doi: 10.18720/MCE.80.1

The improving of the concrete quality in a monolithic clip

Повышение качества бетона в монолитной обойме

A.M. Sychova*,
Military Space Academy named after A.F. Mozhaysky, St. Petersburg, Russia,
L.B. Svatovskaya,
Emperor Alexander I St. Petersburg State Transport University, St. Petersburg, Russia,
D.S. Starchukov,
Military Space Academy named after A.F. Mozhaysky, St. Petersburg, Russia,
V.Y. Soloviova,
Emperor Alexander I St. Petersburg State Transport University, St. Petersburg, Russia,
M.V. Gravit,
Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia

Д-р техн. наук, профессор А.М. Сычева*,
Военно-космическая академия имени А.Ф. Можайского, Санкт-Петербург, Россия,
д-р техн. наук, профессор Л.Б. Сватовская,
Петербургский государственный университет путей сообщения Императора Александра I, Санкт-Петербург, Россия,
канд. техн. наук, доцент Д.С. Старчуков,
Военно-космическая академия имени А.Ф. Можайского, Санкт-Петербург, Россия,
д-р техн. наук, профессор В.Я. Соловьева,
Петербургский государственный университет путей сообщения Императора Александра I, Санкт-Петербург, Россия,
канд. техн. наук, доцент М.В. Гравит,
Санкт-Петербургский политехнический университет Петра Великого, Санкт-Петербург, Россия

Key words: clip; silica Sol; heavy concrete; Gibbs free energy; surface energy; surface hardness; corrosion resistance

Ключевые слова: обойма; кремнезоль; тяжелый бетон; энергия Гиббса; поверхностная энергия; твердость поверхности; коррозионная устойчивость

Abstract. The article deals with the possibility of increasing strength, hardness, frost resistance, water and corrosion resistance of concrete. The reduction of its abrasion resistance and water absorption by creating a layer of nonorganic monolithic high-strength clip on its surface is also considered. The possibility of synthesis of such clip by impregnating the concrete surface with a Sol of SiO2 is shown and thermodynamically substantiated. The mathematical dependence reflecting the strength of concrete in such a clip is developed. The distribution of efforts between the clip and not strengthened kernel in the case of load action is shown. The methods of X-ray, differential thermal analysis, electron microscopy and analysis of pore size were used for researching the phase composition and structure of the clip, as well as its porous structure. It was established experimentally the improvement of the various performance properties of concrete due to the presence of inorganic monolithic clip up to 200 %. Corrosion resistance of concrete in various aggressive environments is demonstrated and the concrete corrosion depth under the age of 50 years is calculated.

Аннотация. В статье показана возможность повышения прочности, твердости, морозостойкости, водонепроницаемости, коррозионной устойчивости, а также снижения истираемости и водопоглощения бетона за счет создания на его поверхности слоя неорганической монолитной высокопрочной обоймы. Показана и термодинамически обоснована возможность синтеза такой обоймы путем пропитки поверхности бетона золем SiO2. Разработана математическая зависимость, отражающая прочность бетона в такой обойме. Показано распределение усилий между обоймой и не упрочненным ядром в случае действия нагрузки. Рентгенографическим, дериватографическим методом, а также методом электронной микроскопии и порометрии исследован фазовый состав и структура новообразований обоймы, а также ее пористая структура. Экспериментально установлено улучшение до 200 % различных эксплуатационных свойств бетона за счет присутствия неорганической монолитной обоймы. Показано коррозионная устойчивость бетона в различных агрессивных средах и рассчитана глубина коррозии бетона в возрасте до 50 лет.

Сычева А.М., Сватовская Л.Б., Старчуков Д.С., Соловьева В.Я., Гравит М.В. Повышение качества бетона в монолитной обойме // Инженерно-строительный журнал. 2018. № 4(80). С. 3–14.

1. Introduction

It is known that there are various ways to increase concrete strength, for example, by the mechanical activation of the concrete mix [1–3]. In addition, methods of physical-chemical and mechanical activation of cement are widely used in practice [4–7]. But it is well known that the introduction of modifying additives in the concrete mixture [8–11] cannot implement the provision of cement completely, and it continues to harden with time.

The use of nanoparticles of different nature to improve the various properties of the concrete follows from the literature review.

TiO_2 nanoparticles effects on physical, thermal and mechanical properties of self-compacting concrete with ground granulated blast furnace slag as binder is shown in [12].

The effect of limewater on strength and percentage of water absorption of Al_2O_3 nanoparticles blended concrete has been investigated was studied. Portland cement was partially replaced by Al_2O_3 nanoparticles with the average particle size of 15 nm. Utilizing up to 2.0 wt. % Al_2O_3 nanoparticles could produce concrete with improved strength and water permeability [13].

Splitting tensile strength of concrete using ground granulated blast furnace slag and SiO_2 nanoparticles as binder was studied in [14].

Abrasion resistance and compressive strength of concrete specimens containing SiO_2 and Al_2O_3 nanoparticles which are cured in different curing media have been investigated was studied [15]. Portland cement was partially replaced by up to 2.0 wt. % SiO_2 and Al_2O_3 nanoparticles and mechanical properties of the produced specimens were measured. Increasing the nanoparticles content has found to increase the abrasion resistance.

The effect of curing medium on microstructure together with physical, mechanical and thermal properties of concrete containing ZnO_2 nanoparticles have been investigated was present in the work [16]. Portland cement was partially replaced by ZnO_2 nanoparticles with the average particle size of 15 nm and the specimens were cured in water and saturated limewater for specific ages. The results indicate that the ZnO_2 nanoparticle up to maximum of 2.0 % produces concrete with improved compressive strength.

The use of nanoparticles in SiO_2 Sol to harden the surface of concrete has not been investigated to date, follows from the review of scientific articles.

Nanocoatings are regarded as the most promising high-performance materials for construction applications [17, 18]. Due to their self-assembly effect, they represent remarkable characteristics against environmental agents compared to conventional coating materials in construction industry. They also show high performance in contradiction of energy efficiency, CO_2 emission, and the air quality improvement.

Active pozzolacic admixtures, such as silica fume (SF) and metakaolin, are used in modern concrete technology to obtain high performance properties [19]. Nano-scale pozzolans helps to achieve more dense microstructural packing and more impermeable cement matrix.

