Kovalchuk, Oleksandr; Zozulynets, Viktoriia

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Oleksandr Kovalchuk,
Viktoriia Zozulynets

DEVELOPMENT OF ALKALINE CONCRETE ON THE BASIS OF ACTIVE AGGREGATES

The object of the research is the process of directed structure formation in the body of alkaline concrete, made using a reactive aggregate, in this case, basalt, and the process of deformation development in such concrete. The problem with using reactive aggregates is that they cause alkaline corrosion. It manifests itself in the form of cracks and layers of gel-like substances that form at the point of contact of the aggregate with the cement stone.

During the research, methods of physical and chemical analysis were used (X-ray phase, differential thermal and thermogravimetric analyzes, electron microscopy, infrared spectroscopy, microprobe analysis). And also methods of mathematical planning of experiments have been used for the dependence of the physical and technical properties of cements and the directions of their structure formation. Also, the research has been carried out based on the analysis of world achievements in solving the problem of alkaline corrosion of concrete.

The possibility of joint operation of the matrix of alkaline cements and active aggregates, represented by basalt, has been determined. The component composition of alkaline cement has been optimized and the need to increase the amount of the alkaline component in the system for the normal course of structure formation processes has been proved. The study of the influence of technical factors and conditions of hardening on the development of processes of structure formation of the investigated compositions has been carried out. The deformation properties of fine-grained concrete based on slag-alkaline cement and basalt aggregate have been investigated. It is shown that the expansion deformations of the samples, which accompany the process of alkaline corrosion of the aggregate in concrete, are directly related to the component composition and hardening conditions of the material.

The obtained research results confirm the possibility of using active aggregates for the manufacture of building materials, in particular, based on alkaline cements. But for the safe course of the processes of structure formation, the component composition of the system has to be adjusted by introducing an active mineral additive and an additional alkaline component. The use of hydrophobizing additives makes it possible to increase the strength of the material even when operating under normal heat and humidity conditions.

Keywords: *alkaline cement, alkaline concrete, reactive aggregate, alkaline aggregate corrosion, alkalinity index (pH).*

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1. Introduction

With the development of industry and social adaptation to environmental changes, the demand for building materials with better physical and mechanical properties in comparison with analog, long-existing products of the construction industry is growing. Creation of new materials and modification of existing key stages of solving this problem. However, another possible option is the development of technologies that allow the use of materials that, for one reason or another, were irrational or unusable.

An excellent example of this is the use of reactive aggregates. Usually they are limited or not used at all in the production of building materials, because they are the cause of alkaline corrosion. It manifests itself in the form of cracks and interlayers of gel-like substances formed at the point of contact of the aggregate with the cement stone.

Alkaline corrosion contributes to the emergence and development of destructive processes in the body of concrete, which significantly reduces its strength, frost-resistant, waterproof, and, accordingly, durability. This occurs through the interaction of cement alkalis and active silica. The products of this reaction significantly increase in volume, due to which internal stresses arise and the material is destroyed. However, the solution to such a problem is possible by rational selection of the percentage of the component composition of the system, as well as by directed control of the structure and properties of such materials.

The implementation of this issue will significantly expand the raw material base for the production of building materials. In particular, this applies to concrete products and structures. And this, in turn, will increase the quantity and improve the quality of the products of the construction complex, which will certainly have a positive effect on economic indicators.

2. The object of research and its technological audit

The object of research is the process of directed structure formation in the body of alkaline concrete, made using a reactive aggregate in this case, basalt, and the process of deformation development in such concrete.

Also, a detailed analysis requires the study of the basic laws of the development of alkaline corrosion of concretes based on traditional cement (Portland cement) and alkaline cements, because they differ significantly from each other.

Studies of the processes of alkaline corrosion in alkaline concretes were studied mainly for systems using an alkaline component in the form of an alkaline solution. In modern conditions, maximum attention is paid to the development of cements and concretes using an alkaline component in the form of dry salt. And the corrosion processes of such systems have not yet been studied.

