

Основою для забезпечення стійкості штучного каменю на основі лужних алюмосилікатних зв'язуючих до змінних умов зовнішнього середовища є формування в його фазовому складі цеоліто- та слюдоподібних гідратних новоутворень.

Управління процесами структуроутворення та, як наслідок, експлуатаційними властивостями лужних гідроалюмосилікатів, можливе за допомогою варіації співвідношення основних оксидів зв'язуючого, дисперсністю частинок та умовами тверднення. Зазначено, що для отримання високих експлуатаційних характеристик каменю на основі лужних алюмосилікатних зв'язуючих існує необхідність у підвищених температурах їх тверднення. В роботі запропоновано забезпечення водостійкості штучного каменю при його твердненні в нормальних умовах за рахунок модифікації зв'язуючого Са-вміщуючими добавками.

Досліджено вплив СаО-вміщуючих модифікаторів різного морфологічного типу на фізико-механічні характеристики штучного каменю на основі лужних алюмосилікатних зв'язуючих. Встановлено, що на 28 добу тверднення при температурі зовнішнього середовища  $20 \pm 2$  °C і незалежно від типу введення Са-вміщуючих модифікаторів, штучний камінь характеризується міцністю при стиску від 14,2 до 42,8 МПа з коефіцієнтом водостійкості від 0,81 до 1,05 за рахунок утворення в продуктах гідратації суміші високо- та низькоосновних гідросилікатів кальцію та цеолітоподібних новоутворень гібридного типу – кальцій-натрієвих гідроалюмосилікатів із незначним вмістом Na- та K-гейландитів. Показано, що водостійкість штучного каменю в ранні терміни твердіння при температурі середовища  $20 \pm 2$  °C забезпечується за рахунок утворення в продуктах гідратації зв'язуючих високо- і низькоосновних гідросилікатів кальцію, що утворюються внаслідок гідратації портландцементу, меленого шлаку і гашеного вапна.

Прискорити кінетику набору міцності з забезпеченням водостійкості штучного каменю можливо при використанні в якості лужного компоненту рідинного скла з силікатним модулем 2,0–2,6 і вмістом вапна пушонки  $2,0 \pm 3,0$  % від маси лужного алюмосилікатного зв'язуючого. Відмічено, що гідравлічна активність Са-вміщуючих модифікаторів зменшується в ряді Шлак > Са(ОН)<sub>2</sub> > СаСО<sub>3</sub> > Портландцемент > Глиноземистий цемент

**Ключові слова:** лужний алюмосилікат, СаО-вміщуючий модифікатор, штучний камінь, фазовий склад, структуроутворення

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# INFLUENCE OF THE CaO-CONTAINING MODIFIERS ON THE PROPERTIES OF ALKALINE ALYUMO-SILICATE BINDERS

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## 1. Introduction

At present, alkaline aluminosilicate binders are an alternative replacement of Portland cement and differ from the latter by unique phase composition, which ensures the formation of artificial stone of high strength, corrosion resistance, thermal resistance and the others due to the formation of analogues of natural and durable zeolite-, mica-like and feldspathoid minerals [1–5]. These properties of artificial stone, including water resistance, are provided by the transition of gel-like phase into the crystalline phase in the temperature range from 60 to 100 °C [6–11]. The need for low temperature treatment of materials based on aluminosilicate binder significantly hinders their use in the construction industry.

At ambient temperature of 20 °C and below, hydration processes slow down in the alkaline aluminosilicate binder,

the gel-like component does not transfer into the crystalline phase and, therefore, proper water resistance of artificial stone is not ensured. Under such conditions, water resistance of artificial stone ( $Cst=0.8$  and above) can be formed within about 9–12 months of hardening. Therefore, conducting research in the area of formation of water-resistant phases with the acceleration of the processes of formation of alkali aluminosilicate binders at ambient temperature of 20 °C and below is a pressing issue, the solution of which will make it possible to significantly expand the area of using the materials on their basis.

## 2. Literature review and problem statement

Papers [6, 8, 9] show the results of research into the formation of water-resistant artificial stone due to the varia-

tion of the ratios of basic oxides at elevated temperatures. It was shown that at the ratio of  $\text{Al}_2\text{O}_3/\text{SiO}_2$  from 2 to 6 and hardening temperature of  $65^\circ\text{C}$ , water resistance of artificial stone is ensured. At hardening at  $25^\circ\text{C}$ , with the highest molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ , strength to compression of artificial stone reaches the values of up to 50.8 MPa within 180 days, and at thermal treatment at  $65^\circ\text{C}$ , it reaches the same strength to compression within 14 days of hardening [12], information regarding indicators of water resistance is not available.

