

USING LOW CLINKER SLAG PORTLAND CEMENT FOR NORMAL WEIGHT CONCRETE

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The paper presents effective ways to increase activity of slag Portland cement with a clinker content of 5-19%. The influence of complex sulfate-fluoride and sulfate-fluoride-alkaline activation is studied. The results obtained at the first stage of the research are used for investigating properties of concrete produced using the above mentioned low clinker slag Portland cement with a clinker content of less than 20%. The influence of different plasticizing additives and heat treatment on the strength characteristics of concrete has been determined. A method for design of concrete compositions using low clinker slag Portland cement is proposed.

Keywords: activating additives, cement clinker, energy saving technology, phosphogypsum, slag Portland cement.

1. Introduction

One of the trends in modern construction industry is using energy-saving technologies for building materials production. The energy consuming industry is Portland cement production due to high fuel consumption for producing Portland cement clinker. The main way of reducing the content of clinker in the Portland cement composition is increasing the active mineral additives content and in particular blast furnace slag. At the world's total Slag Portland cement production is about 20 [1].

According to European standard EN 197-1, low clinker slag Portland cement "CEM III/C" has Portland cement clinker content of 5-19%. Low clinker slag Portland cement (LCSPC) is characterized by relatively low compressive strength at 28 days between 20 to 30 MPa [2]. It is used, first of all, for constructions that should have high corrosion resistance and also for massive constructions with low concrete exotherm [3].

Slag Portland cement strength is formed due to the clinker component, as well as the hydraulic activity of slag, which is provided by interaction with clinker hydration products. In order to achieve high strength of slag Portland cement, it is desirable to use alito-aluminate clinkers ($C_3A + C_3S = 65-75\%$) and to provide a higher specific surface area of cement [2,4].

To increase the cement strength, especially in case of maximum slag content, the optimal sulfate component content has a high importance [5, 6]. A positive effect is achieved by adding plasticizers, alkalis and curing accelerators during

the slag cements milling process [7, 8].

The paper presents results of experimental investigation on complex sulfate-alkaline and sulfate-alkaline-fluoride slag activation for LCSPC production and its further use in concrete with stone siftings.

2. Literature review

Activation of slags binding properties in slag Portland cement is achieved by intensifying their interaction with calcium hydroxide, released as a result of hydrolysis of clinker minerals and gypsum, which is part of the cement. The curing processes intensity, the structure and composition of the hydrate products depend on the hardening conditions and the used slag activator type. Alkaline and sulfate activation are used to increase the slag binders strength [9, 10]. For granulated blast furnace slag acid activation is also possible [11].

In presence of Ca^{2+} and SO_4^{2-} ions hydration of both crystalline and glassy phases of blast furnace slag is accelerated. Moreover, hardening under normal conditions requires presence of both ions, and at heat treatment conditions there is a sufficient excess of Ca^{2+} [5]. At the room temperature, in presence of Ca^{2+} and SO_4^{2-} ions, gelinite and oxermanite are hydrated. Other slag minerals require hydrothermal treatment.

In blast furnace slag - water system hardening in presence of SO_4^{2-} (and also Ca^{2+}) ions, crystals of calcium hydrosulphoaluminates are formed, which prevents formation of waterproof membranes from aluminum hydroxides and silicon

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on glassy particles. In this case, the ion exchange on the particles surface layer, which causes deformation of the glassy structure, is also intensified. The needle-like crystals of calcium hydro-sulfoaluminate [5], contribute to the hardening mass strengthening. Simultaneously, formation of low-alkaline calcium hydrosilicates also occurs.

It should be noted that with double slag activation by calcium hydroxide and sulfate, along with the positive sides, under certain conditions, and in particular at a higher concentration of the latter, such destructive processes as hardening deceleration and even drop of strength may occur [12]. This is because under certain conditions in the system recrystallization processes, associated with formation of compounds may cause an increase in the solid phase volume. This leads to concentration of local stresses, strength loss and even destruction [12]. Therefore, it is necessary to take into account the optimal quantitative ratio of used activators.

Another method of activating slag cements is alkali metals compounds introduction into their compositions. The idea of creating such hydraulic binders was proposed by analyzing geological data about natural mineral and rock formation processes occurring with participation of alkaline and alkaline earth metals, as well as physical and chemical processes of forming a cement stone on their basis [13 - 15]. A corresponding theoretical approach for production of alkaline and alkaline earth aluminosilicate hydraulic binders was proposed. Based on further investigation of these binders, principles for synthesis of alkali (and in particular slag-alkaline) binders with given properties were developed [9].

The composition of slag-alkaline binder hydrate products is determined by that of the blast granular slag, alkaline component type and concentration as well as curing conditions. In general, these hydrate compositions can be divided into three groups: low basic calcium hydrosilicates, alkali -calcium hydrosilicates and hydro-aluminosilicates. As alkaline components, it is most expedient to use alkaline wastes of different industries: soda melt, soda-sulfate mix, sodium aluminates, etc.

An extensive data on the effect of slag-Portland cement grinding fineness on the compressive strength is available [3,7,16]. The strength growth at the initial or subsequent curing periods depends on the slag type and composition. It was found that at separate milling of cements, containing 50 and 60% of slag, the strength at early age is determined by the clinker milling fineness, and at later ages – by that of granulated slag [7]. An increase in the amount of slag to 75% showed that the clinker milling degree does not significantly increase the strength, but the leading

role is played by slag, whose hydraulic properties are largely dependent on the grinding fineness [7].

Adding into a binder system substances with ionic chemical connection nature, as well as those with oxidizing properties yields hydration activation and cement stone strength increase. Adding ion salts like CaF_2 , MgF_2 and Na_2SiF_6 have an activating effect on slag and slag Portland cement curing [17]. The slag activation mechanism by fluorite consists of slag particles surface activation, increasing their reactive ability. Activation by fluorine salts yields chemical modification of the surface and also regulates the electronic processes.

However, in spite of the extensive data available on slag binders properties, improvement of low clinker slag Portland cement technology is an important problem, which requires further research.

3. Research aim and scope

The main purpose of the present study is to find effective ways to activate low clinker slag Portland cement, as well as to propose technology for producing concrete based on this cement and using stone siftings. To achieve this purpose, an experimental study is carried out. The experimental program included three series of tests. First the influence of the clinker content, curing activators, surface area and superplasticizer content on the LCSPC strength is studied. The aim of the second series is finding the optimal LCSPC component content to achieve increased strength. The focus of the third series is development of concrete composition made on the basis of the above mentioned binder and stone siftings.

4. Experimental program

4.1. Materials

For producing LCSPC were used:

- blast furnace granulated slag, which can be attributed to basic slag;
- Portland cement clinker ($\text{C}_3\text{S} = 57.1\%$, $\text{C}_2\text{S} = 21.27\%$, $\text{C}_3\text{A} = 6.87\%$, $\text{C}_4\text{AF} = 12.19\%$), which according to the mineralogical composition can be attributed to typical average aluminate clinkers produced by cement plants.

Phosphogypsum-dihydrate (FG) was used as the sulfate components of slag Portland cement. The chemical composition of the initial materials is given in Table 1.