3. The aim and objectives of research

The aim of research is to develop applied and technological solutions to prevent and counteract alkaline corrosion of concrete.

Among the main objectives of the research are the following:

1. Investigate the properties of concrete using reactive aggregates.
2. Make adjustments to the composition of the concrete mix.
3. Investigate the shrinkage/expansion deformation of alkaline concrete using an active aggregate.
4. To study the influence of technical and technological factors of preparation and placement of concrete mixture on the development of alkaline corrosion of artificial stone.

4. Research of existing solutions to the problem

The solution to this issue is promising for the development of the construction industry all over the world. That is why many specialists have studied the solution to the problem of alkaline corrosion. An analysis of the results of their research allows to highlight the following aspects that are important for further research.

The search for ways to increase the durability and efficiency of compositions based on cement, mineral fibers and other alkaline-reaction aggregates is carried out mainly in the following main directions:

– development of new types of low-alkaline Portland cements and various methods of modification of Portland cements for binding active calcium oxide;
– coating of glassy fibers with protective compounds that protect them from the influence of the alkaline environment of the hardening cement stone;
– development of alkali-resistant fibers and fillers;
– use of new effective binders, in particular, alkaline binders (slag-alkaline, alkaline Portland cements, alkaline aluminosilicate bonds, etc.) with a hydration mechanism fundamentally different from Portland cement and a set of synthesized hydrate formations.

The choice of binders for the preparation of fiber cement compositions is directly related to the issues of their durability and economy.

First, one of the ways to reduce the alkalinity of cements and increase the stability of alkaline-reaction aggregates in the composition is the introduction into the composition of active mineral additives that bind active lime. These include: amorphous microsilica, metakaolin, fly ash, tripoli, diatomite, crushed expanded perlite, pumice and polymer additives [1, 2]. So, according to the data [3, 4], the introduction of microsilica and metakaolin additives into Portland cement made it possible to slightly increase the resistance of the fiberglass of the cement matrix. It was shown that in the control specimens of the samples, complete degradation of fibers occurred between 28 and 56 days during storage of the samples in water with a temperature of 65 °C, while in the samples with the addition of metakaolin and microsilica complete degradation of fibers under the same storage conditions for 6 to 12 months. Although, as is known [5] and as noted above, there are opposite data on an increase in the corrosive expansion of concrete on Portland cement when finely dispersed active silica is introduced into its composition.

In accordance with [6], in order to exclude the expansion of concrete due to the interaction of alkalis of Portland cement with silica of the aggregate, it is proposed to carbonize concrete by injecting gaseous CO_2, using a saturated solution of CO_2 or solid carbon dioxide in the process of preparing concrete. The amount of CO_2 should be 0.05–0.23 kg per 1 kg of C_3S contained in the cement. A side undesirable effect of the method is a decrease in the total pH of concrete and, as a result, a decrease in protective functions in relation to steel reinforcement.

The introduction of additives of lithium compounds is considered to be an effective way of regulating the expansion deformations of concrete due to the interaction between the aggregate and the alkaline medium of the cement stone [7, 8]. Lithium compounds can be introduced both at the stage of cement production into the raw charge and during the preparation of the concrete mixture. But due to the scarcity of these compounds, the method has not been widely used.

There are also known methods of preventing the development of corrosion when the process has already begun – it can be the treatment of the concrete surface with solutions of $Ba(OH)_2$, LiCl, $Na_2O \cdot mSiO_2 \cdot nH_2O$ [9].

In a number of cases [10, 11], there are no or almost no expansion deformations in concrete, although the filler used is quite active alkaline-reaction. Studies of the structure of concrete have shown that this is due to the high porosity of aggregates, the pores in which play the role of a buffer space for the alkaline silica gel formed.

Analyzing the scientific results and achievements of numerous researchers in the field of studying the alkaline corrosion of concrete, it can be noted that most of them are aimed precisely at the issue of modifying the formulation of cements and concrete mixtures. The aim of their research is to level the real threat of the alkaline reaction of the active aggregate. That is, when modeling processes, it is already known in advance that such negative dynamics will be present in the processes of structure formation, and attempts are made to level these harmful processes at the recipe level. This is quite important knowledge, which, however, does not sufficiently meet the problems of the industry, since the use of aggregates containing active ingredients is limited at the level of standards. And such aggregates are deliberately almost never used in the production of concrete mixtures and structures.