The problem regarding ensuring water resistance, and respectively, strength of artificial stone based on alkali aluminosilicate binder at ambient temperature of  $20^\circ\text{C}$  and below is unresolved.

The reason for this can refer to objective difficulties that are associated with the fact that under normal conditions of hardening, artificial stone based on minerals of clay and alkaline compounds in aqueous medium is softened. The variant to overcome this problem may be long thermal treatment. Such an approach was implemented in papers [6, 8, 9], however, the complete formation of water-resistant gel of N(K)-A-S-H composition was not achieved.

Introduction of Portland cement in the amount of up to 15 % into the composition of aluminosilicate binder contributes to an increase in the duration of hardening and more rapid strength gaining due to formation of water resistant high-base calcium silicates. The results show that strength to compression of this cement made up from 33.25 to 51.38 MPa. It grows at an increase in the amount of introduced Portland cement [8–15].

Addition of ground blast furnace slag of up to 10 % to the composition of alkali aluminosilicate binder contributes to the improvement of strength characteristics, but under normal temperature of hardening, artificial stone gains water resistance only after 90 days of hardening [16].

When we introduce up to 20 % of aluminate cement with the concentration of sodium hydroxide of 10, 12 and 14 M to the composition of alkaline aluminosilicate binder, strength to compression increases and water resistance is ensured only on day 28 of hardening. This is due to the fact that the product of dehydration of aluminate cement – aluminum hydroxide, binding with alkali, forms water resistant phases in later time of hardening [17].

Results of research [16] show that the modification of alkaline aluminosilicate binder with the addition of  $\text{Ca}(\text{OH})_2$  increases its resistance to carbonation due to the formation of zeolite-like phases. The effect of adding  $\text{Ca}(\text{OH})_2$  on the mechanical characteristics was not shown.

In papers [18, 19], it was stated that the introduction to the composition of aluminosilicate binder of 50 % thermo-activated limestone, that hardened at ambient temperature, strength at compression within 28 days made up 39.2 MPa but its influence on the water resistance indicator was not noted.

All this allows stating that it is promising to carry out the research into the formation of hydroaluminosilicates of N(K)AS<sub>x</sub>H<sub>y</sub> type under normal hardening temperatures by introducing catalysts of hardening, specifically, Ca-containing modifiers, to their composition. In this case, the basis for ensuring water resistance of artificial stone in the early periods of hardening at ambient temperature of  $20\pm 2^\circ\text{C}$  can be studying the influence of Ca-containing modifiers of alkaline aluminosilicate binder on the processes of structure formation and strength with determining the mechanism of

the formation of water resistant hydroaluminosilicates of the N(K)AS<sub>x</sub>H<sub>y</sub> type.

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### 3. The aim and objectives of the study

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The aim of this study is to establish the relationship between the processes of structure formation and properties of artificial stone based on alkaline aluminosilicate binder modified by Ca-containing additives.

To accomplish the aim, the following tasks have been set:

- exploration of the influence of CaO-containing modifiers of various morphological type on the processes of structure formation of alkali aluminosilicate binders;
- exploration of the influence of CaO-containing modifiers on the kinetics of strength gaining and ensuring water resistance of artificial stone based on the alkali aluminosilicate binders;
- determining the optimum module of liquid glass and the amount of air-slaked lime on the formation of strength and water resistance of artificial stone at hardening under ambient conditions at the temperature of  $20^\circ\text{C}$ .

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### 4. Materials and methods to study the modified binder

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To obtain alkaline aluminosilicate binder having the composition  $(0.8\text{Na}_2\text{O}+0.2\text{K}_2\text{O})\cdot\text{Al}_2\text{O}_3\cdot 4.5\text{SiO}_2\cdot n\text{H}_2\text{O}$ , we used: metakaolin, microsilica, and sodium liquid glass. Calculation of the optimum ratio of oxides was carried out taking into consideration the recommendations of [18]. The composition of the binder by alkaline oxides was adjusted using their aqueous solutions.

We used as CaO-containing modifiers: PC – Portland cement PC I-500 (Ukraine) with the content of  $\text{C}_3\text{S}>50\%$ , S – ground granulated blast furnace slag of Dniprodzerzhinsk metallurgical plant (Ukraine), which refers to basic  $M_o=1.21>1$ , with the content of glass phase of about 75 %, saturated compound of methyl –  $\text{C}_2\text{MS}_2$ ,  $\text{C}_2\text{AS}$ ,  $\text{CAS}_2$  and orthosilicate composition –  $\text{C}_2\text{S}$ ,  $\beta\text{-C}_2\text{S}$ ,  $\text{C}_3\text{S}_2$ , AC – alumina cement Istra 40 (Croatia),  $\text{Ca}(\text{OH})_2$  – air-slaked lime (Ukraine) and  $\text{CaCO}_3$  – calcium carbonate (Turkey). The modifiers were added in the amount of 5 % of the weight of alkaline aluminosilicate binder, carefully stirring it with dry components.