From a review of existing methods of construction hardening it follows that there are many scenarios of their strengthening, including through the implementation of the clip effect [20]. Nowadays there are different variants of clips such as metal and concrete which are used as the individual reinforcing layers [21]. But modification options for creating of a monolithic nonorganic clip in the surface layer of the concrete at the expense of its impregnation with the solution based on nanoparticles (a colloidal solution) are not discussed. In addition, from the literature review it follows that the mechanical hardening of the concrete core due to the creation of such a monolithic durable clip in its surface layer has not been investigated yet.

The purpose of the research. The development of a method to improve the quality of heavy concrete by impregnating it with a colloidal solution.

The object of the research. The concrete quality indicators in a monolithic inorganic clip obtained in the surface layer of concrete due to its impregnation with a colloidal solution.

The subject of the research. Physical and chemical hardening processes occurring in the surface layer of concrete impregnated with a colloidal solution.

The research problems.

1. Research of physico-chemical and thermodynamic processes of hardening the concrete surface when it is impregnated with a colloid solution.
2. Research of the value of mechanical hardening of the concrete core due to the effect of the resulting monolithic clip and the factors affecting it.
3. The evaluation of the concrete quality obtained.

2. Methods

We have investigated and scientifically grounded the following idea: when creating high-performance concrete it is possible to strengthen not the whole volume of concrete but only its surface layer. It can be done by means of its impregnation with sol solution with particle sizes of 1...100 nm. This process is called Sol-impregnate [22].

In this case two mechanisms will operate, the enabling to improve the concrete strength and other physico-mechanical characteristics of concrete. The first mechanism is the physical-chemical hardening of the concrete surface layer, resulting in the creation of a monolithic inorganic ultra strong clips. The second one is connected with the fact that in the case of the load action the synthesized monolithic clip will mechanically strengthen the concrete core. In addition to hardening synthesized clip can give concrete the new operational properties, such as hardness, abrasion resistance, etc.

Figure 1 shows a concrete cube under the action of load *P*, which consists of a hardened part – inorganic monolithic ultra-strong clips and nonhardened part – concrete core.

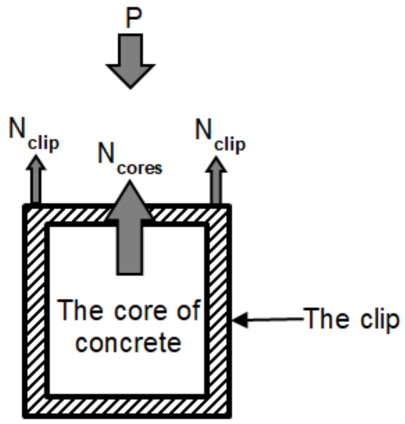


Figure 1. The concrete cube in the monolithic ultra-strong clip

In the first stage, the calculation of load redistribution R between the synthesized clip and concrete core for the sample of 100 x 100 x 100 mm has been done. The calculation has shown that when the layer thickness of the synthesized clips is up to 10 mm and in the case of exceeding its strength in relation to the concrete core 1.5 times there will be 0.65 *R* on a concrete core and 0.35 *P* on a monolithic inorganic clips.

Then, we have developed a mathematical dependence (1). It takes into account the influence of the following factors on the compressive strength of the sample *R* which is located in the clip: the load redistribution between the clip and the concrete core; the number of Sol-impregnate faces; cross-sectional form of the sample and the distance between the upper and lower Sol-impregnate faces.

$$R_{str}=((0.35R)_{\text{clips}}+(0.65R)_{\text{core}})\cdot K_f\cdot n\cdot 1.7(h/a)^{-0.4} \qquad (1)$$

where K_f – is the coefficient taking into account the cross-sectional form of the sample:

if a cube with sides of 100 mm, then $K_f = 1$

if the cylinder, then $K_f = 1.15$;

n – is the number of Sol-impregnate faces:

if there are 6 faces, then $n = 1.7$,

if there are 4 faces (lateral), then $n = 1.5$

if there are 2 faces (top and bottom), then $n = 1.3$;

h/a – is the ratio of sample's height to its width.

The developed formula allows for the first time to calculate and predict the compressive strength of concrete located in the inorganic monolithic clip.

Then the theoretical principles are given. Their implementation will allow to realize physico-chemical synthesis of ultra-strong monolithic clips and to obtain concretes with high performance properties.

1. One of the thermodynamic parameters for solid phases of concrete, in accordance with the third law of thermodynamics is the Gibbs free energy, ΔG^0_{298}, kJ/mol. The Gibbs free energy reflects the part of the energy directed into the system from outside (for example, surface energy) which can be converted into the useful work. The lower the value of the Gibbs free energy of solid phases of concrete, the more

work is performed by the system in the process of hardening. Figures 2 and 3 show that lower values of the Gibbs energy and such high physical and mechanical characteristics as compressive strength and hardness [23, 24] correspond to the low-basic hydrosilicates (CaO/SiO_2 ratio < 1.2).

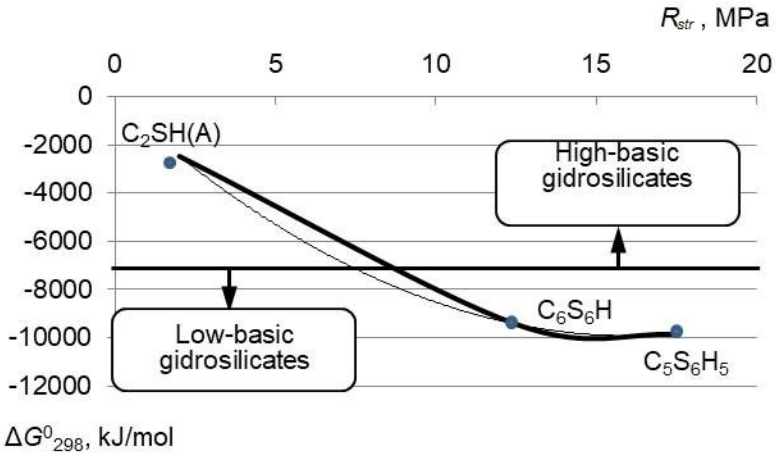


Figure 2. The interrelation of the Gibbs energy with compressive strength of hydrosilicates