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5. Methods of research

During the research, the following was used:
– methods of physical and chemical analysis (X-ray phase, differential thermal and thermograviometric analyzes, electron microscopy, infrared spectroscopy, microprobe analysis);
– methods of mathematical planning of experiments on the dependence of the physical and technical properties of cements and the directions of their structure formation.

The specific surface area of the raw materials and finished cements was determined by the Blaine device (Germany) in accordance with DSTU B V.2.7-188.

The determination of the technological characteristics of the cement paste (dough of normal density, setting time) was carried out according to DSTU B V.2.7-185.

The physical and mechanical characteristics of cement-sand mortars were determined according to DSTU B V.2.7-181 and DSTU B V.2.7-187 on samples of prisms with a size of 160×40×40 mm made of cement-sand mortar in an IP-100 hydraulic press (Russia).

The system alkalinity (pH) was determined after 1, 2, 3, 4, 5 and 24 hours of curing by measuring the characteristics of a 10 % aqueous extract on a PL-700al pH meter (Taiwan) (pH/ORP/Conductivity/TDS/Salt/DO/Temp).

Optimization of recipe solutions was carried out using the methods of mathematical planning of the experiment. The calculations were performed in the STATISTICA software environment and Microsoft Office Excel.

The study of the shrinkage deformations of cements was determined in a cement-sand mortar of beams 4×4×16 cm according to the Giprocement method. Sample measurements were performed on days 8, 14 and 28 of curing.

The radiological properties of the artificial stone were determined using high-frequency germanium detectors from CANBERRA (USA).

Investigations of the shrinkage deformations of alkaline concretes were carried out in bulk: the samples were made from a cement-sand mortar in a ratio of 1:2.25 in accordance with DSTU B V.2.7-185 on a planetary mixer of the Hobart type (Germany). The tests of the samples were carried out in accordance with the recommendations of DSTU B V.2.7-181. The beams were removed from the molds after 2 days and placed for further curing in a water seal, as well as thermostats with a temperature of 20, 38, and 65 °C and a relative humidity of about 100 %.

Self-deformations were determined on specimens-beams 2.5×2.5×25.4 cm with the above ratio «binder: filler». Measurement of linear deformations was carried out on a device with a dial indicator IP-04 (Russia) with a division price of 0.01 mm. The baseline measurement was performed 2 days later (immediately after the samples were removed from the mold) from the moment the samples were formed. Subsequently, the indicators were taken in accordance with the test schedule for the samples.

According to the methodology for studying the effect of storage conditions, samples of fine-grained concrete using slag-alkaline cement were kept under normal conditions (20±2 °C and relative humidity 95±5 %) until the manifestation of expansion deformations.

6. Research results

6.1. Study of the influence of the alkaline component on the change in the alkalinity of the system. The studies carried out show that the use of active aggregates can significantly complicate or stop the processes of structure formation of one-component cements using active aggregates (for example, basalt). Thus, it has been established that the usual alkali content in such systems is insufficient for the normal course of the processes of structure formation, and the total alkalinity of the system already decreases in the initial period and subsequently has a steady tendency to decrease.

To determine the optimal content of the alkaline component in a one-component cement system using an active filler, LTsEM-1 alkaline cement according to DSTU B V.2.7-181 was used, into which an alkaline component was additionally introduced in the form of soda ash in an amount of 2, 4, 6, 8 and 10 %.

The test results are shown in Table 1 and Fig. 1.

These results indicate that without the additional introduction of alkali, the total pH value already at the initial stage is 10 and rapidly decreases over time. The optimal additional alkali content in the system to eliminate this problem is 6–8 %, which ensures high initial pH values (11.5–11.7), as well as maintaining the pH value over time (up to 11 within 4–24 hours).