For cement - sand mortar (1:3 by mass) standard sand [18] was used. Naphthalene - formaldehyde type SP-1, lignosulfonate type LST and polycarboxylic type Sika VC 225 plasticizers were used.

In the study of concrete based on LCSPC were used granite crushing siftings. The physical properties of the siftings are given in Table 2.

Table 1

Materials type	Oxides content, wt. %							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	MnO	P ₂ O ₅
Blast furnace slag	39.52	6.49	0.12	47.13	3.10	1.74	1.15	-
Phospho-gypsum	-	0.36	0.15	38.4	0.003	59.7	-	0.67
Clinker	22.47	5.26	4.07	66.18	0.64	0.46	0.29	-

Table 2

Property	Value
Density, g/cm ³	2.7
Bulk density, g/cm ³	1.48
Volume of voids, %	45.1
Fineness modulus	3.49
Content of dust particles, %	15.8

Table 3

No.	Factors		Variation levels		
	Natural	Coded	Lower (-1)	Main (0)	Upper (+1)
1	Clinker content, %	X ₁	5	12	19
2	Content of phosphogypsum in terms of SO ₃ , %	X ₂	3.03	4.5	5.97
3	Specific surface of the binder, m ² /kg	X ₃	350	450	550
4	Hardening activator content (Na ₂ SiF ₆), %	X ₄	0	2	4
5	Content of SP-1 superplasticizer, %	X ₅	0	0.5	1

4.2. Experiments planning

At the first stage of the present study, tests were carried out using experiments planning method [19]. As a result of specimens testing and data statistical processing, experimental statistical models of the water-cement ratio and strength LCSPC in the form of regression equations were obtained:

$$y = b_0 + \sum_{i=1}^k b_i x_i + \sum_{i=1}^k b_{ij} x_i x_j + \sum_{i=1}^k b_{ii} x_i^2, \quad (1)$$

where y is the output parameter; b_0 , b_i , b_{ij} , b_{ii} are regression coefficients; x_i , x_{ij} , x_{ii} are the investigated factors; k is the number of factors.

As an experimental plan, at this research stage, a three - level five - factor Ha₅ - type plan with properties close the D – optimal was used [19]. The contents of clinker, phosphogypsum in terms of SO₃, the binder specific surface, as well as the content of hardening intensifier (Na₂SiF₆) and SP-1 superplasticizer were selected as varied factors. Experiment planning conditions and the factors variation range are given in Table 3.

The LCSPC strength characteristics were obtained by testing 40 × 40 × 160 mm cement - sand specimens. The water-cement ratio was assigned from the condition of ensuring the required mortar standard cone fluidity that ranged between 106 and 115 mm after 30 shakes on the shaking table. The specimens before the tests were cured in a special chamber at a temperature of 20 ± 2 °C and relative humidity of 90%.

The second stage was focused on experimental confirmation of the LCSPC properties improvement due to adding a complex curing activator admixture, consisting from phosphogypsum, sodium silicofluoride and lime.

As an experimental plan for the third research stage, a three - level two - factor B₂- type plan was used [19]. The contents of binder and plasticizer admixture were chosen as varied factors. Strength characteristics of concrete were obtained by testing standard 15 × 15 × 15 cm cubic samples.

5. Results and discussion

5.1. The complex sulfate-fluoride activation of low clinker slag Portland cement

In accordance with the experiments planning conditions (Table 3), the following characteristics were identified: binder normal consistency, water - cement ratio and compressive strength of standard mortars. After experimental data processing and statistical analysis, mathematical models a form of polynomial regression equations were determined (Table 4).

Analysis of the obtained models shows that, as expected, the most significant reduction in normal cement paste consistency is observed at adding naphthalene - formaldehyde type superplasticizer SP-1 in an amount of 1% by the binder weight (Figure 1(c, d, h)). The paste normal consistency of cement is reduced to 20 - 22%. As it was expected, increase in the specific surface of the low clinker slag Portland cement has a

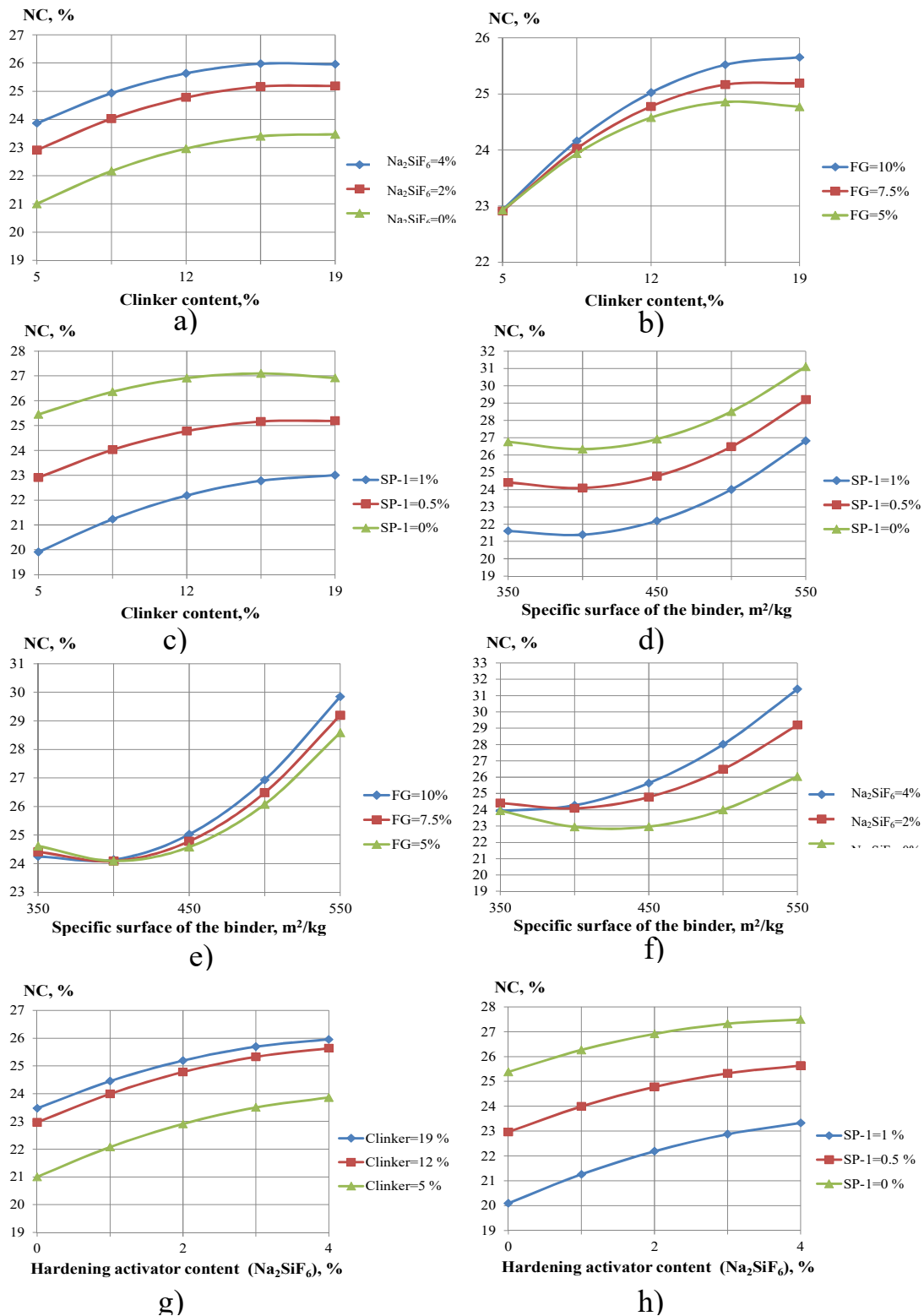


Fig.1- Influence of technological factors on normal consistency of low clinker slag Portland cement:

