

## HEAT-RESISTANT ASH AND SLAG CONCRETE WITH ACTIVATING ADMIXTURES

LEONID DVORKIN<sup>1</sup>, VADIM ZHITKOVSKY<sup>1\*</sup>, YURI RIBAKOV<sup>2</sup>

<sup>1</sup>National University of Water and Environmental Engineering, 11, Soborna st., Rivne 33028, Ukraine

<sup>2</sup>Department of Civil Engineering, Ariel University, Ariel, 40700, Israel

*The paper shows the use of activators for the hardening of cement-ash concrete, incl. passing when heating concrete. Such an activator is a composition of sodium fluorosilicate and naphthalene-formaldehyde superplasticizer. The addition of sodium fluorosilicate makes it possible to increase the early strength of the cement-ash binder, enhance the kinetics of pozzolanic reaction and reduce the drop in the strength of the cement-ash stone when it is heated to 800°C. Experimental dependences of concrete mixture water demand and concrete strength on the cement and aggregates consumption for different workability mixtures have been obtained. These dependences take into account the influence of complex admixtures of superplasticizer and sodium fluorosilicate that enabled to propose a method for design of ash and slag concrete compositions. The positive role of the proposed complex activating admixture on the change in strength and shrinkage of ash and slag concrete after drying and subsequent heating has been experimentally confirmed. A complex of experimental-statistical models of ash and slag concrete properties has been obtained, taking into account the influence of activation admixture, superplasticizer and sodium silicon fluoride consumption, cement-water ratio, temperature and the number of heating and cooling cycles.*

**Keywords:** heat-resistant concrete, fly ash, ash and slag mixture, superplasticizer, sodium fluorosilicate

### 1. Introduction

One of the common heat-resistant materials is Portland cement concrete, which contains active dispersed additives [1-4]. Such additives must bind free calcium oxide, which is formed during thermal decomposition of cement hydration products. At the same time they should not allow the formation of fusible substances with minerals of Portland cement.

A number of materials characterized by hydraulic activity can be used as such additives, and depending on their type, heat-resistant binders with various properties can be obtained [5-7].

One of such additives for cement heat-resistant concrete is fly ash. The properties of ash as a component of heat-resistant materials are determined by its Al<sub>2</sub>O<sub>3</sub> content (normalized Al<sub>2</sub>O<sub>3</sub> content of at least 20...25%), the recommended total content of free calcium oxide CaO and magnesium MgO up to 3%, carbonates – 2%, sulfates are not allowed in terms of SO<sub>3</sub> more than 4% and losses on ignition should be less than 8% [8-12].

The role of aggregate in heat-resistant concrete can be performed by ash and slag mixtures from hydraulic handling systems. For ash and slag mixtures it is necessary that the content of SiO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub> be at least 75%, including SiO<sub>2</sub> at least 40 %, sulfates in terms of SO<sub>3</sub> – up to 3 %, free CaO and MgO in the amount of less than 4 %, loss on ignition – up to 5% [3].

The ash activity at elevated temperatures correlates with that at normal temperature. The hydraulic activity of ashes, as well as other pozzolanic type materials, is mainly due to the chemical interaction of silicon and aluminum oxides included in them with calcium hydroxide, which is released during the hydrolysis of clinker minerals with formation of calcium silicate and calcium aluminate hydrates.

One of the methods for chemical activation of cements with addition of ash and slag is introduction of fluoride salts [13-16]. In accordance with theoretical concepts [14], substances containing fluorine ion can act in two directions:

- activating the breaking of Si-O bonds and transfer of silicon ions into solution;
- affecting the surface of minerals, replacing the OH-group.

For heat-resistant Portland cement concrete fluoride salts can be considered as activators and mineralizers. These salts intensifying the cement hardening processes at normal temperatures and facilitating the interaction of CaO with the glassy phases of ash at elevated temperatures [16]. The mineralizing effect of fluoride salts was studied mainly during the firing of cement clinker. The experience of using fluorosilicate admixture in the production of refractory concrete using liquid glass is known.

In the literature on the production of heat-resistant Portland cement concretes, the experience of using fluorosilicate compounds is insufficiently shown.

\* Autor corespondent/Corresponding author,  
E-mail: [v.v.zhitkovsky@nuwm.edu.ua](mailto:v.v.zhitkovsky@nuwm.edu.ua)

Table 1

| Material             | Chemical composition of the initial materials |                                |                                |       |                  |      |                  |                 |                  |
|----------------------|---|--------------------------------|--------------------------------|-------|------------------|------|------------------|-----------------|------------------|
|                      | Oxide content, %                              |                                |                                |       |                  |      |                  |                 |                  |
|                      | SiO <sub>2</sub>                              | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | CaO <sub>B</sub> | MgO  | R <sub>2</sub> O | SO <sub>3</sub> | Loss on ignition |
| Portland cement      | 21.47   | 5.26                           | 4.07                           | 66.38 | 0.32             | 0.62 | 0.29             | 1.46            | –                |
| Fly ash              | 54.2  | 25.5                           | 9.1                            | 2.5   | 0.5              | 1.5  | 1.2              | 2.5             | 2.9              |
| Ash and slag mixture | 60.8  | 22.1                           | 6.4                            | 2.4   | 1.6              | 1.4  | 1.3              | 2.3             | 3.2              |

The scientific hypothesis underlying the present study is possibility of a significant increase in initial and residual strength of heat-resistant concrete with ash and slag, improvement of a number of its other properties by using cement-ash binder with reduced water demand due to addition of superplasticizer and fluorosilicate activator.

## 2. The purpose of the work, materials and research methods

The purpose of this work is research possibility of improving the properties of heat-resistant cement concrete with addition of fly ash and use of ash and slag mixture as aggregate. For this purpose, it is used superplasticizer and sodium fluorosilicate admixtures.

The raw materials for investigating of heat-resistant ash and slag concrete are Portland cement, fly ash and ash and slag mixture of hydraulic removal-waste from a thermal power plant.

The chemical composition of the raw materials is given in Table 1.

The mineralogical composition of Portland cement is: C<sub>3</sub>S – 59.3%, C<sub>2</sub>S – 20.5%, C<sub>3</sub>A – 6.9%, C<sub>4</sub>AF – 11.1%.

