micropores and conditionally closed

pores. This indicates the denser and impermeable structure of composites, which positively affects the performance and durability of concretes.

In accordance with the results shown in Fig. 8, the lower basicity of the cement, the lower the value of the initial porosity and the more intense the process of pore closing over time.

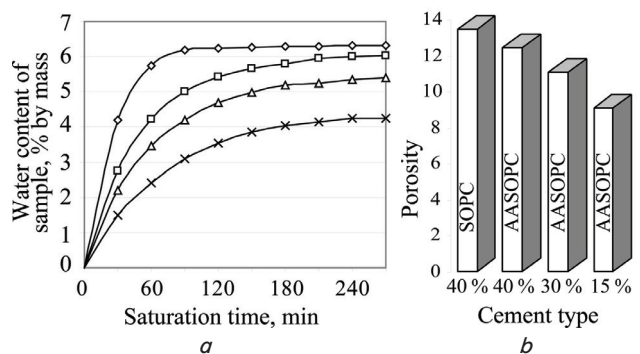


Fig. 7. Characteristic of a porous structure of samples with a different content of clinker at the age of 28 days: a – kinetics of capillary saturation, b – porosity

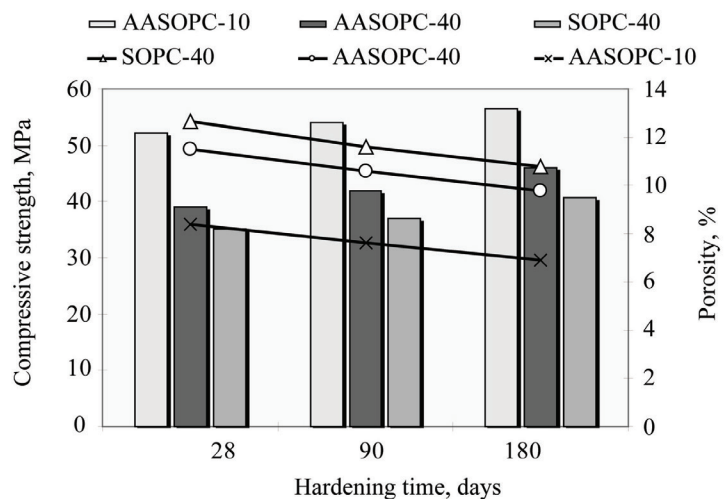


Fig. 8. Development of strength and porosity of artificial stone with a different content of clinker

5.6. The role of alkalis in the process of structure formation of artificial stone of the alkali activated cement

The introduction to the composition of cement of compounds of alkali metals in the amount greater than that required, according to the principles of compositional arrangement of traditional cements based on compounds of calcium and magnesium, allows us to argue that the compounds of alkali metals are not only the activators of hardening, but they also act as self-functioning components of the cement system $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, basic structure-forming products of low-base calcium hydrosilicates and zeolite-like new formations (where $\text{Me}_2\text{O}_3-\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$). Images of the surface of the chip from an artificial stone are shown in Fig. 9.

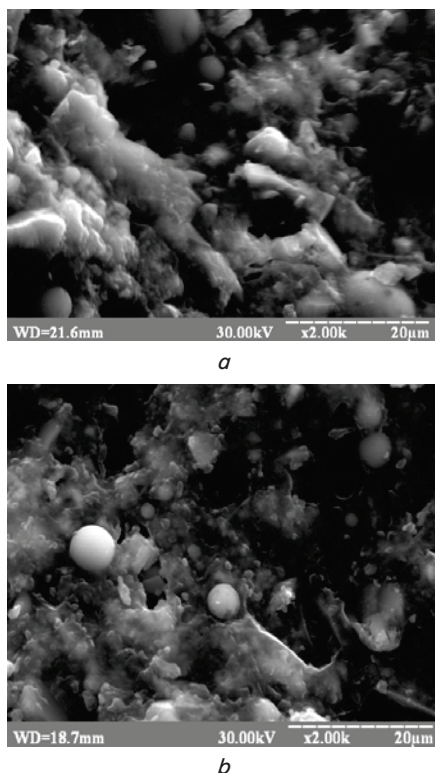
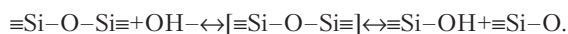