The samples of artificial stone at dimensions  $20\times 20\times 20$  mm and  $10\times 10\times 60$  mm hardened within 28 days at temperature  $T=20\pm 2^\circ\text{C}$  and a humidity of the environment of  $W=65\pm 5\%$ . The samples were tested for strength to compression and water resistance on day 2, 7, and 28 of hardening. Water resistance of the stone was determined by the change in strength at compression of samples after full water saturation and assessed by the coefficient of water resistance ( $K_{wr}=R_c^{wet}/R_c^{dry}$ ). The required number of samples to assess the above listed indicators for each composition of the binder was not less than 3.

Determining the phase composition of artificial stone based on alkaline aluminosilicate binder was studied using an X-ray phase analysis. X-ray phase analysis was carried out at the diffractometer DRONE-4-07 with a copper tube at a voltage of 30 kW, current of 10...20 mA and the range of angles  $2\theta=10\text{...}60^\circ$ . The neo-formations were identified based of the data [20, 21], as well as using DataBase PDF-2 with software module JCPDFWIN.

As the criteria for evaluation of the properties of artificial stone based on alkali aluminosilicate binders, its strength at compression ( $R_c$ ) and water resistance (softening coefficient,  $K_{wr}$ ) were selected. Softening coefficient describes the ratio of strength at compression of artificial stone, kept in water (full water saturation), to strength of the stone under dry conditions.

As the criteria for evaluation of the properties of artificial stone based on alkaline aluminosilicate binders, its strength at compression ( $R_c$ ) and water resistance (coefficient of softening,  $K_{wr} \leq 0.8$ ).

## 5. Results of experiment on the modification of the binder by Ca-containing additives

### 5.1. Features of structure formation processes

Fig. 1 shows the results of X-ray phase analysis of the process of structure formation of artificial stone based on alkaline aluminosilicate binder after 28 days of hardening, depending on the type of CaO-containing modifiers and conditions of hardening – environment, ambient temperature of 20 °C with variable humidity within the time of hardening.

According to the RFA data, diffraction surges of neo-formations, such as quartz  $\text{SiO}_2$ , (PDF2 #046-1045),  $\text{Na}_4\text{Ca}_4\text{Si}_6\text{O}_{18} \cdot n\text{H}_2\text{O}$ , (PDF2 #079-1084), C-N-A-S-H, C-K-A-S-H [1–4, 8] and zeolite-like of the type of analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ; #PDF2 2-417), gismondite ( $\text{CaSi}_2\text{Al}_2\text{O}_8 \times 4\text{H}_2\text{O}$ , PDF2 #020-452), zeolite K-M ( $\text{K}_2\text{Si}_3\text{Al}_2\text{O}_{10} \cdot 3\text{H}_2\text{O}$ , PDF2 #030-902) are observed after the introduction of Portland cement to the composition of the alkali aluminosilicate binder (Fig. 1).