Physical mechanical properties of Portland cement are: specific surface area ( $S_{sp}$ ) – 280 m<sup>2</sup>/kg, normal consistency – 25,3%, setting time, initial - 2 hours 15 minutes, final - 3 hours 51 minutes; strength at 7 days – flexural 5.1 MPa, compressive 32.2 MPa, 28 days – flexural 6.8 MPa, compressive 51.8 MPa.

The experiments used fly ash from the Burshtyn thermal power plant (Ukraine). This fly ash refers to type IV ashes which are used for structures operating under severe conditions [17].

Physical properties of fly ash: specific surface area 250 m<sup>2</sup>/kg, normal consistency – 25.9 28,1%, CaO absorption activity – 38.4 mg/g. Fly ash was also used, after grinding in a laboratory ball mill (specific surface area 350 m<sup>2</sup>/kg, normal consistency – 28.1%).

According to the value of the loss on ignition (Table 1), represented mainly by unburned carbonaceous particles, the ash can be classified as category B. According to the value of the dispersion index for the residue on a sieve with a mesh size of less than 45 μm, ash belongs to class 2 [17].

The ash-and-slag mixture used in the production of heat-resistant concretes as an aggregate met the requirements [18] and was a mixture of ash and fuel slag from hydraulic handling systems.

The maximum size of slag grains in the mixture was 5 mm, its content was 10% by weight. The specific surface area of the mixture was 150 m<sup>2</sup> / kg, the total residue on the sieve was 0.08-25%.

Total specific efficiency of natural radionuclides in fly ash was 110 Bq/kg, ash and slag mixture - 120 Bq/kg, which is significantly less than the permissible ( $A_{eff} < 370$  Bq/kg) for the production of building materials without restrictions [19].

The content of heavy metals in ash and ash and slag mixture (vanadium, copper, molybdenum, nickel, manganese, etc.) was within 0.05...0.07% of their mass, which ensures compliance with the established sanitary standards [20].

Ash and slag mixture was used as aggregate, the ash and slag fractions were <0.315 mm and 0.315...4 mm, respectively and their weight ratio was 1:3.

Powdered superplasticizer SP-1 Polyplast (SP) – a condensation product of naphthalene sulfonic acid and formaldehyde was used. The content of "active substance" in SP was at least 69%, pH of 2.5% aqueous solution – 7...9. An aqueous solution of SP-1 does not change its properties when heated to 85°C.

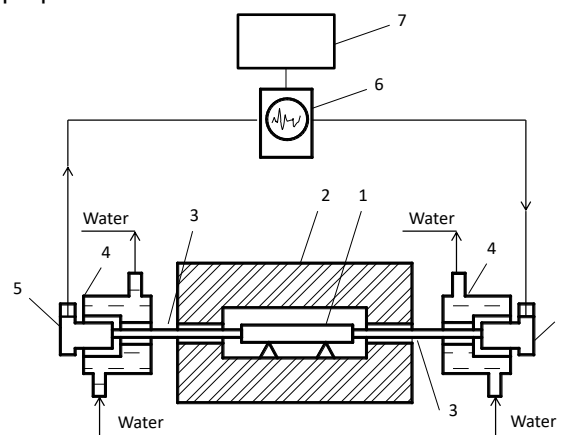


Fig. 1 - A scheme of device for measuring strength and dynamic modulus of elasticity at heating: 1 – tested specimen, 2 – electric furnace, 3 – high-temperature pipelines, 4 – water-cooled chambers, 5 – electro-acoustic transducers, 6 – ultrasonic device, 7 – digital printing device.

Table 2

Composition and physico-mechanical properties of activated cement–ash binder at normal hardening

| No | Binder composition, % |         |                                  | Flexural strength, MPa |        |         | Compressive strength, MPa |        |         |
|----|-----------------------|---------|----------------------------------|------------------------|--------|---------|---------------------------|--------|---------|
|    | Portland cement       | Fly ash | Na <sub>2</sub> SiF <sub>6</sub> | 1 day                  | 3 days | 28 days | 1 day                     | 3 days | 28 days |
|    |                       |         |                                  |                        |        |         |                           |        |         |
| 1  | 100                   | -       | -                                | 1.7                    | 3.4    | 6.2     | 18.7                      | 25.7   | 53.5    |
| 2  | 70                    | 30      | -                                | 1.2                    | 2.5    | 5.5     | 11.8                      | 18.7   | 46.5    |
| 3  | 60                    | 40      | -                                | 1.1                    | 2.2    | 5.0     | 10.7                      | 16.1   | 41.7    |
| 4  | 70                    | 30      | 0.5                              | 1.6                    | 4.5    | 5.6     | 15.0                      | 24.1   | 48.6    |
| 5  | 70                    | 30      | 1                                | 2.2                    | 4.8    | 5.8     | 16.5                      | 26.2   | 51.1    |
| 6  | 60                    | 40      | 0.5                              | 1.45                   | 3.9    | 5.5     | 12.3                      | 21.5   | 42.3    |
| 7  | 60                    | 40      | 1                                | 1.73                   | 4.1    | 5.9     | 13.5                      | 23.6   | 45.1    |

Table 3

The content of Ca(OH)<sub>2</sub> and CaO<sub>free</sub> in the cement-ash stone after heating

| No. | Cement stone composition, %  | Ca(OH) <sub>2</sub> content, % |        | CaO <sub>free</sub> content, % |        |        |
|-----|--|--------------------------------|--------|--------------------------------|--------|--------|
|     |  | 400 °C                         | 500 °C | 600 °C                         | 700 °C | 800 °C |
| 1   | Portland cement – 70; fly ash – 30<br>(S <sub>sp</sub> =280 m <sup>2</sup> /kg);                                     | 11.7                           | 11.2   | 6.1                            | 4.3    | 2.6    |
| 2   | Portland cement – 70; fly ash – 30<br>(S <sub>sp</sub> =280 m <sup>2</sup> /kg); Na <sub>2</sub> SiF <sub>6</sub> -1 | 9.5                            | 7.4    | 3.9                            | 2.1    | 1.5    |
| 3   | Portland cement – 70; fly ash – 30<br>(S <sub>sp</sub> =350 m <sup>2</sup> /kg)                                      | 10.3                           | 9.4    | 5.2                            | 2.7    | 1.4    |
| 4   | Portland cement – 70; fly ash – 30<br>(S <sub>sp</sub> =350 m <sup>2</sup> /kg); Na <sub>2</sub> SiF <sub>6</sub> -1 | 8.2                            | 5.9    | 2.8                            | 1.4    | -      |

\*- hardening at normal conditions before heating is 3 days.