- a) clinker and hardening activator content (Na_2SiF_6);
- b) clinker and phosphogypsum content;
- c) clinker and SP-1 superplasticizer content;
- d) specific surface of the binder and SP-1 superplasticizer content;
- e) specific surface of the binder and phosphogypsum content;
- f) specific surface of the binder and hardening activator content (Na_2SiF_6);
- g) hardening activator (Na_2SiF_6) and clinker content;
- h) hardening activator (Na_2SiF_6) and SP-1 superplasticizer content.

Table 4

Experimental-statistical models of cement paste normal density, water-cement ratio and strength of low clinker slag Portland cement mortar

Parameters	Regression equation
Normal cement paste consistency , %	$NC = 24.8 + 1.1X_1 + 0.2X_2 + 2.4X_3 + 1.3X_4 - 2.4X_5 - 0.7X_1^2 + 2X_3^2 - 0.5X_4^2 - 0.2X_5^2 + 0.2X_1X_2 + 1.1X_1X_3 - 0.1X_1X_4 + 0.4X_1X_5 + 0.4X_2X_3 + 0.6X_2X_4 + 1X_2X_5 + 0.013X_3X_4 + 0.2X_3X_5 + 0.3X_4X_5$ (2)
Water-cement ratio	$W/C = 0.36 + 0.01X_3 + 0.01X_4 - 0.03X_5 - 0.01X_2^2 + 0.02X_3^2 - 0.02X_4^2 + 0.01X_1X_2$ (3)
Compressive strength at 7 days, MPa	$f_m^7 = 19.8 + 1.8X_1 - 2.2X_2 + 2.9X_3 - 0.1X_4 + 0.9X_5 - 3.1X_1^2 - 1.4X_2^2 - 1.1X_3^2 - 2.3X_4^2 + 3.5X_5^2 - 0.7X_1X_2 - 0.4X_1X_3 - 1.9X_1X_4 - 0.3X_1X_5 + 0.3X_2X_3 - 0.8X_2X_4 - 0.5X_2X_5 + 0.7X_3X_4 - 0.4X_3X_5 + 1.9X_4X_5$ (4)
Compressive strength at 28 days , MPa	$f_m^{28} = 44 + 5.73X_1 - 0.7X_2 + 1.49X_3 + 0.22X_4 + 1.19X_5 - 6.32X_1^2 - 2.42X_2^2 - 3.22X_3^2 - 4.17X_4^2 + 1.33X_5^2 - 0.65X_1X_2 - 1.53X_1X_3 - 2.69X_1X_4 - 0.55X_1X_5 + 1.28X_2X_3 + 0.4X_2X_4 - 3.65X_2X_5 - 0.86X_3X_4 + 0.2X_3X_5 + 2.91X_4X_5$ (5)

significant impact on the cement paste normal consistency. When the specific surface (S) increases from S = 400-450 m²/kg to S = 500 - 550 m²/kg., the cement paste normal consistency is

increased by 20 - 23% (Figure 1(d, e, f)).

It is known that using finely dispersed filler in a form of blast granular slag contributes to reducing the water demand of mortars and

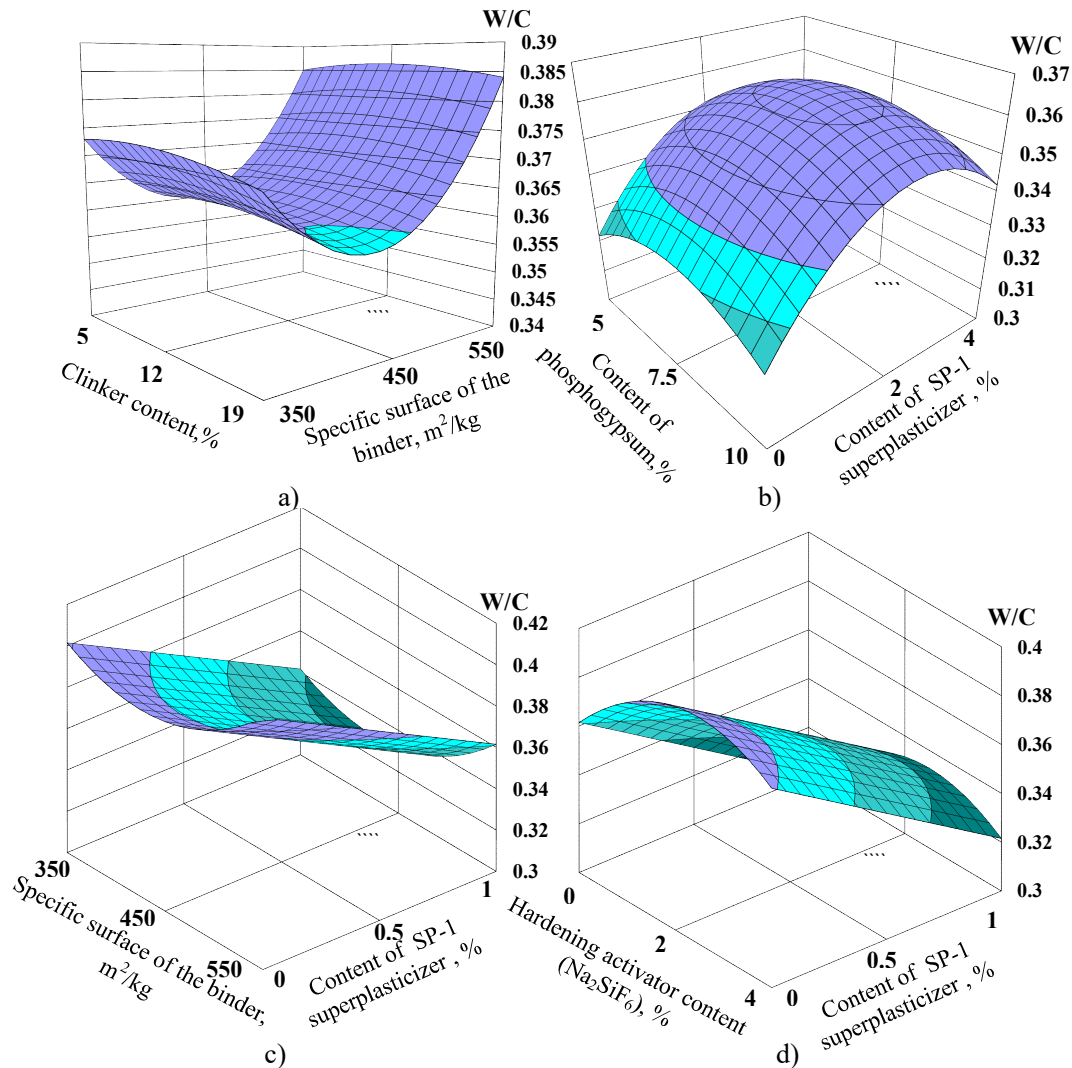


Fig. 2 - Influence of technological factors on water - cement ratio of mortars based on low clinker slag Portland cement: a) clinker content and specific surface of the binder; b) phosphogypsum and SP-1 superplasticizer content; c) specific surface of the binder and SP-1 superplasticizer content; d) hardening activator (Na₂SiF₆) and SP-1 superplasticizer content.

concretes [2]. This can be explained by a decrease in the amount of capillary water that is contained in filler particles (Figure 1(a, b, c)).