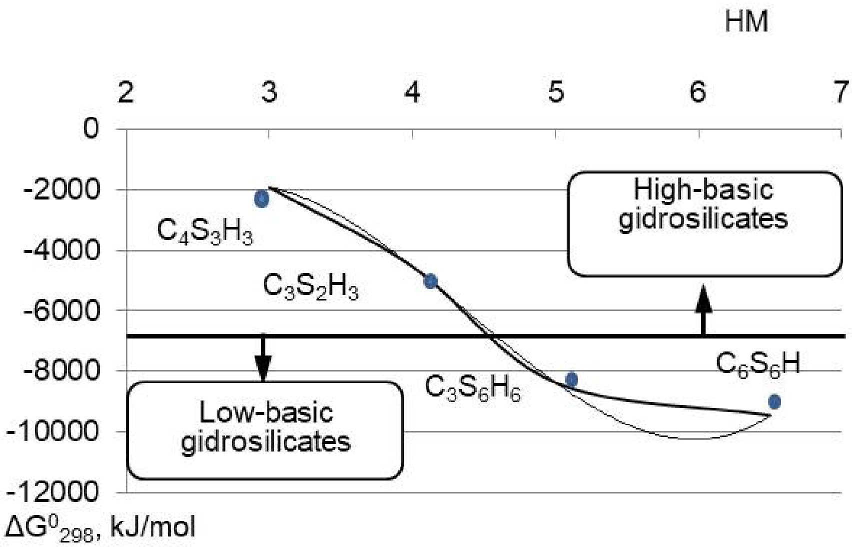


Figure 3. The interrelation of the Gibbs energy with the hardness of hydrosilicates

We are to specify the synthesis of the high strength clip so that the cement system would make the maximum useful work, i.e. low-basic hydrosilicates with low values of the Gibbs energy possessing high strength and high hardness would originate on its basis.

2. As well known, nanoparticles have a huge surplus surface energy. In the impregnation with the sol solution containing nanoparticles in the concrete surface will occur spontaneous reset of this energy (ΔG^0_{298} process < 0). Then, in accordance with the third law of thermodynamics, it will be additional useful work, which is expressed in the formation of low-basic hydrosilicates and improving physical and mechanical properties of high strength concrete Figure 4.

3. The use of the ability of high-strength concrete to the spontaneous capillary liquid absorption (ΔG^0_{298} physical process < 0) will allow to achieve ultra-high concentration of sol additives in the surface layer of the concrete at its impregnation. This, in its turn, will increase the intensity of spontaneous hardening process and speed up their flow, Table 1.

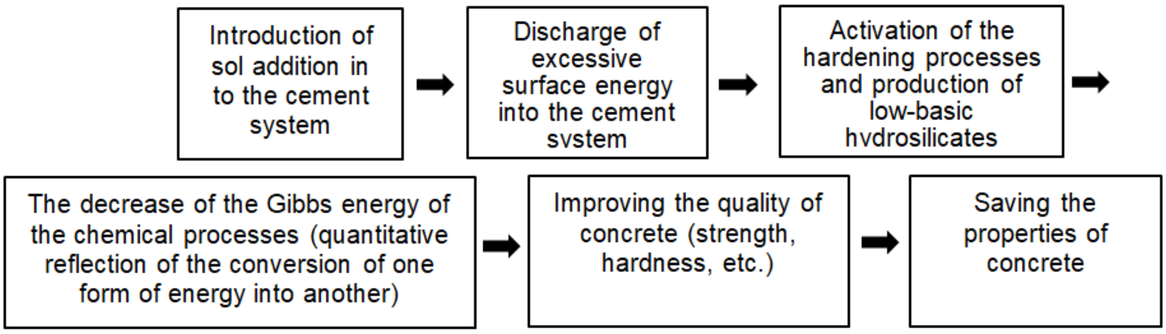


Figure 4. The scheme of realization of the law of energy conservation while obtaining a high-strength clip by impregnating the concrete surface with sol solution

Table 1. Spontaneous processes occurring during impregnation of concrete surface with the sols

The type of process	ΔG^0_{298}, kJ/mol
Capillary ascent	$\Delta G^0_{298}<0$
Discharge of the excessive surface energy of sol nanoparticles	$\Delta G^0_{298}<0$
The process of hardening of concrete with the formation of low-basic hydrosilicates	$\Delta G^0_{298}<0$
Corking of pores with particles of SiO_2 gel and new low-basic hydrosilicates	$\Delta G^0_{298}<0$

4. Extraction of the additional cement reserves at the expense of the energy nanoparticles of the injected sols will allow to obtain high-strength monolithic clip by spontaneous physico-chemical processes (ΔG^0_{298} process<0):

- binding of $Ca(OH)_2$ resulting from the basic reactions of hardening, in additional low-basic hydrosilicates, table 2;
- the increase of the number of the cement having reacted and the decrease of basicity of hydrosilicates;
- the acceleration of the hardening process in time.

Table 2. The results of thermodynamic calculation of the Gibbs energy, ΔG^0_{298}, kJ/mol of the possible solid phases formed in the surface layer of concrete

The chemical reaction of hardening	**The estimated ΔG^0_{298}, kJ/mol**
The main reaction of cement hardening	
$3CaO \cdot SiO_2 + 3H_2O \rightarrow 2CaO \cdot SiO_2 \cdot 2H_2O + Ca(OH)_2$	–356
$2(2CaO \cdot SiO_2) + 3H_2O \rightarrow 3.3CaO \cdot 2SiO_2 \cdot 2.3H_2O + 0.7Ca(OH)_2$	–218
Additional reactions of cement hardening for the technology of Sol-impregnate	
$Ca(OH)_2 + SiO_2 \cdot H_2O \rightarrow 2CaO \cdot SiO_2 \cdot 1.17H_2O + 1.83H_2O$	–95
$2CaO \cdot SiO_2 \cdot 1.17H_2O + 2(SiO_2 \cdot H_2O) \rightarrow 2CaO \cdot 3SiO_2 \cdot 2.5H_2O$ ($C_2S_3H_{2.5}$) + + $0.67H_2O$	–180
$Ca(OH)_2 + 2(SiO_2 \cdot H_2O) \rightarrow CaO \cdot 2SiO_2 \cdot 2H_2O + H_2O$	–169
$6Ca(OH)_2 + 6(SiO_2 \cdot H_2O) \rightarrow 6CaO \cdot 6SiO_2 \cdot H_2O$ (C_6S_6H) $+ 11H_2O$	–117.0
$5Ca(OH)_2 + 6(SiO_2 \cdot H_2O) \rightarrow 5CaO \cdot 6SiO_2 \cdot 5.5H_2O$ ($C_5S_6H_5$) $+ 5.5H_2O$	–585

The implementation of the sum of these theoretical positions will allow to create energy-saving technology of Sol-impregnate (surface hardening) of concrete without using additional energy from outside. The use of such technology will allow to obtain an inorganic mineral super strong clip and the bulk of fundamentally important performance characteristics of concrete such as strength, hardness, abrasion resistance, frost resistance, water absorption and integrity of the protective properties of concrete over time (corrosion resistance).