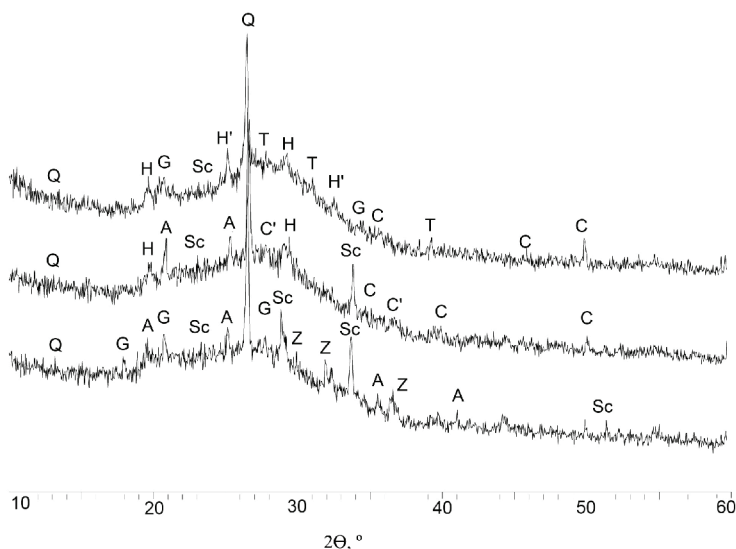


Fig. 1. X-ray patterns of artificial stone of composition  $(0.8\text{Na}_2\text{O} + 0.2\text{K}_2\text{O}) \cdot \text{Al}_2\text{O}_3 \cdot 4.5\text{SiO}_2 \cdot 15\text{H}_2\text{O}$  after hardening for 28 days under conditions of  $T = 20 \pm 2$  °C,  $W = 65 \pm 5$  % (lime, slag, PC I-500 downwards, respectively). Designations: Q – quartz; C –  $\text{Ca}_6\text{Si}_6\text{O}_{16} \cdot \text{H}_2\text{O}$ ; C' –  $\text{Ca}_6\text{Si}_3\text{O}_{12} \cdot 2\text{H}_2\text{O}$ ; Sc –  $\text{Na}_4\text{Ca}_4\text{Si}_6\text{O}_{18} \cdot n\text{H}_2\text{O}$ ; Z – zeolite K-M; T – thomsonite; G – gismondine; H – Na heulandite; H' – K heulandite

In the composition of hydration products after the introduction of 5 % ground slag to the composition of alkaline aluminosilicate binder, diffraction surges of neo-formations were detected, such as quartz  $\text{SiO}_2$  (PDF2 #046-1045),

C-N(K)-A-S-H,  $\text{Ca}_6\text{Si}_3\text{O}_{12} \cdot 2\text{H}_2\text{O}$  (PDF2 #003-735),  $\text{Ca}_6\text{Si}_6\text{O}_{16} \cdot \text{H}_2\text{O}$  (PDF2 #015-313),  $\text{Na}_4\text{Ca}_4\text{Si}_6\text{O}_{18} \cdot n\text{H}_2\text{O}$ , (PDF2 #079-1084) and zeolite-like – zeolite Na-A ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ; #PDF2 2-417) and sodium heulandite ( $\text{Na}_6\text{Si}_{27}\text{Al}_{36}\text{O}_{72} \cdot 24\text{H}_2\text{O}$ , PDF2 #022-1563) (Fig. 1).

In the composition of hydration products after the introduction of 5 % of air-slaked lime to the composition of alkali aluminosilicate binder, diffraction surges of neo-formations were detected, such as quartz, thomsonite  $\text{NaSi}_5\text{Al}_5\text{O}_{20} \cdot 6\text{H}_2\text{O}$  (PDF2 #009-490),  $\text{Ca}_6\text{Si}_6\text{O}_{16} \cdot \text{H}_2\text{O}$  (PDF2 #015-313) and zeolite-like – sodium heulandite ( $\text{Na}_6\text{Si}_{27}\text{Al}_{36}\text{O}_{72} \cdot 24\text{H}_2\text{O}$ , PDF2 #022-1563), potassium heulandite ( $\text{K}_6\text{Si}_{27}\text{Al}_{36}\text{O}_{72} \cdot 24\text{H}_2\text{O}$ , PDF2 #022-1721) (Fig. 1).

In the composition of hydration products after the introduction of 5 %  $\text{CaCO}_3$  and alumina cement (RFA curves are not shown) to the composition of alkali aluminosilicate binder, according to the data of paper [19], diffraction surges of crystallized hydro aluminates of the type –  $\text{CAH}_x$ , hydrogranates of type –  $\text{C}_3\text{SAH}_4$  and calcium hydro aluminates, containing  $\text{CaCO}_3$  were detected

### 5.2. Influence of additives on physical and mechanical properties

Fig. 2 and Fig. 3 show graphic dependences of the influence of Ca-containing modifiers on the kinetics of gaining strength at compression and water resistance by artificial stone based on alkaline aluminosilicate binder, depending on the period of hardening.

In general, the kinetics of strength gaining is positive. Ca-containing modifiers contribute to gaining strength of alkaline aluminosilicate binder both in earlier periods (day 2 and 7), and on day 28 of samples hardening at ambient temperature of  $20 \pm 2$  °C. Additives of ground slag, air-slaked lime and calcium carbonate that provide for obtaining artificial stone based on alkaline aluminosilicate binder with strength at compression, respectively, of 42.8, 41.6 and 32.7 MPa, manifest themselves most actively.

The influence of additives on water resistance of artificial stone based on alkaline aluminosilicate binder is somewhat ambiguous.

Thus, in the early periods of hardening, on day 2 and 7 (the samples were in the aqueous medium), water resistance of artificial stone ( $K_{wr} > 0.8$ ) is ensured by additives of air-slaked lime, ground slag and Portland cement (Fig. 3).

Fluctuation of water resistance coefficient in the early periods of hardening is related to the peculiarities of flow of the hydration process in the studied binding compositions.