Analysis of Eq. 3 in Table 4 and graphic dependencies shown in Figure 2 shows that increase in clinker content does not significantly affect the water - cement ratio of mortars made using LCSPC (Figure 2(a)). Significant influence on the water - cement ratio has the binder specific surface. With the surface area becomes 420 - 450 m²/kg, the binder water demand decreases due to higher mortar plasticity and increase in the binder particles dispersion. Excessive increase in surface area leads to a sharp W/C growth (Figure 2(a, c)). An increase in the content of sodium silico fluoride as hardening activator leads to some increase in water demand (Figure 2(d)). The impact of these two factors has an extreme character.

Increasing the phosphogypsum content to 7.5% (4.5%, of SO₃ equivalent) in the total binder weight leads to a slight increase of W/C. This

increase is due to formation of higher ettringite amount as a result of interaction between the aluminate component of cement clinker and the sulfate component of phosphogypsum. However, when the aluminate component is completely consumed for ettringite formation, further increase in the phosphogypsum content leads to a slight decrease of W/C (Figure 2(b)).

The most significant reduction effect of W/C without changing the consistency of the mortar is achieved when superplasticizer is added. SP-1 superplasticizer allows to reduce the W/C of the mortar made using LCSPC from 0.39 to 0.33 and accordingly increases the specimens strength. As it follows from the analysis, the influence of superplasticizer content on W/C, of the obtained model, is practically linear ((Figure 2(b, c, d)).

Reducing the binder water demand by adding superplasticizer and increasing the specific surface can significantly increase its strength. Strength at 7 days is positively affected by

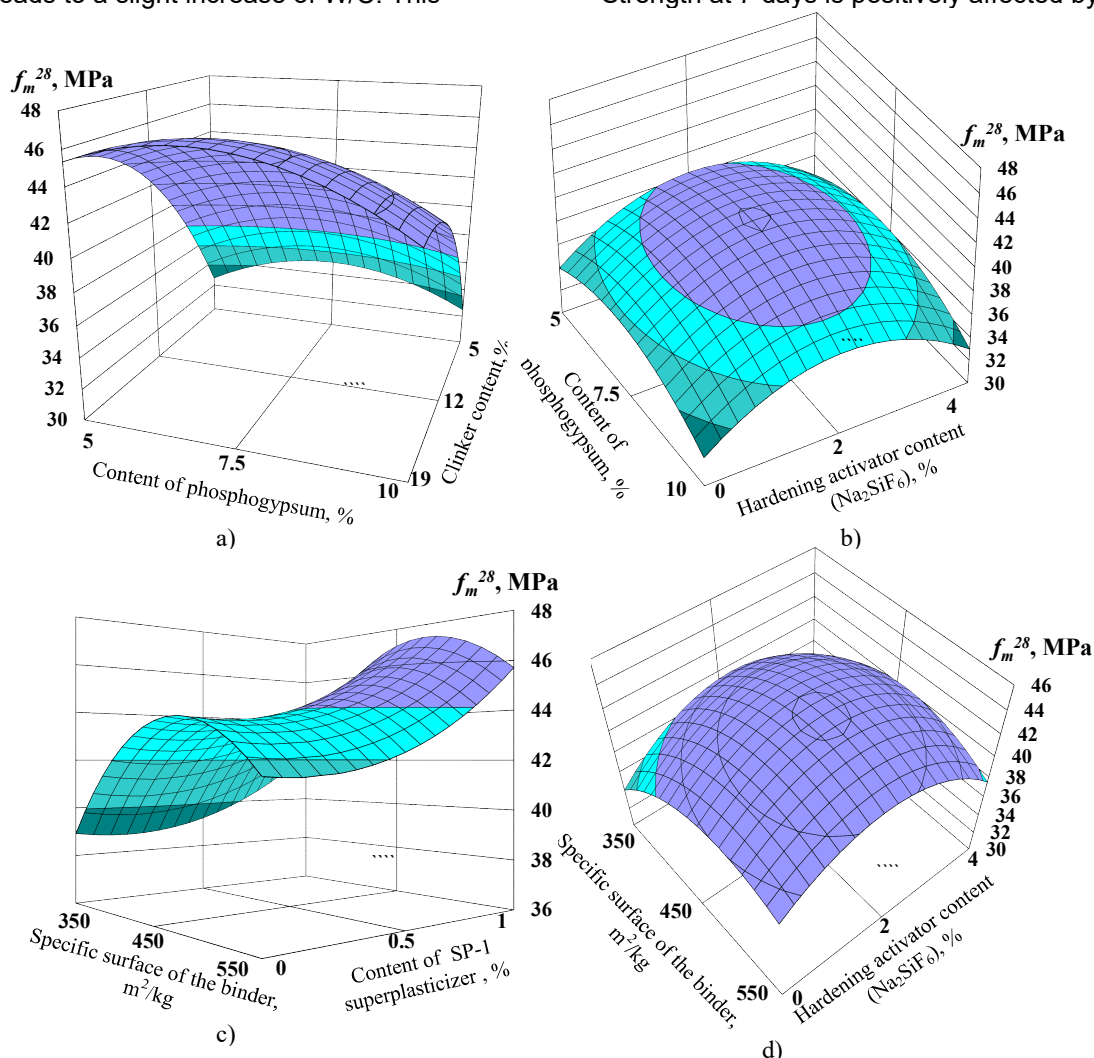


Fig.3 - Influence of technological factors on strength of mortars based on low clinker slag Portland cement at 28 days:

- a) clinker and phosphogypsum content and specific surface of the binder;
- b) phosphogypsum and hardening activator (Na₂SiF₆) content;
- c) specific surface of the binder and SP-1 superplasticizer content;
- d) specific surface of the binder and hardening activator (Na₂SiF₆) content.

increasing the content of hardening intensifier (Na_2SiF_6) up to 2% of the binder weight. As a result, acid - base reactions (in particular, the hydration reaction) are activated. Further increase in the content of this additive leads to a decrease in strength.

Following Figure 3, simultaneous increase in content of clinker, phosphogypsum and sodium silicon fluoride in the total weight of binder, with increasing its specific surface have a positive effect on the LCSPC strength. This is because due to presence of Ca^{2+} and SO_4^{2-} ions and high dispersion of particles, hydration of the blast granular slag glassy phase is accelerated. As a result, formation of low - calcium hydrosilicates occurs. However, it should be noted that with double activation of the slag by calcium hydroxide and the sulfate component, destructive processes are possible – hardening deceleration and some decrease in strength, caused by the hydrosulfoalluminates recrystallization processes (Figure 3 (b, d)). Therefore, as follows from the obtained model (Figure 3), it is necessary to take into account the optimal quantitative ratio of the used activators.