In the next part of the work the synthesis of monolithic high -strength clips was carried out. According to the previous calculation the task of the synthesis was to obtain the strength characteristics of monolithic inorganic clip 1.5 times higher than of not hardened concrete core.

In accordance with the earlier developed method silica Sol (SiO_2) was chosen for the impregnation, because previous studies showed its activating effect on the concrete.

At the beginning the most rational conditions of hardening necessary for obtaining a high strength of the concrete surface layer due to its impregnation with a Sol of SiO_2 were stated. For this purpose, samples of heavy concrete class B30 with the size 100 x 100 x 100 mm have been produced. In the process of their production Portland cement CEM 42.5, granite crushed stone of 5–10 mm and pit sand with a fineness modulus of *Mr* = 2.26 were used. The composition of concrete are shown in table 3.

Table 3. The consumption of the components per 1 m3 of concrete mix, kg

Cement	Sand	Crushed stone	Water
370	802	1063	155

In order to achieve a well-developed pore structure, providing spontaneous capillary inflow of the sol into concrete surface, the time of concrete hardening was investigated under normal conditions before the impregnation. The time period was twenty four hours because the mass of the absorbed silica sol in this case was maximum.

Then the assessment of the rational time of impregnation of concrete samples in the SiO_2 Sol solution with their subsequent hardening under normal conditions (temperature = 20 ± 2 ºC and humidity = 95 %) for 28 days was made. The impregnation time was 3 days. For impregnation of concrete surfaces the industrial silica Sol SITEK of 3 % concentration was used.

3. Results and Discussion

The quality indexes developed by the concrete which has been obtained by the technology of Sol-impregnation are given in the Table 4. The table shows that in comparison with the control samples hardness increases by 30 %, the compressive strength of concrete increases by 78 %, tensile strength in bending of 76 %, the water resistance increases by 75 %, frost resistance increases by 200 %, the water absorption decreases by 60 %.

Table 4. Quality indexes of the concrete developed on the basis of surface strengthening by Sol-impregnation

The name of index	**Control sample**	**Strengthen of the sol SiO_2 sample**	**Increase of quality, %**
Hardness number by Moos	4	6	75
Compressive strength	39.3 MPa	69.9 MPa	78
Tensile strength in bending	5.2 MPa	9.2 MPa	76
Index of crack resistance	0.132	0.153	16
Abrasion resistance	0.89 g/cm^2	0.67 g/cm^2	25
Water resistance	0.8 MPa	1.4 MPa	75
Frost resistance, cycles	200	600	200
Water absorption	4.7 %	1.9 %	60
Elastic strength, MPa·10^{-3}	32.5	44.5	37

Further work was connected with physico-chemical investigation of sol strengthen concrete layer.

In accordance with the carried out X-ray investigations, and differential thermal analysis, Figures 5, 6, Table 5, it was revealed [25] that the increase of the mechanical properties is connected with the formation of the concrete low-basic hydrosilicates of type C_6S_6H, CSH(I), $C_2S_3H_{2.5}$, $C_3S_2H_3$ with low values of the Gibbs energy in the surface sol strengthen concrete layer, table.2. Besides that, $Ca(OH)_2$ and C_3S are absent in the samples, which confirmed the previous assumption that with the injection of sol SiO_2, calcium hydroxide is bound in the additional low-basic hydrosilicates and the main cement reserve is exhausted.

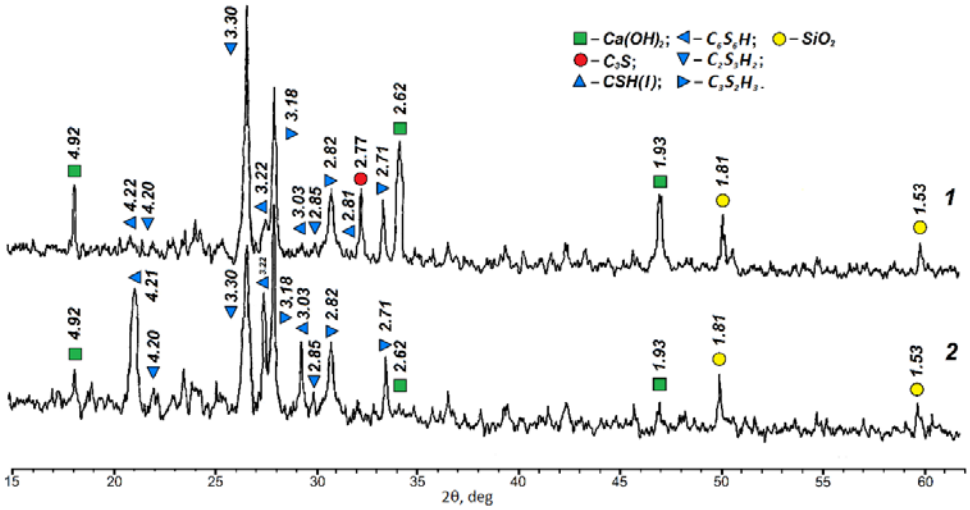


Figure 5. X-ray analyses of samples of cement stone:
1 – control sample; 2 –sample impregnated with silica Sol