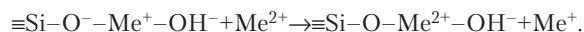
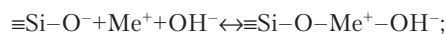
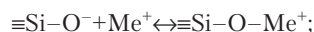
Fig. 9. Images of the surface of the chip from a cement stone during hardening of the system «clinker – granulated blast furnace slag – fly ash – soda ash». Age: *a* – 28 days; *b* – 180 days

Because of the low basicity of a solid phase, it is impossible that the hydration process should proceed at the expense of protonation of ionic bonds $\text{Me}^{2+}-\text{O}$. That is why it was hypothesized [4] that under conditions of a highly-alkaline environment there is a destruction of the aluminosilicate frame via the break of covalent bonds $\text{Si}-\text{O}-\text{Si}$, $\text{Me}^{3+}-\text{O}-\text{Me}^{3+}$, $\text{Si}-\text{O}-\text{Me}^{3+}$ in line with the following rule:

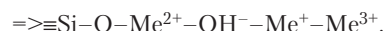


$\equiv\text{Si}-\text{O}^-$ anions can participate in the inverse reaction of poly-condensation. However, in the presence of alkali metals (Me^+ anions) this process does not occur because they neutralize $\equiv\text{Si}-\text{O}^-$ anions. We established the occurrence of bonds of type $\equiv\text{Si}-\text{O}-\text{Me}^+$, preventing the inverse reaction of forming the siloxane connections. $\equiv\text{Si}-\text{O}^-$ anions leave the reaction with subsequent conversion into the colloidal phase. Over time, the resulting alkaline silicates may enter

the cation-exchanging reactions with Me^{2+} ions in line with the following:



This assumption was confirmed by studying the curve that acquires a wave-like character (Fig. 10), continuously linking the alkaline oxide with the available amphoteric oxide Me^{3+} , which leads to the formation of insoluble compounds in line with the following pathway:



Thus, at the initial stage of hydration (dispersion) of cement the alkaline cation acts as a catalyst that retains the ionic strength of the liquid phase, which is necessary for destroying strong covalent bonds, and is involved in transforming the products of destruction during colloid phase.

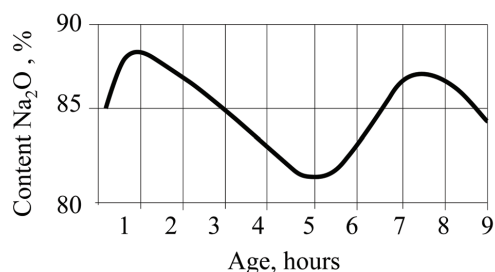


Fig. 10. The content of Na_2O in a disperse medium of the system «C-A-S glass + NaOH» over time

It was established that the accumulation of products of destruction caused by the adsorption and chemical dispersion of the solid phase creates the retaining state for the formation of a dispersion-coagulation structure, in which the processes of poly-condensation develop.

A decisive role in the formation of a condensation structure belongs to the Ca^{2+} cations that are able to interact with the silicon and aluminum-sols and participate in solid-phase reactions through a cation exchange with the alkaline cations of type Me^+ . It was established that the amount of an alkaline activator affects this process, as well as the composition and stability of phases of hydration products in the resulting composition. According to [3], phase composition is represented by $\text{Ca}(\text{OH})_2-\text{SiO}_2-\text{H}_2\text{O}-\text{NaOH}$ with molar ratio $\text{Ca}(\text{OH})_2/\text{SiO}_2=1$:

(I) at $\text{NaOH}/\text{SiO}_2 < 1$, tobermorite 1.13 nm with the degree of condensation of siloxo anions in the intermediate state between the chain and semi linked;

(II) at $\text{NaOH}/\text{SiO}_2 = 1-5$ – tobermorite with the chains of silica anions;

(III) at $\text{NaOH}/\text{SiO}_2 > 5$ – sodium-substituted tobermorite – NaCaHSiO_4 with isolated orthoanions.