On day 28 of hardening under conditions of aqueous medium, artificial stone based on alkaline aluminosilicate binder, modified with Ca-containing additives, is water resistant.

The composition that contains 5 % of alumina meets the normative value of  $K_{wr} = 0.81$ , others considered compositions have resistance coefficient from 0.94 to 1.05, which exceeds the normative value by 1.2–1.3 times.

According to the influence on the change of strength to compression and water resistance, the considered Ca-containing additives can be arranged in the following series:  $\text{S} > \text{Ca}(\text{OH})_2 > \text{CaCO}_3 > \text{PC} > \text{AC}$ .

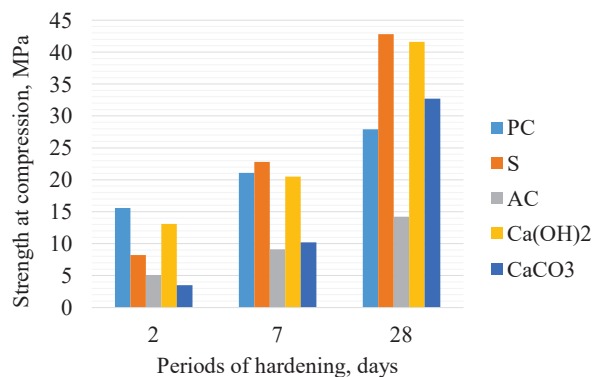


Fig. 2. Influence of Ca-containing modifiers on change of strength of artificial stone based on alkali aluminosilicate binder, depending of duration of hardening (the samples were kept under conditions of environment at the temperature of 20±2 °C)

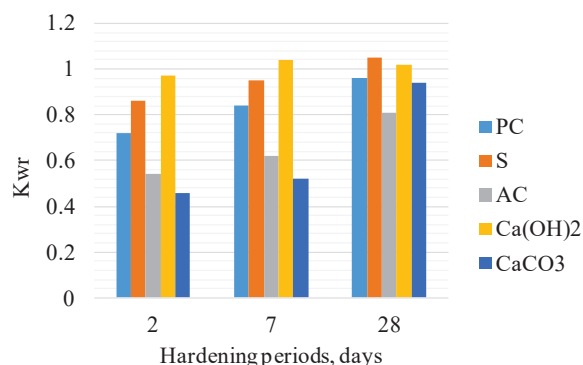


Fig. 3. Influence of modifiers on the change of coefficient of water resistance of artificial stone based on the modified alkaline aluminosilicate binder, depending on the period of hardening (the samples were kept under conditions of environment at temperature of 20±2 °C)

### 5. 3. Optimization of composition of alkali aluminosilicate binder

To control the structure formation and to ensure high indicators of physical and mechanical properties of artificial stone, it was necessary to determine the optimal composition of the modified alkaline aluminosilicate binder.

In order to accelerate the processes of structure formation, air-slaked lime was used as CaO-containing modifier, liquid glass with different silicate module (2.0; 2.5; 3.0) was used as alkaline aqueous solutions of silicates. Air-slaked lime was introduced by careful stirring with dry ingredients in the amount of 1.0; 2.0; 3.0 % in conversion to CaO of the weight of the binder.

Table 1 shows the experiment planning matrix in encoded and natural magnitudes and the research results.

Strength to bending/compression and coefficient of softening (water resistance), the magnitude of which should not be less than 0.8, were accepted as the input parameters.

As a result of the conducted modeling, the regression equations (are not given in the article), that describe mathematical models of influence of the composition of modified alkaline aluminosilicate binder on its properties were obtained.

The analysis of regression equations showed that varying factors X<sub>1</sub> and X<sub>2</sub> are significant, factor X<sub>1</sub> the main factor of influence on the properties of artificial stone, while factor X<sub>2</sub> has a significant impact in the early periods of hardening of the alkali aluminosilicate binder. The joint influence of factors X<sub>1</sub>X<sub>2</sub> is quite low and does not make a significant contribution to the improvement of the properties of artificial stone.

It is shown that on day 7 of hardening, the artificial stone, obtained during the application of liquid glass with silicate module Ms=2.0 (factor X<sub>2</sub>) and the content of air-slaked lime in the amount of 3 % by the weight of the binder (Fig. 4, a, c, e), is characterized by the maximum values of strength at bending/compression. The specified parameters ensure water resistance at the level of 1.21. An increase in the above-mentioned indicators occurs at a simultaneous increase in factor X<sub>1</sub> from 1.5 to 3 % and in silicate module of liquid glass from 2 to 3 (factor X<sub>2</sub>).