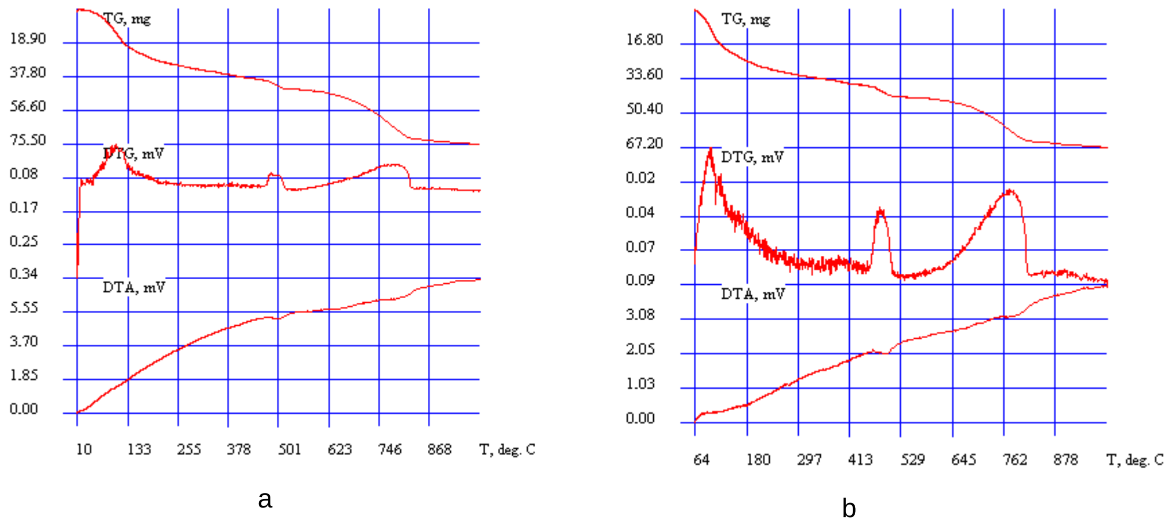


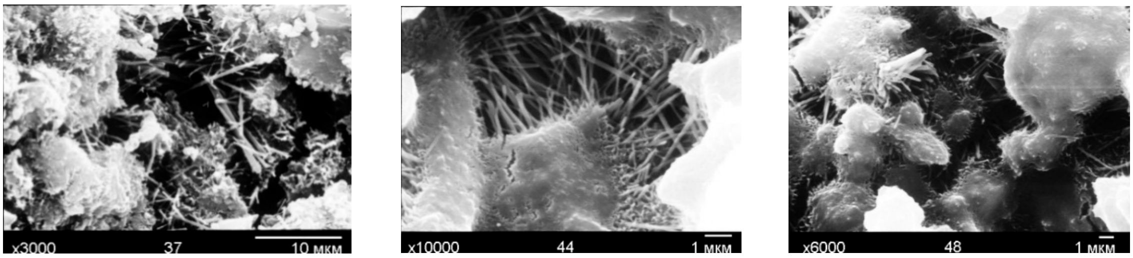
Figure 6. Diversional thermal analysis of the cement stone samples: a – control sample, b – sample, impregnated with silica Sol

Table 5. Results of calculation differential thermal analysis of the cement stone samples

The composition of the impregnate	**Endothermic effect T, ºC**			**Total mass loss on the effects, mg**	**Loss of water in the gel phase, mg**
	Loss of water, mg				
	(30-170)	(470-530)	(680-820)		
–	15.00	7.60	15.20	37.80	37.70
Sol SiO_2	31.70	5.30	24.60	61.60	8.70

The data shown in the Table 5 confirm the data of X-ray studies. Endothermic effects in the region of 30 to 170 °C, 470–530 ºC, 680–820 ºC correspond to dehydration of $C_2S_3H_{2.5}$, endothermic effect in the field of 680-820ºC also corresponds to the dehydration of C_6S_6H and endothermal effect in the field 400^{0}C corresponds to the dehydration of $C_3S_2H_3$ [25]. The total mass loss on the effects increases 1.6 times, indicating a deeper degree of cement hydration in the presence of silica sol. The loss of water in the gel phase of the Sol sample decreases 4 times, which confirms that the redistribution of water in the direction of its increase in the crystalline phase takes place.

By means of the electron microscopy it was revealed that the new phases of hydrosilicates are concentrated in the surface layer of 1 sm depth and in the pores, causing their blockage, Figure 7. The largest concentration takes place in the layer the thickness of which is up to 7 mm.



1 2 3

Figure 7. Photographs of the slice of the sample impregnated with silica Sol, in secondary electrons at different magnification: the 1 – low-basic hydrosilicates at the depth of h=1 mm; the 2 – low-basic hydrosilicates at the depth h=2 mm; the 3 – low-basic hydrosilicates at the depth h=3 mm

New phases form the "bridges" that binds the grains of the cement stone. At the depth of 1 cm the composition of the sol strengthen concrete is equal to the composition of the control sample.

Then, the authors investigated the porous structure of concrete samples of the class B30. Studies have shown, table 6, that in the samples impregnated with SiO_2 Sol the specific surface area of the pores decreases 2.14 times, the volume of sorbenting pores with a radius ≤ 50 nm reduces 1.3 times, the volume of macropores with a radius of ≥ 50 nm decreases 1.28 times. These results confirm the data of microscopic researches and shows that new phases fill the pores of the cement stone, which makes the structure more dense and also contributes to the increase of the strength, hardness, frost resistance, water resistance, corrosion resistance and durability of concrete.

Table 6. The results of determining the pores structure of the concrete samples

The name of the sample	The specific surface of pores, S_{sp}, m^2/g	The volume of sorbent pores, V_s, cm^3/g	The volume of macropores, V_m, cm^3/g	The total volume of the pores, V_Σ, cm^3/g
Control	3.0	0.04	0.09	0.13
Strengthened with the sol SiO_2	1.4	0.03	0.07	0.10

Thus, it was proved experimentally and based scientifically that the technology of surface hardening of concrete with a Sol of SiO_2 leads to production of inorganic high-strength clip. The effect of its action allows to increase the strengthen of the concrete core mechanically and to get the bulk of fundamentally important performance properties.

Then the degree of the preservation in time of the achieved level of the concrete properties was evaluated.

The assessment includes two stages. The first stage estimates the corrosion resistance of concrete after surface hardening, because physico-chemical studies have shown that the technology of surface hardening of concrete $Ca(OH)_2$ transforms into the new phases concentrated in the pores of the surface layer and increasing its strength and density. Thus, the created inorganic high-strength clip acts as a protective corrosion barrier. It eliminates two main causes of the corrosion: chemical – due to the reaction $Ca(OH)_2$ with the reagents of the environment [26], and physical – due to the formation slightly soluble salts in the pores and capillaries of the concrete, causing considerable stress and , contributing to the destruction of the concrete structure [27, 28].

The evaluation of corrosion resistance was made in three types of aggressive environments causing the cement stone corrosion: 1 medium-5% solution of $MgCl_2$-causes the magnesia corrosion, 2 medium-5 % H_2SO_4 solution-causes the acid corrosion, 3 medium-5% Na_2CO_3 solution - causes the alkaline corrosion, table 7. As a result the coefficient of corrosion resistance (2) in different physical environments k_i was calculated.

$$k_i=R_1/R_2 \quad (2)$$

where R_1 – tensile strength in bending of surface-hardened sample in the aggressive environment;

R_2 – tensile strength in bending of the control sample at the age of 28 days under the condition of normal hardening.