Sodium fluorosilicate with a Na<sub>2</sub>SiF<sub>6</sub> content of at least 95% was used as a fluoride activator for ash and slag concrete.

Tests were performed using known standard techniques [2].

To determine the strength and dynamic modulus of elasticity of the specimens during heating, ultrasonic method was applied using a device, shown in Figure 1. The strength and dynamic modulus of elasticity of the samples were determined using ultrasonic transducers at a frequency of 60 kHz.

To obtain of experimental-statistical models, the mathematical experiments planning method was used [21].

### 3. Experimental research and analysis of the results

Adding a fluorosilicate activator to the binder composition did not affect the setting time, normal consistency, and cone flow of cement-ash mortars, but yielded an increase in their early strength (Table 2).

To study the fluorosilicate activator influence in a cement-ash stone during heating, cubic specimens 2×2×2 cm (six samples at each test point) were heated in a muffle furnace to a temperature of 400, 500, 600, 700, and 800° C with an isothermal exposure of 1 hour. The content of free CaO was determined by the ethylo-glycerate method.

The data of chemical analysis (Table 3) indicate that there is a reaction of intense binding CaO<sub>free</sub>, which is formed when the cement-ash stone is heated in the range of 600...800° C, depending on the dispersion of the binder. Introduction of 1% of Na<sub>2</sub>SiF<sub>6</sub> admixture makes this process noticeable even at 500° C.

Table 4 presents the values of cement-ash stone specimens' relative compressive strength at 28 days for W/C corresponding to normal consistency and kinetics of its change when heated. As results from the obtained data, up to 100...200°C, the strength of cement and cement-ash stone increases, which can be explained by an additional increase in the cement hydration degree and removal of mechanically bound water. With further increase in temperature, the strength gradually decreases. The degree of reduction in final strength of cement stone at 800° C is not the

Table 4

| No. | Binder composition, % |         |                                  | S <sub>sp</sub> , m <sup>2</sup> /kg | Heating temperature, °C |      |      |      |
|-----|-----------------------|---------|----------------------------------|--------------------------------------|-------------------------|------|------|------|
|     | Portland cement       | Fly ash | Na <sub>2</sub> SiF <sub>6</sub> |                                      | 100                     | 200  | 500  | 800  |
|     | 1                     | 100     | -                                |                                      | -                       | 280  | 79.4 | 87.5 |
| 2   | 70                    | 30      | -                                | 280                                  | 67.5                    | 72.6 | 51.3 | 44.2 |
| 3   | 70                    | 30      | 1                                | 280                                  | 77.4                    | 81.2 | 74.5 | 63.4 |
| 4   | 70                    | 30      | -                                | 350                                  | 85.3                    | 88.8 | 58.5 | 50.1 |
| 5   | 70                    | 30      | 1                                | 350                                  | 88.1                    | 89.4 | 79.9 | 72.4 |

Note: \*cement stone strength at normal hardening is taken as 100%.

same for the studied binders. For a cement-ash binder, it is 50...56%, and with addition of sodium fluorosilicate strength reduction reaches 28...37%. An increase in ash grinding fineness leads to both higher initial cement-ash stone strength.

To study concrete properties, mixtures were made using cement-ash binder (fly-ash –30%, S<sub>sp</sub>=350 m<sup>2</sup>/kg) and ash - slag mixture as an aggregate. The water demand of the investigated fine-grained concrete mixture changed at a given workability depending on the type and content of additives and cement/aggregate ratio (Figure 2).

W, l/m<sup>3</sup>

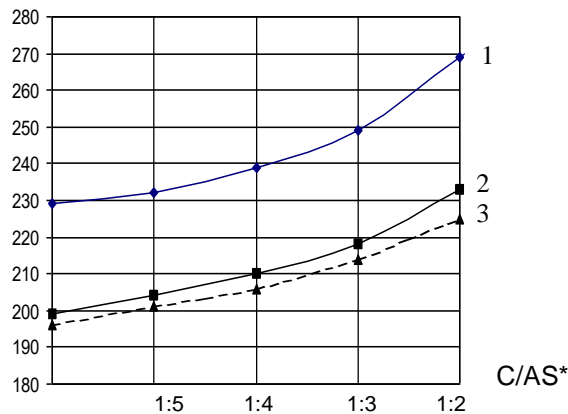


Fig. 2 - Water demand of a fine-grained concrete mixture (SC=1...4 cm) with ash and slag aggregate: 1 – without additives; 2 – with superplasticizer (1 % by binder weight); 3 – with complex admixture (SP – 1% + Na<sub>2</sub>SiF<sub>6</sub> – 1%); AS\* – ash and slag mixture.

Statistical approximation of the results obtained for concrete specimens compressive strength (R<sub>cem</sub>) at 28 days for the given conditions under normal hardening enabled to obtain an equation for concrete with 1% of SP+1% Na<sub>2</sub>SiF<sub>6</sub>:

$$R_c = 0.44R_{cem}(1/(W/C) - 0.1) \quad (1)$$

where R<sub>cem</sub> is the compressive strength of cement-ash binder.

1/(W/C)

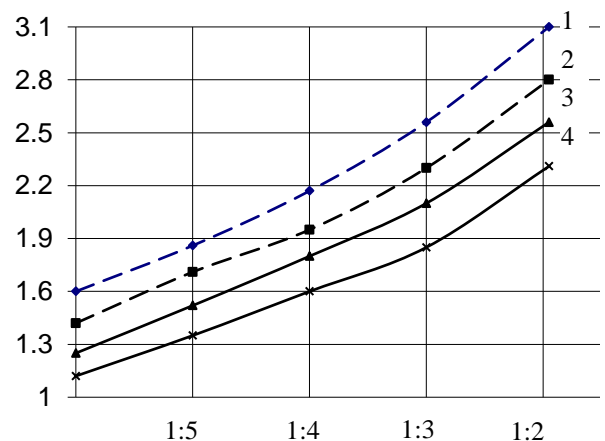


Fig. 3 - Dependence 1/(W/C) vs. C/AS for mixtures of various workability: 1 – mixture with complex admixture SP+Na<sub>2</sub>SiF<sub>6</sub> with V=11...20 sec; 2 – mixture without admixture with V=11...20 sec; 3 – mixture with complex SP+Na<sub>2</sub>SiF<sub>6</sub> admixture with SC=1...4 cm; 4 – mixture without admixtures with SC=1...4 cm.