Starting from a certain moment, the development of strength is accompanied by a decrease in the value of pH of the liquid phase. This can be explained by its interaction with

the products of destruction of the solid phase with the formation of stable zeolite-like hydro silicates with an alkaline or alkaline earth composition, which have lower solubility compared with the products of hydration of a portland cement stone.

At the early stages of hydration and hardening (for example, the alkali activated slag portland cement) the formation of a structure is primarily predetermined by the formation and crystallization of low-base hydro silicates and hydro garnets. The alkaline or alkaline earth hydro aluminosilicates, due to their slow crystallization, are formed at the later stages of hardening. The formation of such structures is mainly predetermined in a pore space, resulting in that they fill it and promote the strengthening of crystallization contacts with primary phases, as well as initiate the formation of a more homogeneous and dense structure. In addition, a high value of pH environment in which the process of hydration proceeds terminates the transition of calcium ions into solution, which explains the absence of $\text{Ca}(\text{OH})_2$; thus, the obtained calcium hydrosilicates typically have the basicity of less than 1. Thus, the phase composition of new formations of the alkali activated slag portland cement is represented mainly by tobermorite-like low-base calcium hydro silicates, hydro garnets of different composition, the alkaline hydro aluminosilicates from the group of zeolites and mica. There is also the presence of alkaline and alkaline earth compounds, which are less soluble in comparison with the high-base minerals and are stable as a result of low basicity. This implies ensuring the stability and durability of cement stone over time not only under normal operating conditions, but also under the corrosive impact of various aggressive environments. High performance properties of artificial stone of the alkali activated cement can be explained not only by its more perfect phase composition of new formations, but also by more sophisticated parameters of its structure (Fig. 9).

6. Discussion of results of studying the development of compositions and studying the properties of alkali activated highly-filled cements

The research results extend and complement the principles of compositional arrangement of alkali activated cements with a clinker content not exceeding 40 % by weight of cement. The developed cements are characterized by a rapid acquisition of strength over early terms (2...7 days), 14...38 MPa, and by the high strength on day 28 of hardening, 40...54 MPa. Such characteristics significantly distinguish the designed materials from analogs (traditional slag portland cement). The results of research into the system «clinker – granulated blast furnace slag» help determine the formulation of compositions according to the Ukrainian and European standards regarding the content of basic and additionally introduced components of cement. The systems containing clinker in the amount from 20 to 40 % by weight of cement, and at the content of additional components, specifically an alkaline activator, not exceeding 4 % by weight of the basic components of the alkali activated cement, match the strength classes M400 (according to the EN standard, class 32,5N) and M500 (according to the EN standard, class 42,5R). The obtained results make it possible to conclude that given the increased content of an alkaline activator (5...6 % by weight) the cements meet the requirements of Ukrainian standard for compressive strength at the age of

28 days for classes M550...600 (according to the EN standard, class 52,5N – 52,5R).

The results obtained are due to the combined use of the alkaline component and surface-active substances, which can increase the hydraulic activity of clinker-free components of cement through the alkaline activation and a decrease in water consumption for the cement-sand mortar via a significant plasticizing effect provided by the surface-active substance from the group of lignosulphonates. Thus, the system «clinker – granulated blast furnace slag – alkaline activator – plasticizer» confirmed the possibility of obtaining cements for general building purposes of grades M400 and M500 in line with DSTU B V.2.7-46.

The results obtained in the study of the system «clinker – ash from thermal power plants» give grounds to conclude that the obtained cements reach the strength on day 28 of hardening of 43...55 MPa, after steaming – 41...66 MPa, after 90 days – 57...66 MPa. The content of the alkaline activator in recalculation for dry salt is 1.72...4.2 % by weight and when recalculated for R_2O – 1.01...2.5 % by weight, which meets the requirements of Ukrainian and European standards for the content of additional components (up to 5 % by weight).