The increase in the binder specific surface as well as the content of curing activator - sodium silicon fluoride have negative effects on the LCSPC strength, which is associated with a sharp increase in W/C. The highest strength of specimens is observed with a surface area of 450 m^2/kg , while the optimum consumption of phosphogypsum and sodium silicon fluoride in the binder is 7.5% (4.5% as SO_3) and 2% respectively (Figure 3 (b, d)). As it should be expected, reducing the water demand of the investigated binders by adding superplasticizer and increasing the specific surface can increase the strength. However, an increase in the total amount of superplasticizer and phosphogypsum in the binder weight above a certain limit negatively affects the strength. This is due to the fact that an increase in the phosphogypsum content leads to formation of an increased amount of ettringite, formation of which requires a relatively large amount of water (Figure 3 (a, b)).

5.2. Sulphate - fluoride-alkaline activation (SFA) of LCSPC

From the results of previous studies [17] follows that addition to binder of ionic nature substances, as well as substances with oxidative properties, contributes to hydration activation and increase of strength. However, the disadvantages of these LCSPC activation ways are low pH of concrete and mortar made using such binder, which does not provide the reinforcing steel passivation.

As known, an effective method for activating slag binders, with simultaneous increase of pH, is adding caustic alkalis [13]. However, the main disadvantage of this method is the very fast setting of the binding system.

It is of interest to determine the possibility of enhancing the effect of sulfate-fluoride activation by adding $\text{Ca}(\text{OH})_2$ into the binder system. From the general chemical positions between these substances should pass the following reaction:



That is, in the cement paste, along with calcium fluoride (CaF_2), an caustic alkali (NaOH) is formed, which provides additional alkaline activation. The results on efficiency of SFA activation are shown in Table 5. All studies were carried out for binder with the following composition: Portland cement clinker – 11.2%, blast furnace granulated slag – 81.8%, phosphogypsum dihydrate - 7% (4.2%, based on SO_3).

Following the obtained results, it can be concluded that addition into the LCSPC composition that contains sulfate activator, complex additive in a form of a mixture of sodium silicon fluoride (Na_2SiF_6) and lime yields an increases in the binder pH from 9 - 10 to 12 - 13 and the binder strength increases. In case of complex sulfate-fluoride-alkaline activation, the LCSPC strength is almost doubled. These results significantly extend the limits of such cement application. It can be used in concrete and reinforced concrete structures.

6. Fine-grained concrete based on activated LCSPC

According to the data given in Table 5, of all the activation types that were investigated the most effective is combined sulfate-fluoride-alkaline (SFL) activation. Therefore, the purpose of the present research at this stage was to study the complex influence on strength of concrete, made on the basis of activated LCSPC, the consumption of cement and various plasticizers. It was also of interest to use stone crushing siftings as an aggregate. At present, these siftings are accumulated in significant amounts in quarries, worsening the ecological situation [20]. The siftings grain composition is given in Table 2. The study was performed using mathematical experiment planning. Three - level two - factor plan [19] was used. Terms of experiments planning are shown in Table 6. All tests were carried out for a LCSPC. In order to provide SFA activation, the following components were added to the binder:

- lime ($\text{Ca}(\text{OH})_2$) in an amount of 3% of the binder weight;
- sodium silicofluoride (Na_2SiF_6) in the amount of 2%.

The strength of the binder with a specific surface of 453 m^2/kg was 45 MPa. Plasticizing additives were:

- technical lingosulfonate;
- naphthalene-formaldehyde SP-1 type superplasticizer;
- polycarboxylic superplasticizer Sika VC 225.

As aggregates for concrete, granite crushing siftings with a fineness modulus of 3.5 (table 2) were used.

After processing and statistical analysis of experimental data, mathematical models of standard concrete cubes compressive strength, in a form of

polynomial regression equations are obtained (Table 7). Graphs illustrating the influence of technological factors on the concrete compressive strength after heat treatment (HT), at 28 days and after HT and 28 days of normal curing are shown in Figures 4, 5 and 6.

Table 5

Results of testing SFA activated LCSPC

No.	Binder type	W/C	Cone slump, mm	Flexural strength, MPa		Compressive strength, MPa	
				at 7 days	at 28 days	at 7 days	at 28 days
1	LCSPC	0.4	130	2.0	5.6	17.0	29.4
2	LCSPC	0.5	215	2.6	3.2	13.3	24.1
3	LCSPC+ Lime (3%)	0.4	120	3.6	8.2	19.9	36.3
4	LCSPC+ Lime (3%)	0.5	205	2.9	5.9	16.3	30.8
5	LCSPC+ Lime (7%)	0.4	200	3.0	6.9	17.8	31.4
6	LCSPC+ Lime (7%)	0.5	120	2.8	6.1	15.5	30.2
7	LCSPC+Na ₂ SiF ₆ (2%)	0.4	120	4.4	6.7	24.7	38.3
8	LCSPC+Na ₂ SiF ₆ (2%)	0.5	205	3.9	6.7	21.3	30.5
9	LCSPC + Lime (3%) + Na ₂ SiF ₆ (2%)	0.4	115	6.7	7.2	28.9	46.7
10	LCSPC + Lime (3%) + Na ₂ SiF ₆ (2%)	0.5	200	6.4	7.5	24.3	39.2
11	LCSPC + Lime (7%) + Na ₂ SiF ₆ (2%)	0.4	115	7.1	8.5	24.9	44.9

Table 6

Experiment planning conditions

№	Factors		Variation levels		
	Natural	Coded	Lower (-1)	Lower (0)	Lower (+1)
1	Binder content, kg/m ³ (C)	X ₁	300	400	500
2	Content of plasticizing admixtures, kg/m ³ : SP-1, SikaVC 225, SikaVC 225+LST(1:1)	X ₂	0	1.5	3