When finding the concrete compositions according to Eq. (1), W/C was calculated, and according to the graph in Figure 3 the mass ratio between binder, ash and slag aggregate (n=C/AS), which ensures the given workability, was found.

The binder consumption was obtained from the absolute volumes conditions (2). Cement, water and ash-slag aggregate were calculated according to Eqs. (3, 4, 5):

$$\frac{C}{\rho_C} + \frac{AS}{\rho_{AS}} + \frac{W}{\rho_W} = 1000 \quad (2)$$

where C, AS, W are the consumption of binder, ash and slag aggregate and water in kg/m<sup>3</sup>, ρ<sub>C</sub>, ρ<sub>AS</sub>, ρ<sub>W</sub> are the densities of these components in kg/m<sup>3</sup>.

$$C = \frac{1000}{\frac{1}{\rho_C} + \frac{W}{C} + \frac{1/n}{\rho_{AS}}} \quad (3)$$

$$W = C \cdot W/C \quad (4)$$

Table 5

The change in concrete specimens strength after drying

| No.   | W/C  | Compressive strength, MPa |                                   |                                   | Bending Strength, MPa |                                   |                                   |
|---|------|---------------------------|-----------------------------------|-----------------------------------|-----------------------|-----------------------------------|-----------------------------------|
|   |      | Normal hardening          | Heating to 150° C at $V_t=20^0/h$ | Heating to 150° C at $V_t=50^0/h$ | Normal hardening      | Heating to 150° C at $V_t=20^0/h$ | Heating to 150° C at $V_t=50^0/h$ |
| <i>Concrete without admixtures</i>                                |      |                           |                                   |                                   |                       |                                   |                                   |
| 1   | 0,73 | <u>10.3</u><br>18.5       | <u>18.0</u><br>26.8               | <u>16.5</u><br>24.1               | <u>3.1</u><br>3.7     | <u>5.0</u><br>4.8                 | <u>4.3</u><br>4.1                 |
| 2   | 0,63 | <u>21.5</u><br>26.5       | <u>34.4</u><br>36.6               | <u>28.0</u><br>27.8               | <u>3.5</u><br>4.3     | <u>4.9</u><br>4.7                 | <u>3.9</u><br>4.1                 |
| 3   | 0,54 | <u>24.5</u><br>30.3       | <u>36.8</u><br>37.9               | <u>29.4</u><br>29.7               | <u>3.9</u><br>4.5     | <u>5.5</u><br>4.7                 | <u>3.9*</u><br>4.1*               |
| 4   | 0,46 | <u>26.4</u><br>36.5       | <u>37.0</u><br>42.0               | <u>28.5</u><br>31.0               | <u>4.2</u><br>5.4     | <u>4.4</u><br>5.1                 | <u>3.6*</u><br>4.2*               |
| <i>Concrete with SP + Na<sub>2</sub>SiF<sub>6</sub> admixture</i> |      |                           |                                   |                                   |                       |                                   |                                   |
| 5   | 0,64 | <u>22.3</u><br>25.8       | <u>37.9</u><br>40.0               | <u>37.9</u><br>38.7               | <u>3.4</u><br>4.9     | <u>6.0</u><br>8.6                 | <u>5.8</u><br>8.3                 |
| 6   | 0,56 | <u>25.1</u><br>31.5       | <u>41.4</u><br>44.1               | <u>40.2</u><br>44.7               | <u>4.2</u><br>5.3     | <u>6.1</u><br>6.6                 | <u>5.9</u><br>6.9                 |
| 7   | 0,48 | <u>28.1</u><br>36.8       | <u>40.7</u><br>44.2               | <u>39.3</u><br>43.4               | <u>4.5</u><br>5.7     | <u>6.1</u><br>6.3                 | <u>6.3</u><br>6.6                 |
| 8   | 0,38 | <u>32.5</u><br>42.5       | <u>43.9</u><br>48.9               | <u>44.5</u><br>46.8               | <u>5.1</u><br>5.1     | <u>6.4</u><br>5.6                 | <u>6.1</u><br>5.6                 |

**Note:** 1. Above the line are test results after 7 days, below the line - after 28 days;

2.\* – cracks were detected after heating the specimens.

$$AS = \frac{1}{n/C} \quad (5)$$

The calculated compositions were adjusted experimentally.

The quality and durability of heat-resistant concrete depends on its drying and first heating. The technological task of drying is to remove moisture from concrete in the shortest possible time while ensuring its integrity. When drying concrete, stresses are caused by temperature gradients and water vapor pressure.

The change in strength of concrete specimens that were previously kept at normal conditions for 7 and 28 days was determined after drying to completely remove of mechanically bound water at 150° C at 20 and 50°/h. The results of the experiments are shown in Table 5. The strength was determined on samples-prisms 40×40×160 mm. At each experimental point, three prisms were tested for bending according to a three-point scheme.

Analysis of the data shows that for soft drying and the rate of temperature increase of  $V_t=20^0/h$  the strength of ash and slag concrete, both without admixtures and with the complex SP+Na<sub>2</sub>SiF<sub>6</sub> admixture, is increasing.

The increase in compressive strength for concrete that previously hardened under normal temperature and humidity conditions for 7 days reaches at  $V_t=20^0/h$  75%, from 7 to 28 days – up to 30%. With an decrease in W/C, the strength growth at drying decreases. The increase in flexural strength under constant drying conditions is significantly lower compared to compression strength. For concrete with a complex admixture, the difference in the increase in compressive and flexural strength is leveled, which may indicate a lower effect of destructive processes during heating. This conclusion is even more obvious with an increase in the rate of temperature rise to 50°/h.

One of the significant destructive factors for heat-resistant concrete is shrinkage, which develops during drying and first heating. There is shrinkage at concrete drying, caused by evaporation of adsorption and capillary-bounded water and fire (thermal) shrinkage, caused mainly by the removal of chemically bounded water during cement stone hardening products dehydration.

For design purposes, the simplest and most convenient equation for concrete shrinkage at it drying is [22]:

$$\varepsilon_{shr} \cdot 10^6 = 0,125W\sqrt{W} \quad , \quad (6)$$

where W – is water demand of concrete mixture.