The study into process of heat release by the alkali activated cement leads to the conclusion that a decrease in the basicity of new formations in the composition of cement helps reduce the indicators of heat release, as well as predetermines an increase in the rate of closing the pores and improves the strength of systems over time.

At the early stages, the compounds of alkali metals activate the process of destruction of the solid phase, which leads to the formation of low-base calcium hydro silicates. At the later stages they participate in the formation of compounds similar to natural zeolites.

Our findings show the possibility of industrial use of the highly-filled alkali activated cements, which in terms of their characteristics are not inferior to traditional analogs. However, this study covers the alkali activated portland cement when using mostly the alkaline activator in the form of a solution, which somewhat complicates the technological process of manufacturing cements and concretes based on them. That is why the further research could address the possibility of employing an alkaline activator in the form of a dry salt of alkali metals (soda ash and sodium metasilicate) and their combinations. That would simplify the process of making cement, its application, and change its technological properties (workability, terms of setting, etc.). The designed cements require further study into the properties of concretes and composite materials based on them.

The proposed field of research makes it possible not only to solve engineering tasks on obtaining cements for general building purposes, but also resolves environmental issues related to the disposal of large industrial waste and production of low-energy cements.

7. Conclusions

1. We show the possibility of obtaining cements for general building purposes with a degree of filling by the related industrial products and industrial waste within 60...95 % by weight of cement. We studied physical-mechanical characteristics of cements in the examined systems and demonstrated that the system «portland cement clinker – granulated

blast furnace slag» has a strength at compression that reaches values of 40.4...58.8 MPa; the system «portland cement clinker – fly ash» – 30.4...58.9 MP; the system «portland cement clinker – granulated blast furnace slag – fly ash from TTP» – 39.2...52.5 MPa; the system «portland cement clinker – granulated blast furnace slag – red mud» – 25...47.5 MPa.

2. We studied processes of heat release in the examined systems and established that the heat release of cement decreases with a decrease in the basicity of cement, which is predetermined by the processes of structure formation of artificial stone, namely, the formation of low-base calcium hydro silicates and zeolite-like new formations. We investigated the porosity of a fine-grain concrete based on the alkali activated slag portland cement and found that the ratio of

macro- and micropores shifted to the side of micropores and conditionally closed pores, which exerts a positive effect on the performance indicators of artificial stone.

3. We studied the role of the alkaline activator in the processes of structure formation of the alkali activated cements at a significant content of related industrial products and found that an increase in the alkalinity of a cement environment leads to a decrease in the basicity of calcium hydro silicates in the structure (to values less than 1). Thus, the phase composition of new formations in the alkali activated slag portland cement is represented mainly by tobermorite-like low-base calcium hydrosilicates, hydro garnets of different composition, alkaline hydro aluminosilicates from the group of zeolites and mica.