Analysis of the data achieved shows that according to the normative classification for chemical resistance of concrete in aggressive environments the concrete sample after surface hardening with a Sol of SiO_2 can be attributed to chemically resistant concrete, because its corrosion resistance coefficient is above 0.8. So the developed anti-corrosion barrier can significantly increase the coefficient of corrosion resistance of concrete at the age of 12 months. It increases up to 27 %.

Table 7. The coefficient of corrosion protection of concrete in various aggressive environments

The kind of simple	**The coefficient of corrosion resistance of concrete in various aggressive environments**								
	Magnesia corrosion, $MgCl_2$			The acid corrosion, H_2SO_4			The alkaline corrosion, Na_2CO_3		
	The time of the samples using in an aggressive environment, months								
	1	6	12	1	6	12	1	6	12
Control	0.84	0.78	**0.72**	0.78	0.73	**0.68**	0.85	0.80	**0.74**
Impregnated with the sol SiO_2	0.97	0.95	**0.92**	0.95	0.90	**0.87**	0.98	0.97	**0.94**

At the second stage, the time of preservation of the achieved level of physical and mechanical properties of high strength concrete is estimated. For this purpose the calculations of the destruction depth of the synthesized concrete in the time *h*, in accordance with the existing formula (3) was made. The calculation showed that at the age of 50 years, the corrosion depth does not exceed 0.74 cm, which is 8 times lower than the allowable corrosion depth of concrete at the age of 50 years in accordance with the building codes. This ensures the preservation of the achieved level of operational properties of concrete in time, Table 8.

$$h=(k\cdot t^{0.5}-\alpha)/(S\cdot P^1_{CaO}) \qquad (3)$$

where *k* – the experimental coefficient, determined by preliminary tests;

t – the time for which the depth of destruction (days) is forecasted;

α – the correction factor taking into account that the initial period of corrosion passes through a diffusion-kinetic mechanism;

S – the consumption of cement in concrete, kg/m^3;

P^1_{CaO} – the content of CaO in cement, %.

Table 8 The results of the calculation of the corrosion depth of concrete after surface hardening with the Sol of SiO_2

Age of concrete, years	**Corrosion depth of concrete impregnated with Sol, cm**
10	0.3
20	0.45
30	0.57
40	0.67
50	0.74

On the basis of obtained results it can be concluded that the forecast expressed previously have been confirmed, and the developed technology allows to obtain such solid phases in the strengthened surface layer of concrete, which have lower values of the Gibbs energy. These phases have increased strength and hardness and lead to the formation of inorganic high-strength clip. It improves the physico-mechanical characteristics of concrete up to 200 %, and allows to preserve them in time.

The proposed technology of concrete surface hardening allows to obtain high-strength concrete. In comparison with other methods of hardening, for example, the use of pozzolanic additives or changes in concrete hardening conditions [29, 30], the efficiency is much higher (the compressive strength increases by 78 %). But other high-strength concrete, do not have high hardness, corrosion resistance, etc.

4. Conclusions

1. This paper proposes the method to improve the quality of concrete at the expense of its surface hardening by impregnating with an inorganic Sol of SiO_2 with the creation of a monolithic inorganic high-strength clips.

2. It is shown that under the action of load P the redistribution of the gains in the sol strengthen sample between the clip and the hardened core takes place: N_{cl} = 0.35 R, N_{core} =0.65 R; the presence of the clip provides an increase in strength of the entire sample up to 50 %.

3. For the first time we have developed a mathematical dependence, allowing to calculate the strength of the concrete sample in the monolithic inorganic clip depending on the cross-sectional form of the sample, the number of Sol-impregnate faces and the ratio of the height of the sample to its width.

4. It is determined that the surface strengthening of concrete with a Sol of SiO_2 results in the creation of a high strength layer. The basis of the layer consists of the low-basic hydrosilicates with lower values of the Gibbs energy, ΔG^0_{298}, kJ/mol and with high values of strength and hardness.

5. It is stated that the surface strengthening technology allows to improve the physical-mechanical properties of concrete such as compressive strength, and tensile strength in bending, frost resistance, hardness, abrasion resistance, water absorption, water resistance up to 200 %.

6. It is shown that the technology of surface hardening of concrete leads to the formation of corrosion-protective barrier, which greatly increases the resistance of concrete to various aggressive environments, the corrosion depth of concrete not exceeding 0.74 cm for 50 years.

References

1. Ibragimov R.A., Pimenov S.I. Influence of mechanochemical activation on the features in the of hydration of cement. *Magazine of Civil Engineering*. 2016. No. 2. Pp. 3–12. doi: 10.5862/MCE.62.1 (rus)
2. Hameed A.H. Effect of superplasticizer dosage on workability of self-compact concrete. *Diyala Journal of Engineering Sciences.* 2012. Vol. 05. No. 02. Pp. 66–81.
3. Naydenov Yu.A., Veprinyak I.A. Innovatsionnaya tekhnologiya aktivirovaniya betonov, osnovannaya na yavlenii kavitatsii [Innovative technology of concrete activation, based on the phenomenon of cavitation]. *Nauka XXI veka.* 2013. No. 4. Pp. 12–15. (rus)
4. Bids V.A., Sir E.A., Kutugin V.A. Physical and chemical processes in the activation of cement-sand mixture in a centrifugal mixer. *Proceedings of the universities. Physics.* 2011. No. 11/3. Pp. 346–349.
5. Bogdanov R.R., Ibragimov R.A. Process of hydration and structure formation of the modified self-compacting concrete. *Magazine of Civil Engineering.* 2017. No. 5. Pp. 14–24. doi: 10.18720/MCE.73.2.
6. Gayfullin A.R., Rakhimov R.Z., Rakhimova N.R. Vliyaniye dobavok glinitov v portlandtsement na prochnost pri szhatii tsementnogo kamnya [The effect of clay additives in Portland cement on the compressive strength of cement stone]. *Magazine of Civil Engineering.* 2015. No. 7(59). Pp. 66–73.(rus)
7. Sychova A.M., Svatovskaya L.B., Mjakin S.V., Vasiljeva I.V. Modification of fillers for cements. *Book Chapter Electron Beam Modification of Solids: Mechanisms, Common Features and Promising Applications*. 2009. Pp. 35–37.
8. Vatin N.I., Barabanshikov Yu.G., Komarinsky M.V., Smirnov S.I. Modifikatsiya litoy betonnoy smesi vozdukhovovlekayushchey dobavkoy [Modification of cast concrete mix by air-entraining admixture]. *Magazine of Civil Engineering.* 2015. No. 04(56). Pp. 3–10.(rus)
9. Taheri Fard A.R., Soheili H., Ramzani Movafagh S., Farnood Ahmadi P. Combined Effect of Glass Fiber and Polypropylene Fiber On Mechanical Properties of Self-