Table 6

Experimental and calculated values of ash and slag concrete shrinkage

| No  | C, kg/m <sup>3</sup> | W, l/m <sup>3</sup> | W/C  | Shrinkage values, $\epsilon_{shr} \cdot 10^5$ |  |  |
|---|----------------------|---------------------|------|---|--|--|
|   |                      |                     |      | Hardening 100 days at normal conditions       | Hardening 28 days at normal conditions, followed by drying | Calculated values according to Eq. (6) |
| <i>Concrete without admixtures</i>                                |                      |                     |      |   |  |  |
| 1   | 320                  | 235                 | 0,73 | 43  | 50   | 45                                     |
| 2   | 380                  | 238                 | 0,63 | 49  | 53   | 46                                     |
| 3   | 460                  | 250                 | 0,54 | 52  | 47   | 49                                     |
| 4   | 600                  | 275                 | 0,46 | 54  | 51   | 57                                     |
| <i>Concrete with SP + Na<sub>2</sub>SiF<sub>6</sub> admixture</i> |                      |                     |      |   |  |  |
| 5   | 320                  | 205                 | 0,64 | 35  | 40   | 37                                     |
| 6   | 380                  | 212                 | 0,56 | 37  | 43   | 39                                     |
| 7   | 460                  | 220                 | 0,48 | 45  | 43   | 41                                     |
| 8   | 600                  | 230                 | 0,38 | 48  | 42   | 44                                     |

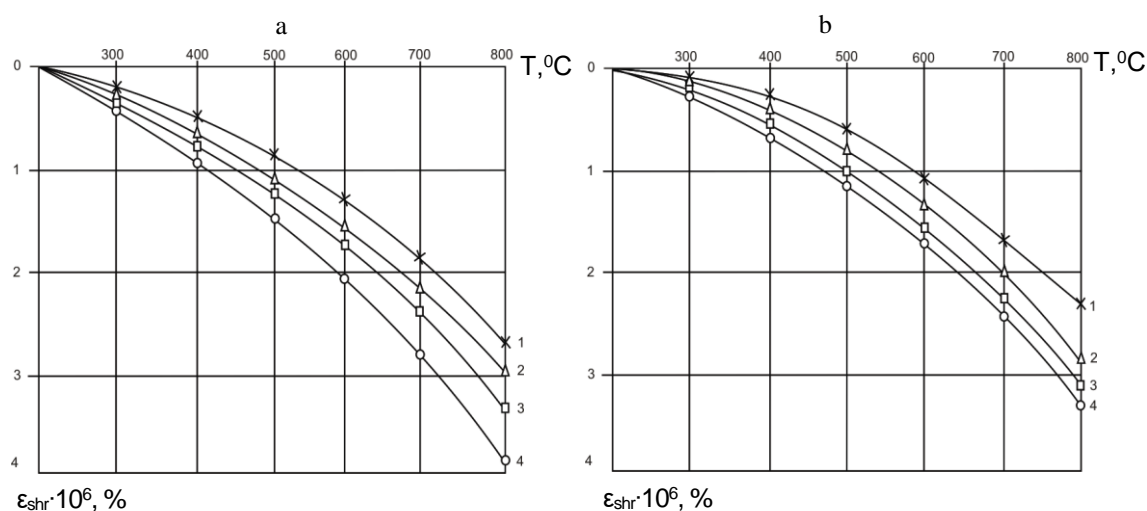


Fig. 4- Fire shrinkage of ash and slag concrete at heating:

**a** – without admixtures (1 – W=230 l/m<sup>3</sup>; W/C=0.74; 2 – W=238 l/m<sup>3</sup>; W/C=0.63; 3 – W=250 l/m<sup>3</sup>; W/C=0.54; 4 – W=275 l/m<sup>3</sup>; W/C=0.45);

**b** – with SP+ Na<sub>2</sub>SiF<sub>6</sub> (1 – W=205 l/m<sup>3</sup>; W/C =0.66; 2 – W=231 l/m<sup>3</sup>; W/C=0.56; 3 – W=220 l/m<sup>3</sup>; W/C =0.48; 4 – W=235 l/m<sup>3</sup>; W/C =0.39).

Table 6 compares the experimental values of ash and slag concrete shrinkage obtained for normal hardening and drying at 150° C ( $V_t=20^\circ\text{C/h}$ ), as well as the calculated values of shrinkage according to Eq. (6). The data were obtained for concrete mixtures of the same workability (cone slump - 1 ... 4 cm) at different cement consumption. The table shows that the value of concrete shrinkage at normal hardening and drying at elevated temperatures is slightly different and differs from the calculated values (Eq.

6). With increasing cement consumption, especially over 450 kg and, accordingly, a decrease in w/c to ensure constant slump, the water content of the concrete mixture increased significantly. This result is consistent with the water demand constancy rule of fresh concrete. [23]. Using a complex admixture helps to reduce the water demand at constant cement consumption and accordingly, reduces shrinkage deformation both at normal hardening and after drying at elevated temperatures.

Table 7

Experiments planning conditions for studying the effect of cyclic heating and cooling on the ash and slag concrete properties

| Factors   |                | Variation levels |     | Range of variation |
|---|----------------|------------------|-----|--------------------|
|   |                | -1               | +1  |                    |
| Admixtures content (1% SP+1% Na <sub>2</sub> SiF <sub>6</sub> )*, Ad, kg/m <sup>3</sup> | x <sub>1</sub> | 0                | 10  | 10                 |
| Water-Cement ratio, W/C   | x <sub>2</sub> | 0.67             | 0.4 | 0.27               |
| Heating temperature, T, °C  | x <sub>3</sub> | 300              | 800 | 500                |
| Number of heating and cooling cycles, N   | x <sub>4</sub> | 15               | 35  | 10                 |

Table 8

Regression equations for ash and slag concrete properties after cyclic heating and cooling

| Parameters                                  | Regression equation   |
|---|---|
| Compressive strength (R <sub>c</sub> ), MPa | $Y_1 = 11.237 + 3.662X_1 + 2.962X_2 - 0.112X_3 - 0.83X_4 + 0.537X_1X_2 - 0.262X_1X_3 - 0.112X_1X_4$ |
| Flexural strength (R <sub>f</sub> ), MPa    | $Y_2 = 2.225 + 0.55X_1 + 0.225X_2 - 0.05X_3 - 0.175X_4 + 0.05X_1X_2 - 0.02X_1X_3$                   |
| Dynamic modulus of elasticity               | $Y_3 = 2.205 + 0.305x_1 + 0.28x_2 - 0.102x_3 - 0.172x_4 - 0.02x_1x_2 - 0.047x_1x_3 + 0.077x_1x_4$   |
| Water absorption (W), %                     | $Y_4 = 11.35 - 1.275X_1 - 1.175X_2 + 0.05X_3 + 0.3X_4 - 0.6X_1X_2 - 0.02X_1X_3 - 0.125X_1X_4$       |
| Conditional elongation (ε <sub>con</sub> )  | $Y_5 = 0.999 + 0.106X_1 - 0.025X_2 - 0.017X_3 - 0.004X_4 + 0.02X_1X_2 - 0.022X_1X_4$                |

Fire shrinkage of heat-resistant concrete is less studied than moisture shrinkage [22]. It is determined at a given temperature by cement consumption, type and content of admixtures [4]. A certain effect on fire shrinkage has the type of aggregate [2]. Fire shrinkage of concrete was determined on dried 40×40×160 mm prism specimens when heated to 300, 500, 700 and 800° C. The experimental results are shown in Figure 4.