Table 1

Influence of the content of the alkaline component on the reduction of the total alkalinity of the system

Time	system pH					
	AC	AC+2 %	AC+4 %	AC+6 %	AC+8 %	AC+10 %
*	10.0	10.0	11.0	11.5	11.7	11.7
1 h	9.0	10.0	11.0	11.5	11.5	11.5
2 h	9.0	9.5	10.5	11.0	11.5	11.5
3 h	9.0	9.2	10.5	11.0	11.2	11.2
4 h	8.7	9.0	10.2	11.0	11.2	11.2
5 h	8.7	9.0	10.2	11.0	11.0	11.2
6 h	8.5	8.7	10.2	11.0	11.0	11.0
24 h	8.5	8.5	9.5	11.0	11.0	11.0

Note: * – initial test time; AC – alkaline cement

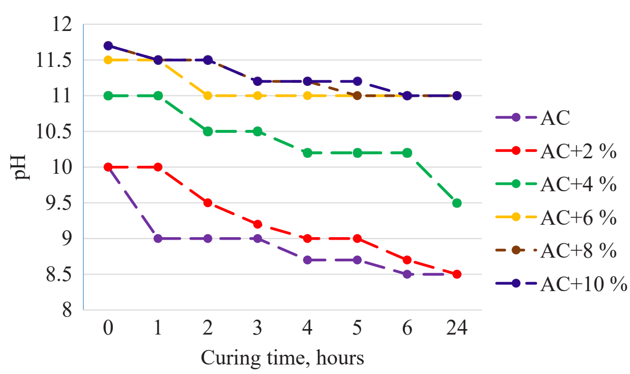

Fig. 1. Change in the pH of the system depending on the content of the alkaline component

However, a pure alkaline system is not enough to eliminate alkaline corrosion. It is necessary to introduce mineral additives that improve the strength characteristics of the material due to the binding of Na+ and K+ ions, and also allow regulating the processes of structure formation. In this case, 10 % metakaolin was used as a mineral supplement.

The results of the influence of the introduction of metakaolin on the alkalinity index pH are shown in Table 2 and Fig. 2.

Table 2

The effect of metakaolin on the pH alkalinity of compositions based on alkaline cement and Portland cement

Time	system pH				
	PC	PC+MK	AC+MK	AC6+MK	AC10+MK
*	11.0	8.5	9.5	11.2	11.6
1 h	10.7	8.5	9.5	11.2	11.6
2 h	10.5	8.7	9.3	11.0	11.6
3 h	10.0	9.4	9.0	11.0	11.5
4 h	9.5	9.5	9.0	11.0	11.5
5 h	9.3	9.7	9.0	11.0	11.2
6 h	9.0	10.0	8.7	10.8	11.2
24 h	11.0	10.5	8.3	10.8	11.2
48 h	11.0	10.7	7.8	10.8	11.2

Note: * – initial test time; PC – Portland cement; AC – alkaline cement; MK – metakaolin

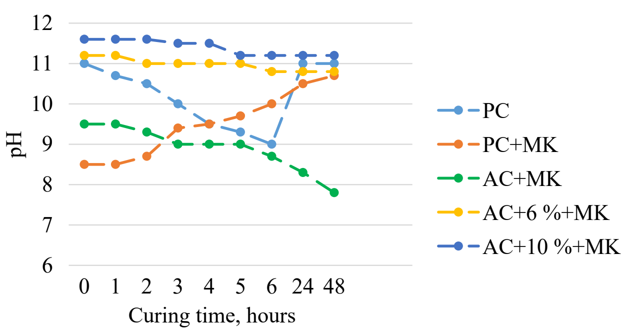

Fig. 2. Change in the pH of the system with the introduction of metakaolin

The results obtained show that the alkalinity of Portland cement systems is slightly higher and is pH=11 at the initial stage. This indicator decreases in the early stages of hardening and returns to around 11 at the age of 1 day. This is what ensures the source of the normal course of the processes of structure formation and curing of materials. The introduction of the metakaolin supplement reduces the total alkalinity at the initial stage to 8.5 with a gradual increase to 10 at the age of 6 hours and 10.5 at the age of 1 day. Such a course of processes of structure formation and hardening is potentially problematic for strength indicators.