References

1. Malhotra V. M. High-Performance High-Volume Fly Ash Concrete // *Concrete International*. 2002. Vol. 24, Issue 7. P. 30–34.
2. Babaevskaia T. V. Chemical and mineral additives of the Relaxol system // *Building materials and articles*. 2005. Issue 3. P. 36–37.
3. Specific features of the compositional build-up of the Portland cements with High contents of mineral additives / Krivenko P. V., Petropavlovskii O. N., Gelevera A. G., Gots V. I., Rostovskaya G. S. // *Building materials*. 2005. Issue 7. P. 2–8.
4. Runova R. F., Kochevykh M. A. The alkaline modification of the composite cements // *Alkaline Cements and Concretes: Proceed. 2nd Int. Conference*. Kyiv, 1999. P. 357–365.
5. Alkali-Activated Mortars for Sustainable Building Solutions: Effect of Binder Composition on Technical Performance / Attanasio A., Pascali L., Tarantino V., Arena W., Largo A. // *Environments*. 2018. Vol. 5, Issue 3. P. 35. doi: <https://doi.org/10.3390/environments5030035>
6. Rathod R. R., Suryawanshi N. T., Memade P. D. Evaluation of the properties of Red Mud Concrete // *IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE)*. 2013. P. 31–34.
7. Ashok P., Sureshkumar M. P. Experimental Studies on Concrete Utilising Red Mud as a Partial Replacement of Cement With Hydrated Lime // *IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE)*. 2013. P. 1–10.
8. Shetty K. K., Nayak G., Vijayan V. Effect of red mud and iron ore tailings on the strength of self-compacting concrete // *European Scientific Journal*. 2014. Vol. 10, Issue 21. P. 168–176.
9. Pan Z. H., Feng Y., Yang N. R. Study on solid alkali- slag-red mud cementitious material // *J. Nanjing Univ. Chem. Technol.* 1998. Vol. 20, Issue 2. P. 34–38.
10. Pan Z. H., Feng Y., Yang N. R. Development of alkali- slag- red mud cement // *J. Chin. Ceram. Soc.* 1999. Vol. 18, Issue 3. P. 34–39.
11. Pan Z. H. Alkali activated slag– red mud cementitious material: thesis of Doctor of Engineering. Nanjing University of Chem. Tech. Nanjing, China, 2011.
12. Alkali-slag-red mud cement / Pan Z. H., Feng Y., Lu Y. N., Yang N. R. // *Cem. Eng.* 2000. Vol. 1. P. 53–56.
13. Hydration products of alkali-activated slag–red mud cementitious material / Pan Z., Cheng L., Lu Y., Yang N. // *Cement and Concrete Research*. 2002. Vol. 32, Issue 3. P. 357–362. doi: [https://doi.org/10.1016/s0008-8846\(01\)00683-4](https://doi.org/10.1016/s0008-8846(01)00683-4)
14. Pu X. C., Gan C. C., Wu L. Properties of alkali– slag cement concrete // *J. Chin. Ceram. Soc.* 1989. Vol. 5. P. 5–10.
15. Radiological characterization and evaluation of high volume bauxite residue alkali activated concretes / Croymans T., Schroyers W., Krivenko P., Kovalchuk O., Pasko A., Hult M. et. al. // *Journal of Environmental Radioactivity*. 2017. Vol. 168. P. 21–29. doi: <https://doi.org/10.1016/j.jenvrad.2016.08.013>
16. Development of alkali activated cements and concrete mixture design with high volumes of red mud / Krivenko P., Kovalchuk O., Pasko A., Croymans T., Hult M., Lutter G. et. al. // *Construction and Building Materials*. 2017. Vol. 151. P. 819–826. doi: <https://doi.org/10.1016/j.conbuildmat.2017.06.031>
17. Radioactivity and Pb and Ni immobilization in SCM-bearing alkali-activated matrices / Alonso M. M., Pasko A., Gascó C., Suarez J. A., Kovalchuk O., Krivenko P., Puertas F. // *Construction and Building Materials*. 2018. Vol. 159. P. 745–754. doi: <https://doi.org/10.1016/j.conbuildmat.2017.11.119>
18. Krivenko P., Kovalchuk O., Pasko A. Utilization of Industrial Waste Water Treatment Residues in Alkali Activated Cement and Concretes // *Key Engineering Materials*. 2018. Vol. 761. P. 35–38. doi: <https://doi.org/10.4028/www.scientific.net/kem.761.35>
19. Applicability of alkali-activated cement for immobilization of low-level radioactive waste in ion-exchange resins / Kryvenko P., Hailin C., Petropavlovskiy O., Weng L., Kovalchuk O. // *Eastern-European Journal of Enterprise Technologies*. 2016. Vol. 1, Issue 6 (79). P. 40–45. doi: <https://doi.org/10.15587/1729-4061.2016.59489>
20. Usharov-Marshak A. V. Calorimetry of cement and concrete. Kharkiv: Fact, 2002. 183 p.