Analysis of the experimental data shows that for the investigated ash and slag concrete without admixtures the maximum shrinkage at the highest possible temperature of 800°C is up to 0.4%.

Using a complex SP+Na<sub>2</sub>SiF<sub>6</sub> admixture allows reducing fire shrinkage by 15...20%, which can be explained by the plasticizing effect and possibility of reducing cement consumption at W/C =const.

In the operation process, heat-resistant concrete is subjected to cyclic heating and cooling effects. In this case, the destructive processes occur, causing accumulation of internal stresses, microcracks formation and a decrease in concrete strength [1-3].

The investigated concrete was cycled at a speed of 150°C/h with an exposure of 4 h and cooling to a temperature of 20°C. The experiments were carried out according to the method of mathematical experiments planning using a two-

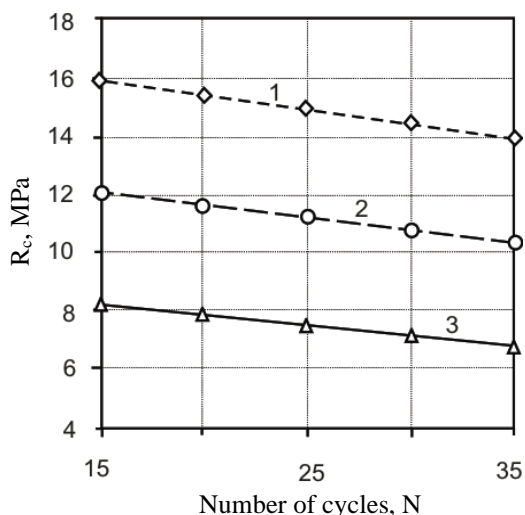


Fig. 5 - Influence of heating and cooling cycles (N) and complex additives (Ad) on compressive strength ( $R_c$ ) of ash and slag concrete ( $W/C = 0.67$ ;  $T=800^{\circ}C$ ): 1 –  $Ad=10 \text{ kg/m}^3$ ; 2 –  $Ad= 5 \text{ kg/m}^3$ ; 3 –  $Ad=0 \text{ kg}$ .

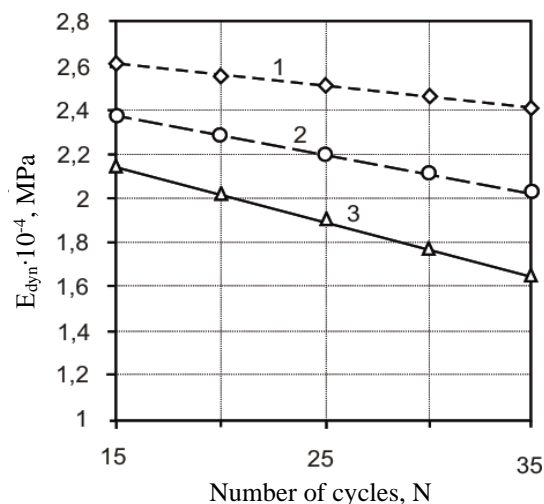


Fig.7- The influence of heating and cooling cycles number (N) and complex additives consumption (Ad) on dynamic modulus of elasticity ( $E_{dyn}$ ) of ash slag concrete ( $W/C=0.67$ ;  $T=800^{\circ}C$ ): 1 –  $Ad=10 \text{ kg/m}^3$ ; 2 –  $Ad= 5 \text{ kg/m}^3$ ; 3 –  $Ad=0 \text{ kg/m}^3$ .

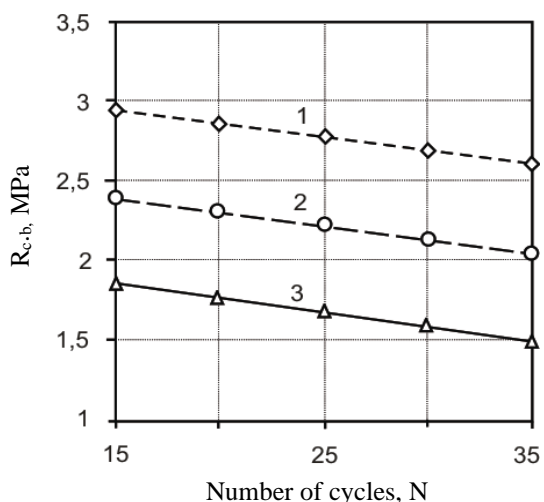


Fig. 6 - Influence of heating and cooling cycles (N) and complex additives (Ad) on flexural strength ( $R_{c,b}$ ) of ash and slag concrete ( $W/C = 0.67$ ;  $T=800^{\circ}C$ ): 1 –  $Ad=10 \text{ kg/m}^3$ ; 2 –  $Ad= 5 \text{ kg/m}^3$ ; 3 –  $Ad=0 \text{ kg/m}^3$ , ( $W/C = 0.67$ ;  $T=800^{\circ}C$ ).