After 28 days of hardening, the artificial stone, obtained when using liquid glass with silicate module Ms=2.0 (factor X<sub>2</sub>) and the content of air-slaked lime in the amount of 3 % of the weight of the binder (Fig. 4, b, d, f), is characterized by the maximum values of strength at bending/compression of 14.3/55.7 MPa. The specified parameters ensure water resistance at the level of 1.12. An increase in the above-mentioned indicators occurs at a simultaneous increase in factor X<sub>1</sub> from 1.2 to 3 % and in silica module of liquid glass from 2 to 3 (factor X<sub>2</sub>).

Table 1

Experiment planning matrix and results of its implementation

No.	Encoded magnitudes		Natural magnitudes		Physical and mechanical characteristics					
	X <sub>1</sub>	X <sub>2</sub>	Ca(OH) <sub>2</sub> , %	Ms	R <sub>b</sub> , MPa	R <sub>c</sub> , MPa	K <sub>wr</sub>	R <sub>b</sub> , MPa	R <sub>c</sub> , MPa	K <sub>wr</sub>
					Day 7			Day 28		
1	1	0	3.0	2.5	8.10	37.50	1.15	13.80	52.50	1.09
2	0	-1	2.0	2.0	7.70	35.50	1.13	13.10	52.10	1.08
3	-1	0	1.0	2.5	5.50	21.40	0.96	9.40	31.20	0.95
4	0	0	2.0	2.5	7.30	32.10	1.09	12.40	48.50	1.05
5	-1	-1	1.0	2.0	6.20	23.10	0.98	10.50	34.10	0.99
6	-1	1	1.0	3.0	4.50	18.90	0.92	7.70	30.10	0.94
7	1	-1	3.0	2.0	8.40	39.80	1.21	14.30	55.70	1.12
8	1	1	3.0	3.0	7.40	31.20	1.10	12.60	49.10	1.07
9	0	1	2.0	3.0	6.80	30.30	1.07	11.60	44.30	1.02

Note: Ms – silicate module of liquid glass, calculated from formula  $Ms = n(\text{SiO}_2) / n(\text{Na}_2\text{O})$ , where  $n(\text{SiO}_2)$  and  $n(\text{Na}_2\text{O})$  are the amount of the substance of oxides SiO<sub>2</sub> and Na<sub>2</sub>O in liquid glass, mole; R<sub>c</sub>, R<sub>b</sub> are the strength at bending and compression; K<sub>wr</sub> is the coefficient of softening (water resistance)