Литература

1. Ибрагимов Р.А., Пименов С.И. Влияние механохимической активации на особенности процессов гидратации цемента // Инженерно-строительный журнал. 2016. № 2(62). С. 3–12.
2. Hameed A.H. Effect of superplasticizer dosage on workability of self-compact concrete // Diyala Journal of Engineering Sciences. 2012. Vol. 05. No. 02. Pp. 66–81.
3. Найденов Ю.А., Веприняк И.А. Инновационная технология активирования бетонов, основанная на явлении кавитации // Наука XXI века. 2013. № 4. С. 12–15.
4. Bids V.A., Sir E.A., Kutugin V.A. Physical and chemical processes in the activation of cement-sand mixture in a centrifugal mixer // Proceedings of the universities. Physics. 2011. No. 11/3. Pp. 346–349.
5. Богданов Р.Р., Ибрагимов Р.А. Процессы гидратации и структурообразования модифицированного самоуплотняющегося бетона // Инженерно-строительный журнал. 2017. № 5(73). С. 14–24.
6. Гайфуллин А.Р., Рахимов Р.З., Рахимова Н.Р. Влияние добавок глинитов в портландцемент на прочность при сжатии цементного камня// Инженерно-строительный журнал. 2015. № 7(59). С. 66–73.
7. Sychova A.M., Svatovskaya L.B., Mjakin S.V., Vasiljeva I.V. Modification of fillers for cements // Book Chapter Electron Beam Modification of Solids: Mechanisms, Common Features and Promising Applications. 2009. Pp. 35–37.
8. Ватин Н.И., Барабанщиков Ю.Г., Смирнов С.И. Модификация литой бетонной смеси воздухововлекающей добавкой//Инженерно-строительный журнал. 2015. № 04(56). С. 3–10.
9. Тахери Фард А.Р., Сохели Х., Рамзани Мовафах С., Фарнуд Ахмади П. Совместное действие стеклянной и полипропиленовой фибры на механические свойства самоуплотняющихся бетонов // Инженерно-строительный журнал. 2016. № 2(62). С. 26–31
10. Низина Т.А., Балыков А.С., Володин В.В., Коровкин Д.И. Дисперсно-армированные мелкозернистые

Compacting Concrete. *Magazine of Civil Engineering*. 2016. No. 2. Pp. 26–31. doi: 10.5862/MCE.62.3

10. Nizina T.A., Balykov A.S., Volodin V.V., Korovkin D.I. Disperse-reinforced fine-grained concrete with a polyfunctional modifying additives. *Magazine of Civil Engineering.* 2017. No. 4(72). Pp. 73–83.(rus)
11. Boikova T., Solovyov D., Solovyova V. Concrete For Road Pavements. *Procedia Engineering.* 2017. Vol. 189. Pp. 800–804.
12. Nazari A., Riahi S. TiO2 nanoparticles effects on physical, thermal and mechanical properties of self compacting concrete with ground granulated blast furnace slag as binder. *Energy and Buildings.* 2011. Vol. 43. Pp. 995–1002.
13. Nazari A., Riahi S. Al2O3 nanoparticles in concrete and different curing media. *Energy and Buildings.* 2011. Vol. 43. Pp. 1480–1488.
14. Nazari A., Riahi S. Splitting tensile strength of concrete using ground granulated blast furnace slag and SiO2 nanoparticles as binder. *Energy and Buildings.* 2011. Vol. 43. Pp. 864–872.
15. Nazari A., Riahi S. Abrasion resistance of concrete containing SiO2 and Al2O3 nanoparticles in different curing media. *Energy and Buildings.* 2011. Vol. 43. Pp. 2939–2946.
16. Riahi S., Nazari A. Physical, mechanical and thermal properties of concrete in different curing media containing ZnO2 nanoparticles. *Energy and Buildings*. 2011. Vol. 43, Pp. 1977–1984.
17. Boostani H., Modirrousta S. Review of Nanocoatings for Building Application. *Procedia Engineering.* 2016. Vol. 145, Pp. 1541–1548.
18. Zhu W., Bartos P.J.M., Porro A. Application of nanotechnology in construction. *Materials and Structures.* 2004. No. 37(9), Pp. 649–658.
19. Shakhmenko G., Juhnevica I., Korjakins A. Influence of Sol-Gel Nanosilica on Hardening Processes and Physically-Mechanical Properties of Cement Paste. *Procedia Engineering.* 2013. Vol. 57. Pp. 1013–1021.
20. Teryanik V.V., Biryukov A.Yu., Borisov A.O., Shipanov R.V. Novyye konstruktivnyye resheniya usileniya szhatykh elementov oboymami [New design solutions for strengthening compressed elements with clips]. *The housing construction.* 2009. No. 7. Pp. 8–9. (rus)
21. Podnebesov P.G., Teryanik V.V. Vnetsentrenno szhatyye kolonny, usilennyye oboymami iz samouplotnyayushchegosya stalefibrobetona [Extra-compressed columns reinforced with clips of self-compacting steel-fiber concrete]. *The Concrete and reinforced concrete.* 2015. No. 3. Pp. 7–10. (rus)
22. Svatovskaya L., Sychova A., Sychov M., Okrepilov V. Quality Improvement of Concrete Articles. *MATEC Web of Conferences* 2016. 53.01024. DOI: 10/1051/matecconf/20165301024.
23. Babushkin V.I., Matveyev G.M., Mchedlov-Petrosyan O.P. *Termodinamika silikatov* [Thermodynamics of silicates] Moscow: Stroyizdat, 1986. 408 p. (rus)
24. Svatovskaya L.B., Solovyeva V.Ya. i dr. *Termodinamicheskiye i elektronnyye aspekty svoystv kompozitsionnykh materialov dlya stroitelstva i ekozashchity* [Thermodynamic and electronic aspects of the properties of composite materials for construction and environmental protection] Saint-Petersburg.: Stroyizdat, 2004. 174 p. (rus)
25. Gorshkov V.S., Timashev V.V., Savelyev V.G. *Metody fiziko-khimicheskogo analiza vyazhushchikh veshchestv* [Methods of physical and chemical analysis of binders]. Moscow: The higher school, 1981. 336 p. (rus)
26. Klueva N, Emelyanov S, Kolchunov V, Maria Gubanova. Criterion of Crack Resistance of Corrosion Damaged

бетоны с полифункциональными модифицирующими добавками // Инженерно-строительный журнал. 2017. № 4(72). С. 73–83.