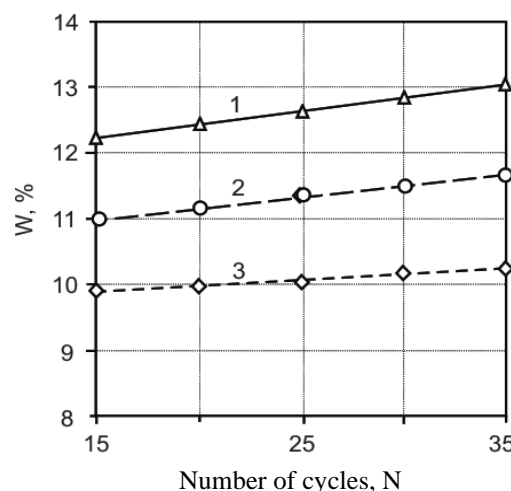


Fig.8 - The influence of heating and cooling cycles number (N) and complex additives consumption (Ad) on water absorption (W) of ash slag concrete ( $W/C=0.67$ ;  $T=800^{\circ}C$ ): 1 –  $Ad=10 \text{ kg/m}^3$ ; 2 –  $Ad= 5 \text{ kg/m}^3$ ; 3 –  $Ad=0 \text{ kg/m}^3$

level plan 2<sup>4-1</sup> [21]. The experimental design conditions are given in Table 7.

The obtained regression equations for compressive and bending strength, dynamic modulus of elasticity and water absorption of ash and slag concrete, which were subjected to cyclic heating and cooling, are given in Table 8.

Additionally, the conditional elongation parameter was calculated as a ratio of flexural strength to dynamic modulus of elasticity ( $R_f/E_{dyn}$ ), characterizing the crack resistance of concrete [24].

Analysis of the obtained regression equations enables to establish the direction and force of the influence of the studied factors, as well

as the effects of their interaction. Using the complex  $SP+Na_2SiF_6$  admixture leads to an increase in compressive and flexural strength, the dynamic elastic modulus value, conditional elongation and a decrease in water absorption (Figure 5-9).

Increasing the number of heating and cooling cycles in a given temperature range causes the opposite effect. Attention is drawn to certain effects of pairwise interactions between factors that characterize the admixture content, water-cement ratio, heating temperature, and the number of heating and cooling cycles.

To characterize the specific influence of each of the factors on the investigated parameter, coefficient  $\chi$  can be used [25]:



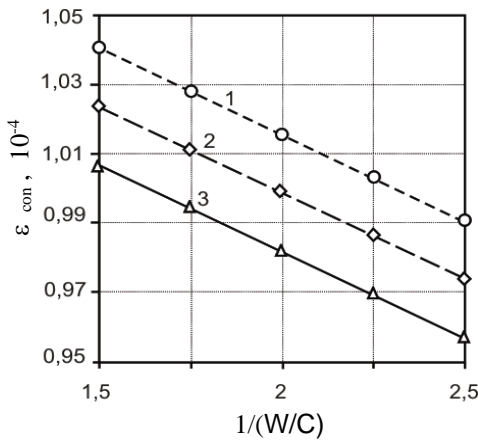


Fig. 9 - The influence of water-cement ratio (1/(W/C)) and heating and cooling cycles number (N) on conditional elongation (ε<sub>con</sub>) of ash and slag concrete (Ad=10 kg/m<sup>3</sup>; T=800° C): 1 – N=15; 2 – N=25; 3 – N=35.

$$\chi = \frac{|b_i + b_{sj}|}{b_0} \tag{7}$$

where b<sub>0</sub>, b<sub>1</sub> and b<sub>sj</sub> are regression coefficients of the corresponding regression equations.

Diagrams of coefficient χ values for indicators of ash and slag concrete properties after their cyclic heating and cooling (Figure 10) enable to rank factors by their relative effect and place them in decreasing order (Table 9).

Analysis of the obtained experimental-statistical models shows that using an admixture including superplasticizer and sodium fluorosilicate is an effective technological method that improves the properties and increases the workability of heat-resistant ash and slag concrete under their cyclic heating and cooling conditions.

Table 9

Factors and their effect on concrete properties

| Concrete properties           | Coded factors   | Natural factors |
|-------------------------------|---|-----------------|
| Compressive strength          | X <sub>1</sub> > X <sub>2</sub> >X <sub>4</sub> >X <sub>3</sub> | Ad>W/C >N>T     |
| Flexural strength             | X <sub>1</sub> > X <sub>2</sub> >X <sub>4</sub> >X <sub>3</sub> | Ad > W/C >N>T   |
| Dynamic modulus of elasticity | X <sub>1</sub> > X <sub>2</sub> >X <sub>3</sub> >X <sub>4</sub> | Ad > W/C >T>N   |
| Water absorption              | X <sub>1</sub> > X <sub>2</sub> >X <sub>4</sub> >X <sub>3</sub> | Ad > W/C >N>T   |
| Conditional elongation        | X <sub>1</sub> > X <sub>4</sub> >X <sub>3</sub> >X <sub>2</sub> | Ad > N>T > W/C  |

#### 4. Conclusions

1. Using sodium fluorosilicate admixture increases the early compressive strength of the cement-ash binder, when hardened under normal conditions, reduces the temperature and intensifies the chemical binding of calcium oxide, which is formed when the cement-ash stone is heated. The compressive strength of cement-ash stone with the Na<sub>2</sub>SiF<sub>6</sub> admixture increases significantly when heated in the temperature range of 500-800° C.

2. A method has been developed for design concrete compositions on a cement-ash binder, activated by addition of Na<sub>2</sub>SiF<sub>6</sub>, and an ash-slag mixture as aggregate with additional introduction of a superplasticizer admixture. For this purpose, experimental dependences of the concrete mixture water demand were obtained. Dependencies for cement/water ratio of concrete with a given strength and the ratio of cement and ash-slag mixture consumptions vs. cement/water ratio were also obtained.

3. A change in slag concrete strength after preliminary hardening at normal conditions and subsequent drying until the mechanically bounded water is completely removed at 150° C at a speed of 20 and 50 %/h was established. A positive effect on the ash and slag concrete strength after drying has been also obtained when the complex admixture of SP superplasticizer and Na<sub>2</sub>SiF<sub>6</sub> is used.

4. Using a complex admixture of superplasticizer and sodium fluorosilicate for ash and slag concrete reduces shrinkage at normal hardening, drying, as well as fire shrinkage after concrete heating to 800° C.

5. Experimental-statistical strength models of ash and slag concrete, their dynamic modulus of elasticity, water absorption and conditional elongation after cyclic heating and cooling are obtained. These models allow predicting the effect of cement-water ratio, temperature, number of heating and cooling cycles on the physic-mechanical properties. Using complex admixtures of superplasticizer and Na<sub>2</sub>SiF<sub>6</sub> has the highest positive effect on the heat-resistant ash and slag concrete properties compared to other factors in the selected variation range.