Table 7

Experimental-statistical models of concrete strength at activated LCSPC

Type plasticizer	Statistical models
Compressive strength at 7 days	
SP-1	$f_{c, cube}^7 = 16.118 + 6.985X_1 + 2.217X_2 + 3.014X_1^2 + 1.114X_2^2 + 1.2X_1X_2$ (9)
SikaVC 225	$f_{c, cube}^7 = 17.656 + 7.552X_1 + 6.651X_2 + 6.969X_1^2 + 1.369X_2^2 + 1.2X_1X_2$ (10)
SikaVC 225 + LST	$f_{c, cube}^7 = 25.372 + 5.251X_1 + 3.817X_2 - 3.618X_1^2 - 2.118X_2^2 - 0.2X_1X_2$ (11)
Compressive strength at 28 days	
SP-1	$f_{c, cube}^{28} = 29.612 + 10.252X_1 + 2.517X_2 - 1.764X_1^2 + 0.236X_2^2 + 0.2X_1X_2$ (12)
SikaVC 225	$f_{c, cube}^{28} = 42.659 + 12.036X_1 + 12.736X_2 + 1.275X_1^2 - 4.625X_2^2 + 1.2X_1X_2$ (13)
SikaVC 225 + LST	$f_{c, cube}^{28} = 38.988 + 9.519X_1 + 6.851X_2 - 5.451X_1^2 - 2.351X_2^2 + 1.575X_1X_2$ (14)
Compressive strength after heat treatment (HT)	
SP-1	$f_{c, cube}^{HT} = 27.31 + 10.035X_1 + 2.851X_2 - 3.313X_1^2 + 0.637X_2^2 + 1.625X_1X_2$ (15)
SikaVC 225	$f_{c, cube}^{HT} = 36.076 + 7.451X_1 + 7.968X_2 - 4.123X_1^2 - 2.473X_2^2 - 2.45X_1X_2$ (16)
SikaVC 225 + LST	$f_{c, cube}^{HT} = 29.921 + 6.118X_1 + 3.934X_2 - 5.789X_1^2 + 0.761X_2^2 + 0.8X_1X_2$ (17)
Compressive strength after heat treatment and 28 days of normal hardening	
SP-1	$f_{c, cube}^{HT 28} = 33.435 + 14.086X_1 + 3.701X_2 - 2.92X_1^2 + 3.53X_2^2 + 2.05X_1X_2$ (18)
SikaVC 225	$f_{c, cube}^{HT 28} = 54.041 + 14.236X_1 + 15.636X_2 - 2.576X_1^2 - 5.736X_2^2 + 2.55X_1X_2$ (19)
SikaVC 225 + LST	$f_{c, cube}^{HT 28} = 45.727 + 10.969X_1 + 6.168X_2 - 7.346X_1^2 - 1.146X_2^2 - 2.4X_1X_2$ (20)

* Heat treatment of concrete (HT) was carried out by steaming at 80°C. The rate of the temperature rise and cooling was 30 °C per hour. The isothermal aging duration is 6 hours.

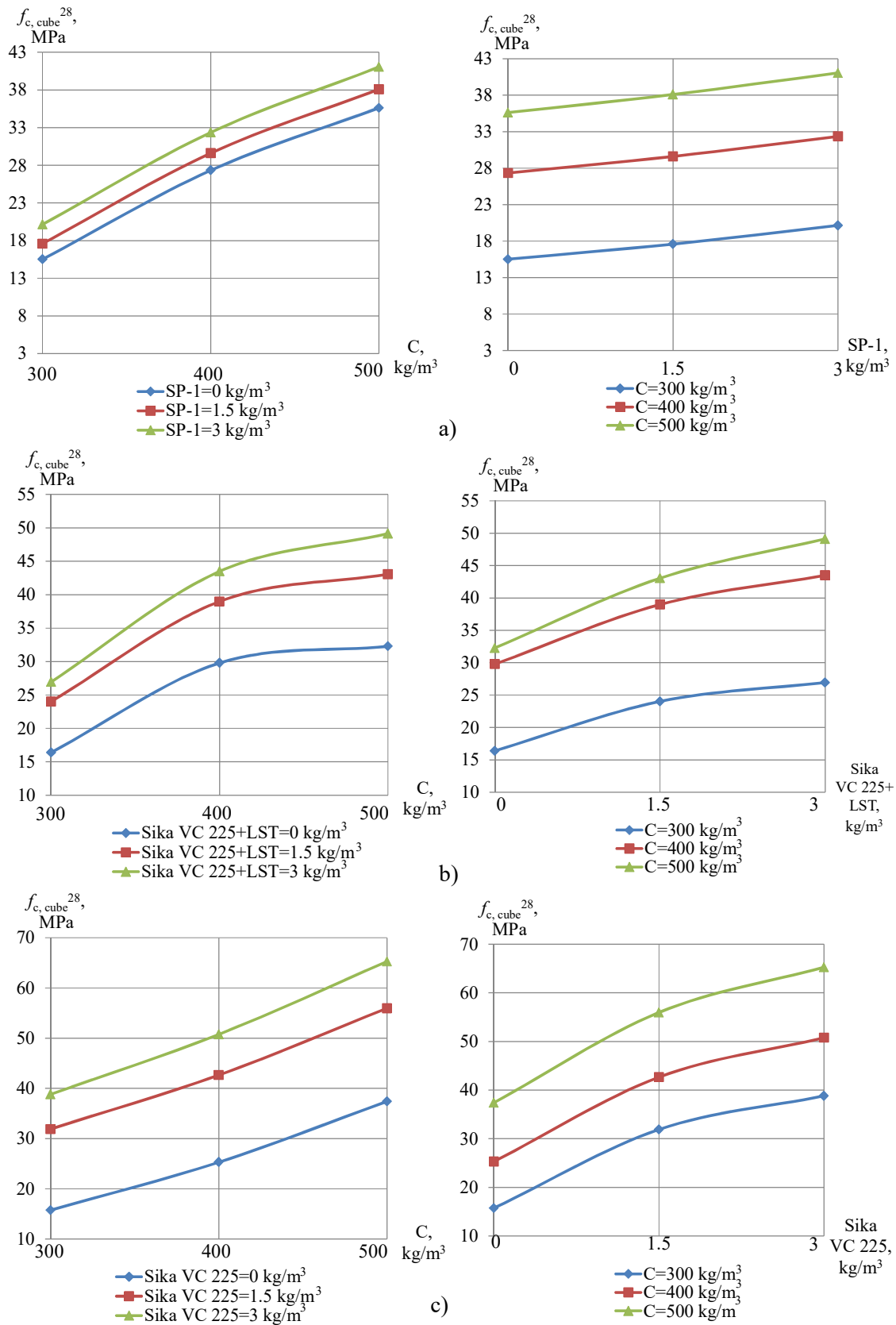


Fig.4 - Influence of technological parameters on LCSPC based concrete strength 28 days: a) SP-1 superplasticizer; b) Sika VC 225+LST (1:1) superplasticizer; c) Sika VC 225 superplasticizer.