The worst system in terms of high alkalinity at the initial stage of hardening is alkaline Portland cement. A low initial indicator of the non-additive system (pH=10.0) causes a slow rate of building up the strength of the system, and the introduction of an active mineral additive (metakaolin) into the composition of an active mineral additive lowers the pH to 9.5 while maintaining this indicator for up to 2 hours of hardening and a subsequent decrease.

6.2. Study of the influence of curing conditions on the kinetics of strength development. This study is aimed at studying the effect of hardening conditions on the kinetics of strength gain of alkaline cements using an active filler (for example, basalt) and the influence of technical factors on the development of structure-forming processes of the studied compositions.

The tested samples were kept under normal conditions for 7 days (compressive strength 10 MPa), after which they were divided into four groups:

1) normal storage;

2) drying with subsequent return to the normal storage chamber;

3) drying and hydrophobization;

3) hydrophobization of samples without drying.

It was found that the worst conditions are drying and hydrophobization (strength on day 28, 10 MPa), and the best conditions are hydrophobization without drying, which provides a hardness of 48 MPa on day 28. The research results are presented in Table 3.

Table 3

Strength indicators of samples depending on storage conditions and exposure factors

Composition	Technical impact factor on the 7th day of curing	Compressive strength, MPa		
		28 days	90 days	180 days
SAC (LTsEM-1)	normal conditions	39.96	73.0	67.1
	drying	14.45	56.9	57.0
	hydrophobization	48.45	78.5	68.3
	drying and hydrophobization	10.95	45.7	28.5
SAC (LTsEM-1)+10 % MK	normal conditions	31.8	16.5	61.7
	drying	3.3	5.2	10.4
	hydrophobization	7.95	12.2	35.7
	drying and hydrophobization	2.7	3.7	4.04
PC (M400)	normal conditions	59.1	68.7	75.96
	drying	48.8	55.94	60.96
	hydrophobization	53.8	67.08	62.4
	drying and hydrophobization	45.4	51.4	52.7
PC (M400)+10 % MK	normal conditions	56.7	60.73	61.8
	drying	50.1	53.96	60.65
	hydrophobization	52.3	59.75	61.04
	drying and hydrophobization	51.5	55.42	58.88

Note: SAC – slag-alkaline cement; PC – Portland cement; MK – metakaolin

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Keeping control specimens-beams measuring 4×4×16 cm under normal conditions allows obtaining a strength of 40 MPa for 28 days. It was also found that drying and hydrophobization of the samples, applied by themselves, are not effective. But the combined action of both factors significantly affects the inhibition of the processes of structure formation of materials and is potentially capable of providing the necessary effect to eliminate moisture in the material during operation.

6.3. Study of shrinkage/expansion deformations. The study of shrinkage/swelling deformations of the system was carried out on the basis of cementing systems selected on the basis of the results of previous studies. The study of shrinkage/expansion deformation of slag-alkaline cements was carried out according to different technological schemes (alkaline component in the form of dry salt and in the form of a solution).

Systems under test:

1. Alkaline Portland cement (PC+liquid glass).
2. Alkaline Portland cement (PC+liquid glass)+10 % MK.
3. SAC (LTsEM-1) with an additional alkaline component.
4. SAC (LTsEM-1) with an additional alkaline component+10 % MK.
5. PC M400.
6. PC M400+10 % MK.

The alkaline component of LTsEM-1systems is presented in the form of a dry sodium carbonate salt. The results of the studies are presented in Table 4 and Fig. 3.

According to the research results, all studied systems are characterized by shrinkage deformations in the entire range of studies. The highest shrinkage indicators are characterized by systems using liquid glass (alkaline Portland cement), and the lowest – alkaline cement LTsEM-1. This can be explained by the presence in systems using water glass of an increased content of gel-like phases, which, at the same time, are present in a much smaller amount in systems using dry alkaline components.