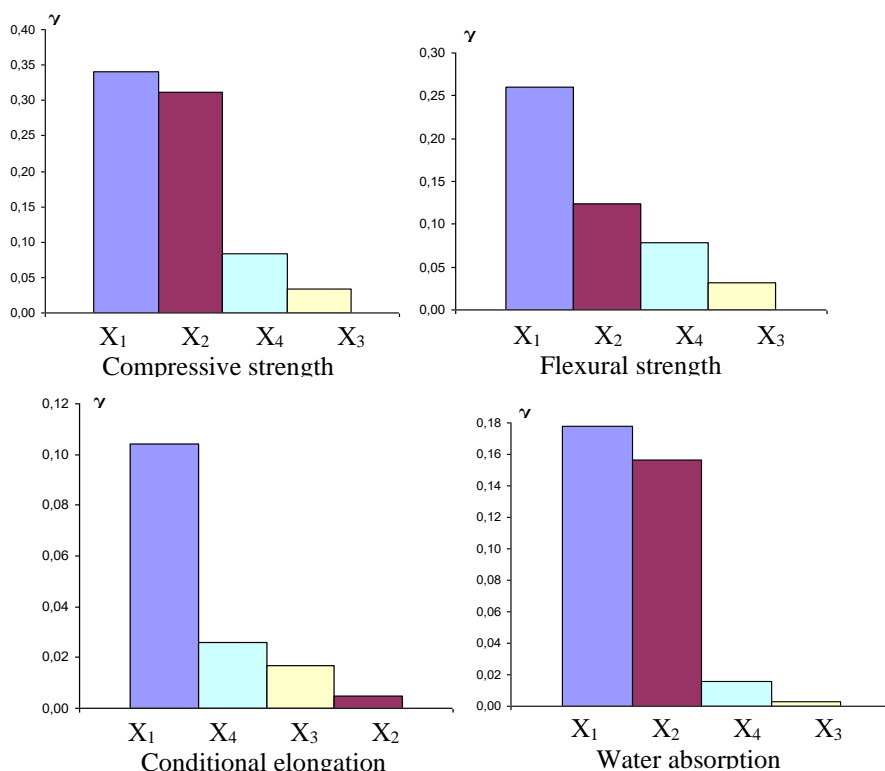


Fig. 10 - The value  $\chi$  coefficient for indicators of ash and slag concrete properties after cyclic heating and cooling:  $X_1, X_2, X_3, X_4$  – variation factors (according to Table 7).

**REFERENCES**

[1]. A. Petzold, M. Rohes, Concrete for High Temperatures, Maclaren, 1970, 235.

[2]. Baifu Luo, Yi Luo, The Effect Of Hold Times On The Stress-Strain Relationship For Steel Fiber-Reinforced Reactive Powder Concrete at Elevated Temperatures, Romanian Journal of Materials, 50 (2), 2020, 274 - 282.

[3]. L. Dvorkin, O. Dvorkin, Special concretes, Infra-Inzheneriya, 2012, 368 (in Russian).

[4]. A. Neville, Properties of Concrete. Prentice Hall, 1995, 864.

[5]. Jayant D. Bapat, Mineral Admixtures in Cement and Concrete, CRC Press Taylor & Francis Group, 2017, 310.

[6]. S. Aidin, B. Baradan, Effect of pumice and fly ash incorporation on high temperature resistance of cement based mortars. Cement and Concrete Research, 37(6), 2007, 988-995.

[7]. M. Tokyay. Cement and Concrete Mineral Admixtures. CRC Press Taylor & Francis Group, 2016, 225.

[8]. S. Aydin, Development of high temperature resistant mortar by using slag and pumice, Fire Safety Journal, 43(8), 2008, 610-617.

[9]. R. Ibrahim, R. Hamid, M. Taha, Fire Resistance of High-Volume Fly Ash Mortars with Nanosilica Addition. Construction and Building Materials, 36, 2012, 779-786.

[10]. R. Sahren, T. Sui, Concrete and Sustainability, CRC Press Taylor & Francis Group, 2014, 413.

[11]. S. Donatello, C. Kuenzel, A. Palomo, A. Fernandez-Jumener, High Temperature Resistance of a Very High Volume Fly Ash Cement Paste, Cement and Concrete Composites, 45, 2014, 234-242.

[12]. L. Dvorkin, O. Dvorkin, Y. Ribakov, Construction Materials Based on Industrial Waste Products. Nova Publishers, 2016, 242.

[13]. V. Fan, S. Yin, Z. Wen, S. Zhong, Activation of Fly Ash and Its Effects on Cement Properties, Cement and Concrete Research, 29(4), 1999, 467-472.

[14]. L. Svatovskaya, M. Sychev, Activated Hardening of Cements, Stroyizdat, 1983, 160 (in Russian).

[15]. B. Volkonskiy, P. Konovalov, S. Malyshev, Mineralizers in the Cement Industry, Stroyizdat, 1964, 198 (in Russian).

[16]. F. Locher, Cement-Principles of Production and Use, Verlag Bau + Technik CmbH, 2006, 535.

[17]. EN 450-1:2012, Fly Ash for Concrete - Part 1: Definition, Specifications and Conformity Criteria.

[18]. GOST 25592-91, Ash and Slag Mixtures of Thermal Power Plants for Concrete, Technical Conditions, 1992, 32 (in Russian).

[19]. GOST 30108-94, Building Materials and Products. Determination of the Specific Effective Activity of Natural Radionuclide, 1994, 45 (in Russian).

[20]. MU 2.1.674-97, Sanitary And Hygienic Assessment Of Building Materials With Additives Of Industrial Waste, 1997, 40 (in Russian).

[21]. L. Dvorkin, O. Dvorkin, Y. Ribakov, Mathematical experiments planning in concrete technology, Nova Science Publishers, 2012, 175.

[22]. O. Berg, U. Shcherbakov, G. Pisanko, High Strength Concrete. Stroyizdat, 1971, 208 (in Russian).

[23]. Dvorkin, O. Dvorkin and Ribakov, Y. Multi-Parametric Concrete Compositions Design, Nova Science Publishers, New York, 2013, 223.

[24]. L. Dvorkin, O. Dvorkin, Basics of Concrete Science, Stroibeton, 2006, 689 (in Russian).

[25]. V. Voznesenski, T. Layshenko, V. Ogarkov, Numeral Methods of Decision of Construction-Technological Tasks on Computer, Vysha Shkola, 1989, 328 (in Russian).

\*\*\*\*\*