11. Boikova T., Solovyova D., Solovyova V. Concrete For Road Pavements // Procedia Engineering. 2017. Vol. 189. Pp. 800–804.
12. Nazari A., Riahi S. TiO2 nanoparticles effects on physical, thermal and mechanical properties of self compacting concrete with ground granulated blast furnace slag as binder // Energy and Buildings. 2011. Vol. 43. Pp. 995–1002.
13. Nazari A., Riahi S. Al2O3 nanoparticles in concrete and different curing media // Energy and Buildings. 2011. Vol. 43. Pp. 1480–1488.
14. Nazari A., Riahi S. Splitting tensile strength of concrete using ground granulated blast furnace slag and SiO2 nanoparticles as binder // Energy and Buildings. 2011. Vol. 43. Pp. 864–872.
15. Nazari A., Riahi S. Abrasion resistance of concrete containing SiO2 and Al2O3 nanoparticles in different curing media // Energy and Buildings. 2011. Vol. 43. Pp. 2939–2946.
16. Riahi S., Nazari A. Physical, mechanical and thermal properties of concrete in different curing media containing ZnO2 nanoparticles // Energy and Buildings. 2011. Vol. 43. Pp. 1977–1984.
17. Boostani H., Modirrousta S. Review of Nanocoatings for Building Application // Procedia Engineering. 2016. Vol. 145. Pp. 1541–1548.
18. Zhu W., Bartos P.J.M., Porro A., Application of nanotechnology in construction // Materials and Structures. 2004. No. 37(9). Pp. 649–658.
19. Shakhmenko G., Juhnevica I., Korjakins A. Influence of Sol-Gel Nanosilica on Hardening Processes and Physically-Mechanical Properties of Cement Paste // Procedia Engineering. 2013. Vol. 57. Pp. 1013–1021.
20. Теряник В.В., Бирюков А.Ю., Борисов А.О., Щипанов Р.В. Новые конструктивные решения усиления сжатых элементов обоймами // Жилищное строительство. 2009. № 7. С. 8–9.
21. Поднебесов П.Г., Теряник В.В. Внецентренно сжатые колонны, усиленные обоймами из самоуплотняющегося сталефибробетона // Бетон и железобетон. 2015. № 3. С. 7–10.
22. Svatovskaya L., Sychova A., Sychov M., Okrepilov V. Quality Improvement of Concrete Articles // MATEC Web of Conferences 53.01024. 2016. DOI: 10/1051/matecconf/20165301024.
23. Бабушкин В.И., Матвеев Г.М., Мчедлов-Петросян О.П. Термодинамика силикатов. М.: Стройиздат, 1986. 408 с.
24. Сватовская Л.Б., Соловьева В.Я. и др. Термодинамические и электронные аспекты свойств композиционных материалов для строительства и экозащиты. СПб.: Стройиздат, 2004. 174 с.
25. Горшков В.С., Тимашев В.В., Савельев В.Г. Методы физико-химического анализа вяжущих веществ. М.: Высшая школа, 1981. 336 с.
26. Klueva N, Emelyanov S, Kolchunov V, Maria Gubanova. Criterion of Crack Resistance of Corrosion Damaged Concrete in Plane Stress State // Procedia Engineering. 2015. Vol. 117. Pp. 179–185.
27. Eskandari H., Mozafari Nic A., Ghanei A. Effect of Air Entraining Admixture on Corrosion of Reinforced Concrete // Procedia Engineering. 2016. Vol. 150. Pp. 2178–2184.
28. Sulikowskia J., Kozubal J. The Durability of a Concrete Sewer Pipeline Under Deterioration by Sulphate and Chloride Corrosion // Procedia Engineering. 2016. Vol. 153. Pp. 698–705.

Concrete in Plane Stress State. *Procedia Engineering*. 2015. Vol. 117. Pp. 179–185.

27. Eskandaria H., Mozafari Nicb A., Ghaneia A. Effect of Air Entraining Admixture on Corrosion of Reinforced Concrete. *Procedia Engineering.* 2016. Vol. 150. Pp. 2178–2184.
28. Sulikowskia J., Kozubal J. The Durability of a Concrete Sewer Pipeline Under Deterioration by Sulphate and Chloride Corrosion. *Procedia Engineering.* 2016. Vol. 153. Pp. 698–705.
29. Sumrerng R., Prinya C. Use of ternary blend of Portland cement and two pozzolans to improve durability of high-strength concrete. *KSCE Journal of Civil Engineering.* 2014. Vol. 18. Pp. 1745–1752.
30. Fanghui H., Zengqi Z. Hydration, mechanical properties and durability of high-strength concrete under different curing conditions. *Journal of Thermal Analysis and Calorimetry.* 2018. Vol. 132. Pp. 823–834.

29. Sumrerng R., Prinya C. Use of ternary blend of Portland cement and two pozzolans to improve durability of high-strength concrete // KSCE Journal of Civil Engineering. 2014. Vol. 18. Pp.1745–1752.
30. Fanghui H., Zengqi Z. Hydration, mechanical properties and durability of high-strength concrete under different curing conditions // Journal of Thermal Analysis and Calorimetry. 2018. Vol. 132. Pp. 823–834.

Anastasia Sychova,
+7(921)857-22-17; amsychova@yandex.ru

Larisa Svatovskaya,
+7(911)919-54-84; lbsvatovskaya@yandex.ru

Dmitriy Starchukov,
+7(904)519-85-43; starchukov@mail.ru

Valentina Soloviova,
+7(921)353-05-07; 9046185117@mail.ru

Marina Gravit,
+7(912)912-64-07; marina.gravit@mail.ru

Анастасия Максимовна Сычева,
+7(921)857-22-17;
эл.почта: amsychova@yandex.ru

Лариса Борисовна Сватовская,
+7(911)919-54-84;
эл. почта: lbsvatovskaya@yandex.ru

Дмитрий Сергеевич Старчуков,
+7(904)519-85-43; эл. почта:
starchukov@mail.ru

Валентина Яковлевна Соловьева,
+7(921)353-05-07;
эл. почта: 9046185117@mail.ru

Марина Викторовна Гравит,
+7(912)912-64-07;
эл. почта: marina.gravit@mail.ru