It should be noted that all systems are characterized by a decrease in shrinkage indicators over time, which indicates the development of expansion processes of the system due to alkaline corrosion of the filler.

The LTsEM-1 alkaline cement systems have proven themselves in the best way. And both in pure form and on the introduction of an active mineral additive in the form of metakaolin, which are characterized by a smooth development of shrinkage deformations and a slight inflection of the function due to the corrosion of the filler and the manifestation of expansion deformations.

The study of the influence of the conditions of hardening and storage of samples on the deformative properties of fine-grained concrete was carried out in the system of slag-bore cement (LTsEM-1) in pure form and with the addition of 10 % metakaolin. The results of the studies are presented in Table 5.

The results obtained indicate that the curing conditions significantly affect the change in shrinkage deformations. Thus, it has been shown that when the samples are dried to constant weight, the expansion of the samples stops. This may indicate the termination of structure-forming processes inside the material due to the disappearance of the liquid phase, which is a necessary condition for the occurrence of reactions. At the same time, it should be noted that the difference between dried samples and samples hydrophobized after drying, in terms of deformation characteristics, is extremely small. This may also indicate that the hygroscopicity of the samples is insufficient to saturate sufficiently with moisture upon returning the samples to normal storage conditions after drying. Hydrophobization in such a process can serve as a guarantee of maintaining low material moisture content and reducing the risk of reactions occurring in long-term storage periods.

Table 4

Shrinkage/swelling deformations of fine-grained concrete using basalt aggregate

No.	Composition	Shrinkage/expansion deformation of the material, mm/m, at the age, days				
		2 days	7 days	28 days	90 days	180 days
1	Alkaline portland cement (PC+liquid glass (SS))	–0.23	–0.45	–0.63	–0.55	–0.51
2	Alkaline portland cement (PC+liquid glass (SS))+10 % MK	–0.30	–0.49	–0.61	–0.49	–0.36
3	SAC (LTsEM-1)	–0.21	–0.33	–0.44	–0.43	–0.40
4	SAC (LTsEM-1)+10 % MK	–0.15	–0.26	–0.31	–0.33	–0.32
5	PC M400	–0.25	–0.41	–0.50	–0.44	–0.40
6	PC M400+10 % MK	–0.19	–0.27	–0.41	–0.30	–0.23

Note: SAC – slag-alkaline cement; PC – Portland cement; MK – metakaolin

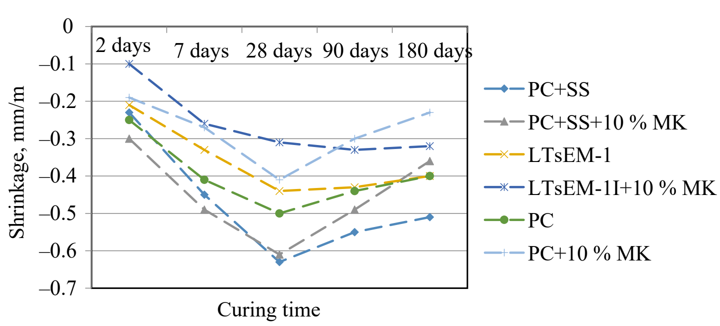

Fig. 3. Shrinkage/expansion deformations of fine-grained concrete using basalt aggregate

Table 5

Shrinkage/swelling deformations of fine-grained concrete depending on storage conditions

Composition	Storage conditions	Shrinkage/expansion deformations of the material, mm/m, at the age, days		
		28 days	90 days	180 days
SAC (LTsEM-1)	normal conditions	–0.44	–0.43	–0.40
	drying	–0.44	–0.44	–0.43
	hydrophobization	–0.3	–0.24	–0.12
	drying and hydrophobization	–0.44	–0.44	–0.43
SAC (LTsEM-1)+10 % MK	normal conditions	–0.31	–0.33	–0.32
	drying	–0.31	–0.31	–0.31
	hydrophobization	–0.28	–0.23	–0.21
	drying and hydrophobization	–0.31	–0.31	–0.31

Note: SAC – slag-alkaline cement; MK – metakaolin

The hydrophobization of fine-grained concrete without drying leads to an increase in the expansion rate of the samples. Combining this information with the strength characteristics of similar systems studied earlier, it can be argued that the processes of structure formation of the system are activated under the conditions of self-steaming of hydrophobized samples. This may contain a potential hazard, given the traditional methods of protecting reinforced concrete structures, namely, covering the structure with a coating of paints and varnishes.