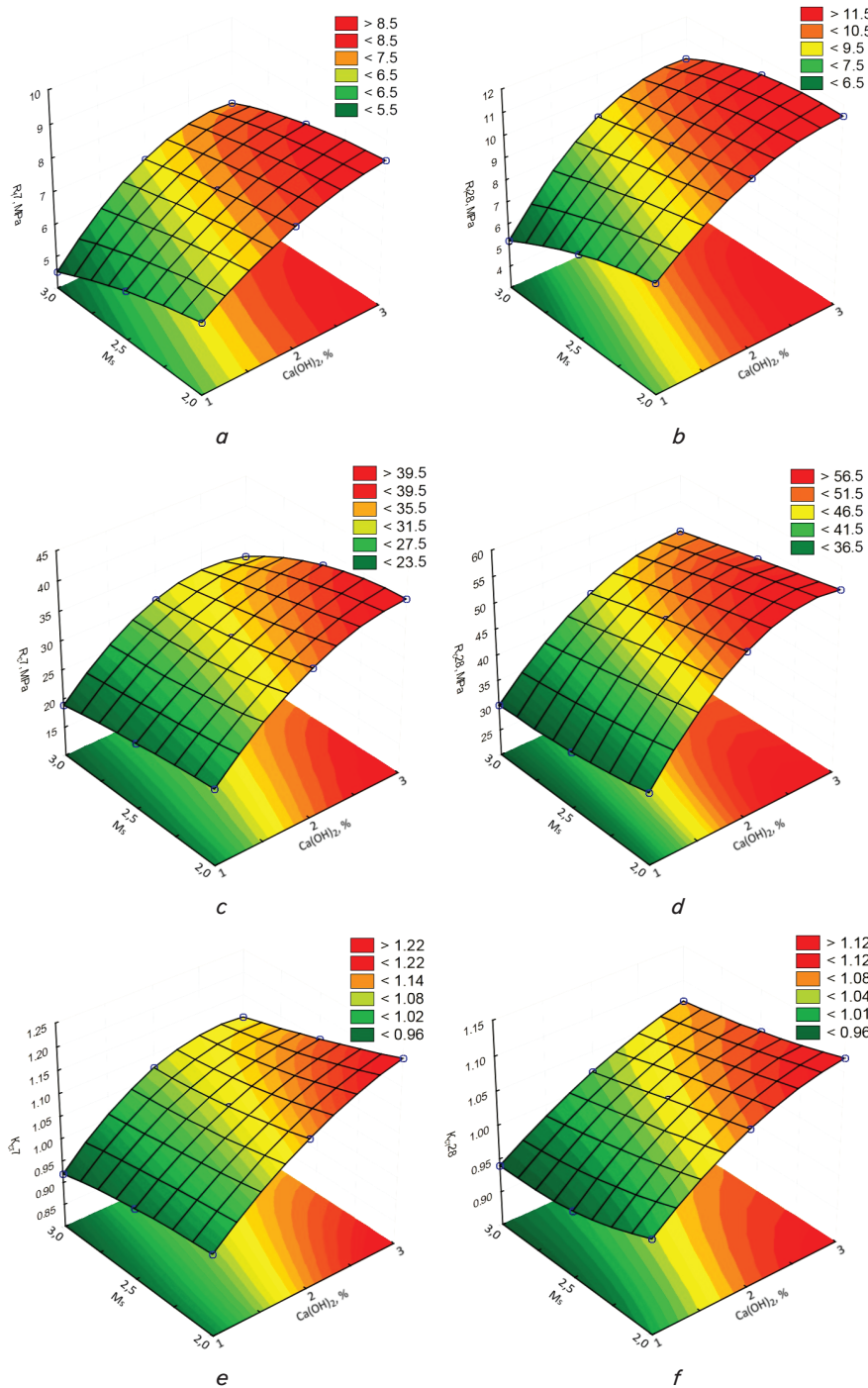


Fig. 4. Response diagrams of the influence of composition of the binder on: *a, b* – strength at bending, *c, d* – strength at compression and *e, f* – water resistance of artificial stone after hardening within: *a, c, e* – 7 days and *b, d, f* – 28 days

A low content of introduction of air-slaked lime in the amount of 1±2 % to the composition of alkali aluminosilicate binder has a significant impact on the improvement of properties of artificial stone from 10 to 40 %.

### 6. Discussion of results of experiment on modification of the binder by Ca-containing additives

Rapid gaining of strength by artificial stone when adding 5 % of PC I-500 in the early period on day 2 and 7 of

hardening from 15.6 to 21.1 MPa is explained by high reactivity of  $Ca(OH)_2$  as a result of hydration of three-calcium silicate  $C_3S$  in alkaline medium (Fig. 2). The interaction of  $Ca(OH)_2$  with alkaline components of the composition leads to the early formation and increasing the crystallinity degree of C-S-H gel with low indexes of water resistance coefficient  $K_{wr}$  from 0.54 to 0.84 (Fig. 3). During the interaction of gels of C-S-H and N(K)-A-S-H and in the presence of active groups  $[AlO_4]^{5-}$  and  $[SiO_4]^{4-}$ , there appear adjacent neo-formations of the type of C-N-A-S-H and C-K-A-S-H [1–4, 8], which considerably increase water resistance coefficient  $K_{wr}$  up to 0.96. Rapid hardening of the mixture causes fast strength gaining and the development of the homogeneous structure of the stone due to the formation of zeolite-like phases of the type of analcime, gismondite, zeolite K-M and sodium calcium silicate (Fig. 1), which explains the low indicators of strength – 27.9 MPa on day 28 (Fig. 2).

Slow gaining of strength by artificial stone when adding 5 % AC in the early periods on day 2 and 7 of hardening from 5.1 to 9.1 MPa is caused by the low hydrolytic activity of hydration product  $Al(OH)_3$  as a result of dehydration of CA and  $C_{12}A_7$  in an alkaline medium (Fig. 2). The interaction of  $Al(OH)_3$  with alkaline compounds in the presence of amorphous silica forms weakly crystallized hydro aluminates of the type  $CAH_x$  and hydrogranates –  $C_3SAH_4$ , which are characterized by low values of water resistance coefficient  $K_{wr}$  from 0.54 to 0.62 (Fig. 3). At the subsequent interaction of gel N(K)-A-S-H with groups  $[AlO_4]^{5-}$  and  $[SiO_4]^{4-}$  at  $T=20\pm 2$  °C, C-N(K)-A-S-H is formed, which on day 28 of hardening leads to the formation of water resistant artificial stone with strength of 14.2 MPa with water resistance coefficient  $K_{wr}=0.84$  (Fig. 2).