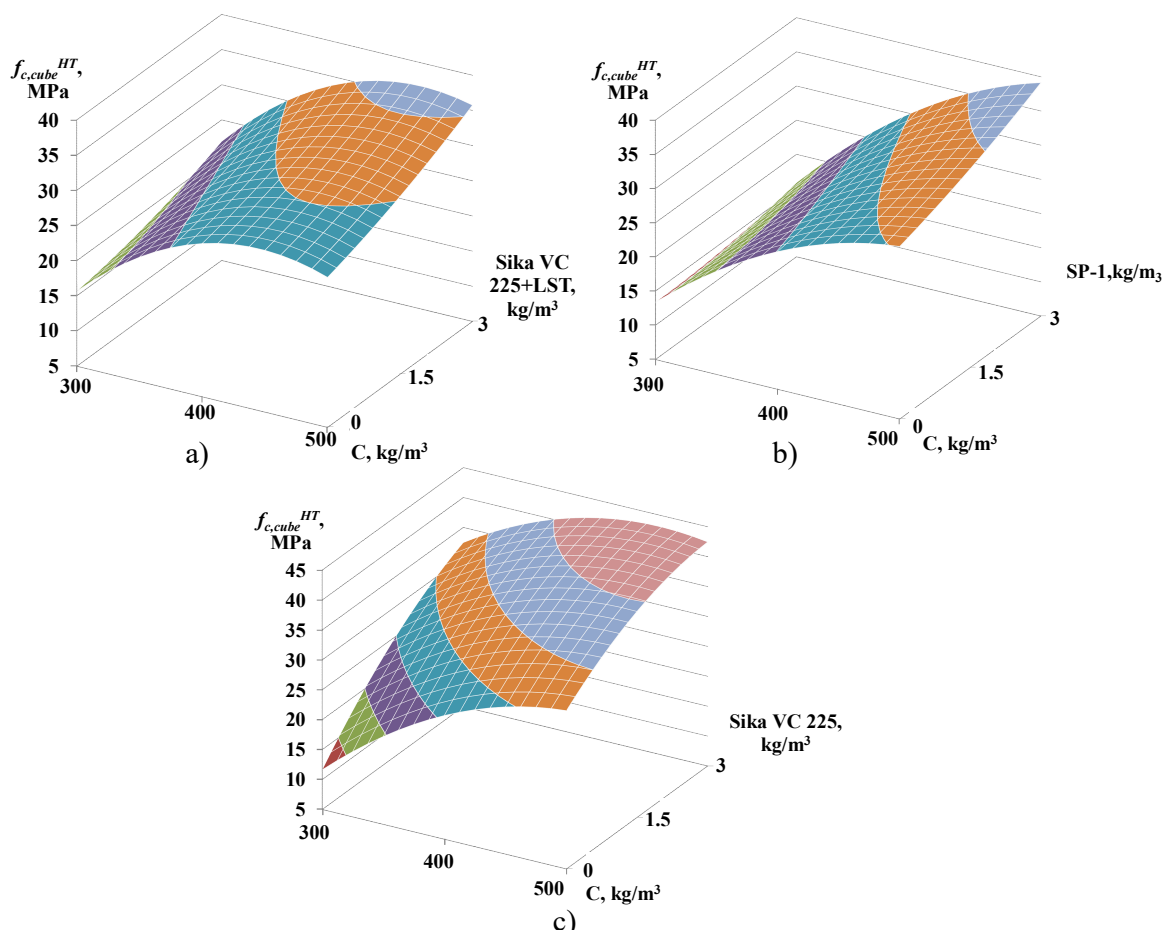


Fig.5 - Influence of technological parameters on LCSPC based concrete strength after heat treatment:

- a) Sika VC 225+LST (1:1) superplasticizer;
- b) SP-1 superplasticizer;
- c) Sika VC 225 superplasticizer

LCSPC – based concrete strength at 7 and 28 days increases most significantly with decreasing W/C. Increasing the content of SikaVC 225 to 3 kg/m³ increases concrete strength twice. The obtained strength values are 40 MPa at 7 days and more than 60 MPa at 28 days (Figure 4 (c)). Using SikaVC 225 + LST allows achieving nearly 30 MPa at 7 days and about 45 MPa at 28 days (Figure 4 (b)). For SP-1 the strength at 7 and 28 days corresponds to 30 MPa and 40 MPa (Figure 4 (a)).

Relatively high strength of concrete, based on LCSPC, can be explained by high reactivity of the binder that has very fine milling, yielding higher activation effect of cement and sulphate compounds of the binder for the blast furnace slag. Achieving low W/C by using plasticizing admixtures promotes cement hydration in “cramped conditions” that yields a more rapid formation of oversaturated solution, at which new hydrate substances are formed in a most rapid way (Dvorkin et al., 2015).

More valuable effect of using fine milled LCSPC is observed at heat curing (Figures 5, 6). A characteristic feature of concrete based on LCSPC is intensive strength growth after steaming. The specimens strength 4 h after steaming is 45 MPa

(Figure 5 (c)) and at 28 days steamed specimens, made using Sika VC 225 plasticizing admixture, achieve strength of 80 MPa (Figure 6 (c)). At adding to the concrete Sika VC 225 + LST the strength values are 35 MPa (Figure 5 (b)) and 50 MPa after 4 h steaming and at 28 days (Figure 6 (b)), respectively, whereas for SP-1 – 40 MPa and 50 MPa, correspondingly (Figure 5 (a), Figure 6 (a)).

In calculation-experimental methods for concrete compositions design that are widely used in practice, the required values of W/C are usually obtained for normal curing temperature and humidity conditions. The most useful equation has the following form [21]:

$$f_c = AR_c(1/(W/C) - b), \text{ [MPa]} \quad (2)$$

where f_c and R_c are correspondingly concrete compressive strength and cement strength, MPa; W/C is the water to cement ratio; A and b are empirical coefficients that take into account the particularities of the used materials and concrete age.