7. SWOT analysis of research results

Strengths. Undoubtedly, a positive aspect of these studies is the development of applied and technological solutions to prevent and counteract alkaline corrosion in concrete. This will significantly expand the raw material base for the manufacture of building products and structures, which will have a positive effect on the economic development of the country.

Weaknesses. In the course of research, it was found that the use of active aggregates significantly complicates or even stops the processes of structure formation of one-component cements. It was also revealed the need for additional introduction of an alkaline component into the system, since the usual alkali content in such systems is insufficient for the normal course of the structure formation process.

Opportunities. The obtained research results confirm the possibility of using active aggregates for the production of building materials, in particular, based on alkaline cements. And additional processing of hydrophobic materials allows to increase the strength of products and structures even during operation under normal heat and humidity conditions.

Threats. The risks of this technology lie in the handling of structures that have been affected by destructive processes associated with alkaline corrosion of the aggregate. Indeed, for them today there is a single approach – the structure is taken out of service, disassembled and manufactured anew. This approach is very capital and resource intensive and requires significant time and logistics costs. To implement the technology for eliminating alkaline corrosion, its implementation is necessary at the initial stage of the construction – planning.

8. Conclusions

1. Studies have been carried out on the properties of concretes using reactive aggregates. For this, the optimal compositions of alkaline cements (LTsEM-1) and PC M400 were selected, which additionally introduced metakaolin in an amount of 10 %. Strength values of 40 and 67 MPa were obtained for 28 and 180 days of curing, respectively, for compositions based on slag-bog cement and 50 and 60 MPa for 28 and 180 days of curing, respectively, for compositions based on Portland cement.
2. Correction of concrete mix samples has been carried out and the need for additional introduction of an alkaline component into the system has been determined. The optimal additional alkali content in the system is 6–8 %, which ensures high initial pH values (11.5–11.7), as well as maintaining the pH value over time (up to 11 within 4–24 hours). Concrete research has been carried out in optimized warehouses.
3. Research has been carried out to determine the shrinkage/expansion deformations of alkaline concrete using active aggregates. It has been determined that from the point of view of shrinkage deformations, systems based on alkaline cement LTsEM-1 have shown the best side. Moreover, both in pure form and with the introduction of an active mineral additive of metakaolin (–0.44 and –0.31 mm/m, respectively, at the age of 28 days of normal curing). In addition, they showa minimal decrease in shrinkage in the longer periods of hardening, which may indicate a decrease in the intensity of the development of alkaline corrosion of the aggregate in the composition of such systems.
4. The influence of technical and technological factors of preparation and placement of concrete mixture on the development of alkaline corrosion of artificial stone has been investigated. It has been found that drying and hydrophobization of samples, used by them, are not effective. But the combined action of both factors significantly affects the inhibition of the processes of structure formation of materials and is potentially capable of providing the necessary effect to eliminate moisture in the material during operation.

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Oleksandr Kovalchuk, *PhD, Senior Researcher, V. D. Glukhovsky Scientific Research Institute for Binders and Materials, Kyiv National University of Construction and Architecture, Kyiv, Ukraine, ORCID: https://orcid.org/0000-0001-6337-0488*

✉ ***Viktoriia Zozulynets,*** *Postgraduate Student, Department of Technology of Building Structures and Products, Kyiv National University of Construction and Architecture, Kyiv, Ukraine, e-mail: zozulinets555@gmail.com, ORCID: https://orcid.org/0000-0002-8066-2033*

✉ *Corresponding author*