Strength gaining by artificial stone when adding 5 % of ground slag in the early periods on day 2 and 7 of hardening from 8.2 to 22.8 MPa is caused by the high reactivity of glass phase of slag (Fig. 2) [1, 2, 4, 9]. The interaction of the components of glass phase of ground slag with alkaline components of the composition leads to a rapid formation of C-S-H gel with high indicators of water resistance coefficient  $K_{wr}$  from 0.86 to 0.92 (Fig. 3). At lower basicity of silicates and in presence of active groups  $[AlO_4]^{5-}$  and  $[SiO_4]^{4-}$  in alkaline medium, the amount of formation of adjacent hydrate phases of type C-N-A-S-H and C-K-A-S-H increases [1–4, 8, 9].

The high strength characteristics of 42.8 MPa at  $K_{wr}=1.05$  (Fig. 2, 3) can be explained by the presence in the composition of artificial stone of hydrate phases – C-N(K)-A-S-H, calcium hydro silicates of various basicity, sodium-calcium hydro silicate, as well as zeolite-like phases, specifically: zeolite Na-A and sodium heulandite (Fig. 1).

Rapid strength gaining by artificial stone when adding 5 % of lime in the early periods on day 2 and 7 of hardening from 13.1 to 20.5 MPa at water resistance coefficient  $K_{wr}$  from 0.97 to 1.04 is caused by high reactivity of  $\text{Ca}(\text{OH})_2$  in alkaline medium (Fig. 2, 3) with the formation of less amount of calcium hydro silicates compared with the introduction of Portland cement to the composition of alkaline aluminosilicate binder. High average strength characteristics of 41.6 MPa at  $K_{wr}=1.02$  (Fig. 2, 3) on day 28 of hardening can be explained by existence of hydrate zeolite-like neo-formations of the type of gismondite, thomsonite, sodium heulandite and potassium heulandite in the composition of artificial stone (Fig. 1).

Slow strength gaining by artificial stone when adding 5 % of  $\text{CaCO}_3$  in the early periods on day 2 and 7 of hardening from 3.5 to 10.2 MPa is caused by low hydrolytic activity of calcite as a result of its low solubility in alkaline medium (Fig. 2). The interaction of products of dissociation of  $\text{CaCO}_3$  with alkaline components of the composition is quite slow, which affects water resistance coefficient of artificial stone  $K_{wr}$  from 0.46 to 0.52 (Fig. 3). On day 28 of hardening, strength of artificial stone increases up to 32.7 MPa, water resistance increases up to 0.94 (Fig. 2, 3) due to the formation of Na-Ca zeolite-like phases containing  $\text{CaCO}_3$  [19].

Generalization of the results of mathematical planning indicates that the introduction of air-slaked lime in the amount of 2.0÷3.0 % of the weight of alkali aluminosilicate binder using liquid glass with the silicate module of 2.0–2.6 is optimal. At the specified quantitative and qualitative characteristics, high strength and water resistance of artificial stone at hardening under conditions of environment at the temperature of  $20\pm 2$  °C is ensured.

The conducted studies may not give a complete idea concerning the influence of CaO-containing modifiers on deformation processes which take place during hardening of the samples under conditions of the environment, especially

at fluctuation of temperature and humidity fields. Therefore, further research will be directed at studying the impact of these modifiers on the development of deformation processes over time, depending on the phase composition of alkali aluminosilicate binders.

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## 6. Conclusions

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1. Regardless of the type of Ca-containing modifiers, the phase composition of products of hydration of alkaline aluminosilicate binder is presented by the mixture of high- and low-base hydro silicates of calcium and zeolite-like neo-formations of the hybrid type, specifically: calcium-sodium hydro aluminosilicates with insignificant content of Na- and K-heulandites; hydraulic activity of Ca-containing modifiers decreases in series  $\text{S} > \text{Ca}(\text{OH})_2 > \text{CaCO}_3 > \text{PC} > \text{AC}$ .

2. Regardless of the type of Ca-containing modifiers, the above composition of hydration products provides for high indicators of strength from 14.2 to 42.8 MPa and water resistance from 0.81 to 1.05 on day 28 of hardening. In the early periods of hardening at ambient temperature of  $20\pm 2$  °C, these indicators are ensured only due to the introduction of 5 % of Portland cement, ground slag and air-slaked lime.

3. Under normal temperature of hardening ( $20\pm 2$  °C), it is possible to accelerate the kinetics of gaining strength and water resistance of artificial stone by using liquid glass of silicate module of 2.0–2.6 with the content of air-slaked lime of 2.0÷3.0 % of the weight of alkaline aluminosilicate binder as an alkali component.

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