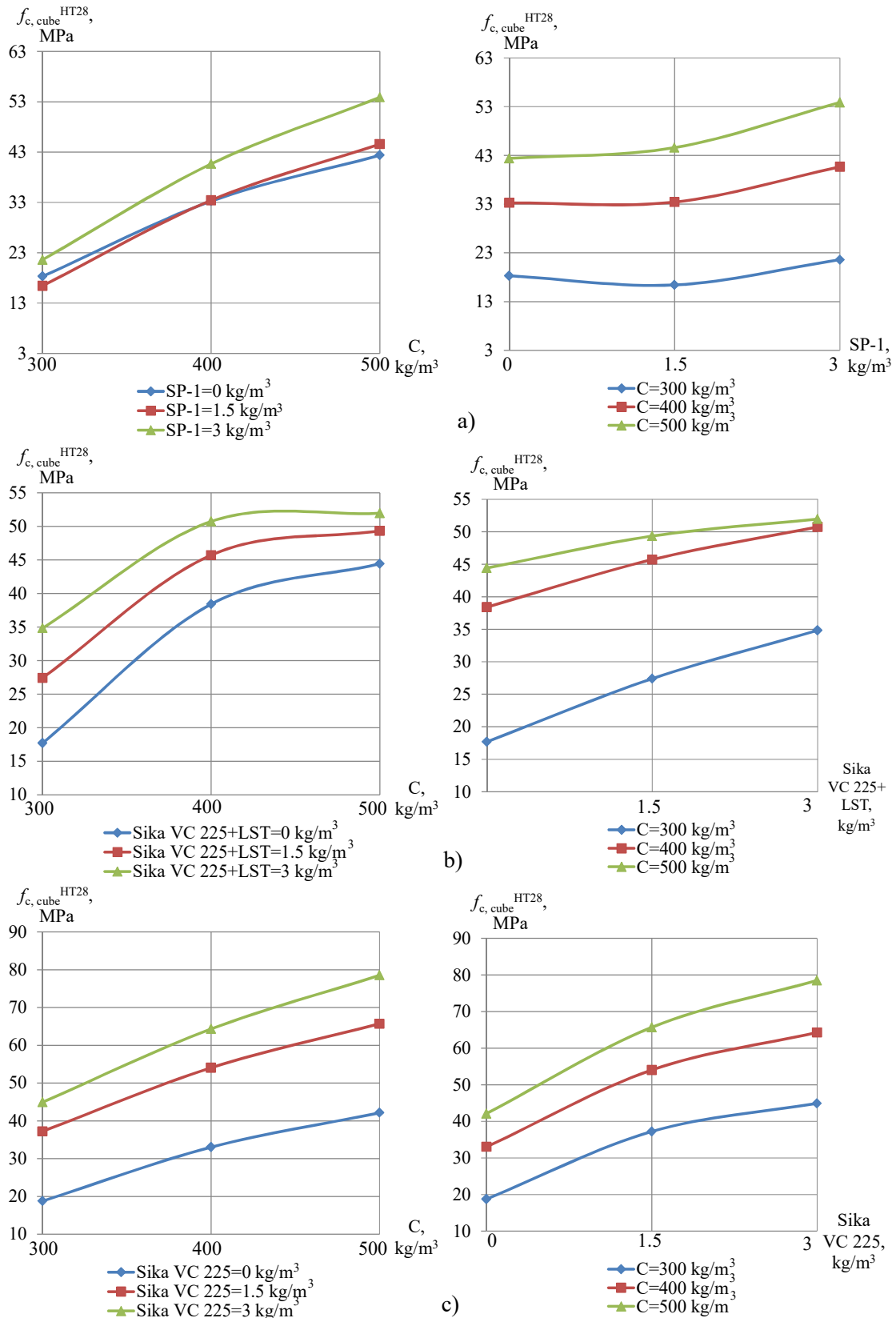


Fig. 6 - Influence of technological parameters on LCSPC based concrete strength after heat –humid processing:
 a) SP-1 superplasticizer;
 b) Sika VC 225+LST (1:1) superplasticizer;
 c) Sika VC 225 superplasticizer.

Table 8

The coefficients A and b in the Eq. (21) for the calculation of the concrete strength made at the activated LCSPC

Duration and hardening conditions	The kind of plasticizer additive					
	SP-1		Sika VC 225		Sika VC 225+LST	
	A	b	A	b	A	b
Compressive strength at 28 days	0.36	0.49	0.43	0.72	0.31	0.22
Compressive strength after heat treatment	0.37	0.67	0.27	0.13	0.20	-0.3
Compressive strength after heat treatment and 28 days of normal hardening	0.51	0.79	0.52	0.72	0.31	-0.23

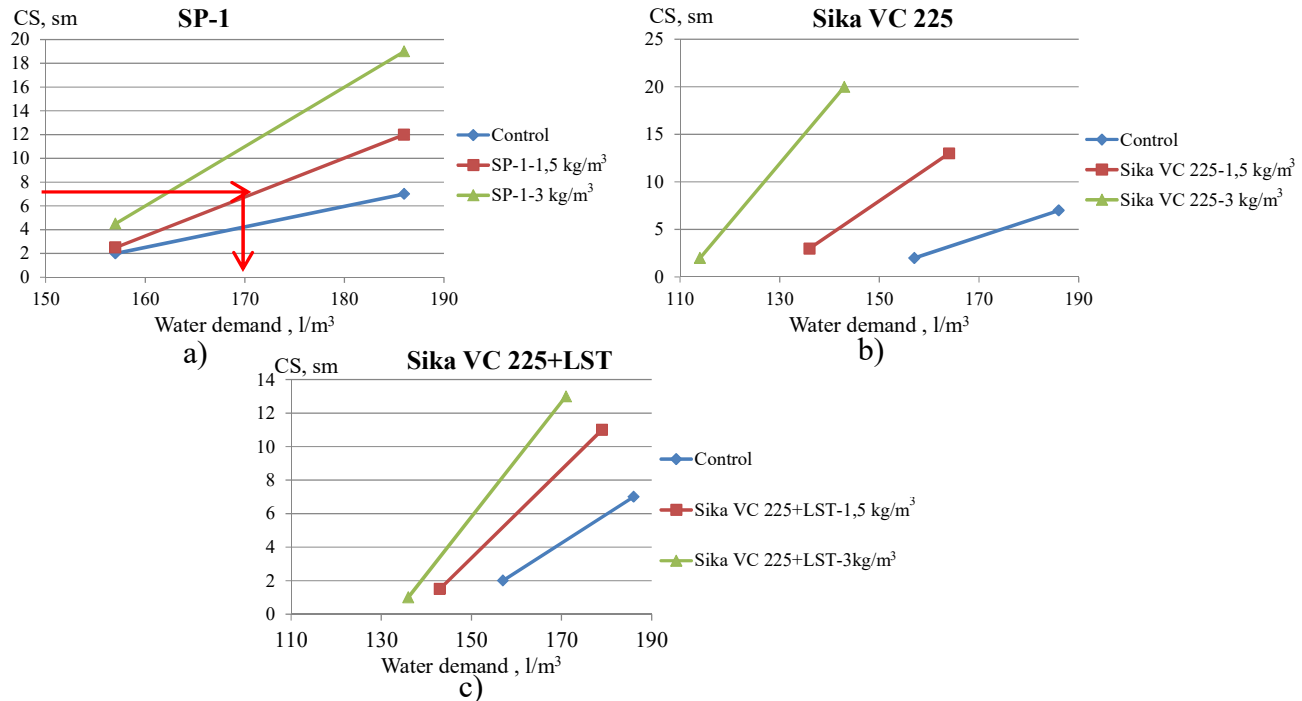


Fig. 7. Dependences of cone slump for LCSPC based concrete vs. water demand per m³:

- a) SP-1 superplasticizer;
- b) Sika VC 225 superplasticizer;
- c) Sika VC 225+LST (1:1) superplasticizer

In order to obtain the coefficients in Eq. (2) for concrete, based on LCSPC and applying various plasticizers, the data for compressive strength and corresponding W/C and different technological factors were approximated. Average values of coefficients A and b for Eq. (2) are presented in Table 8.

Eq. (2) enable to calculate compositions of fine-grained concrete based on LCSPC with the required workability and strength. The methodology includes the following steps:

1. Selecting the type and content of plasticizer and the concrete mix workability.
2. Using the experimentally obtained dependences of the water demand (W) (Figure 7), for a given concrete mix workability value, plasticizer type and content.
3. Finding the concrete mix W/C using Eq. (2), with coefficients A and b from Table 8.

4. Finding the cement content (C):

$$C = W \frac{1}{W/C}, [\text{kg/m}^3] \tag{3}$$

5. Finding the quantity of aggregate (A):

$$A = \left(1000 - \left(\frac{C}{\rho_{cem}} + W \right) \right) \times \rho_A, [\text{kg/m}^3] \tag{4}$$

where ρ_{cem} and ρ_A is the density of the cement and aggregate, respectively.

7. Numerical example

Design composition of fine-grained concrete based on LCSPC with the required compressive strength at 28 days 40 MPa, the concrete mix cone slump is 7 sm. As plasticizing admixture is used SP-

1 in a quantity of 1.5 kg/m³. The LCSPC strength is 45 MPa.

1. According to Figure 7 (a), for the given concrete mix workability (7 cm), plasticizer type (SP-1) and content (1.5 kg/m³), the water demand is 170 l per m³.

2. Using Eq. (2) and coefficients A and b from Table 8, find the W/C ratio, providing the required concrete strength (40 MPa):

$$40 = 0.36 \cdot 45(1/(W/C) - 0.49); W/C = 0.34$$

3. Following Eq. (3), the cement consumption:

$$C = 170/0.34 = 503 \text{ kg/m}^3$$

4. According to Eq. (4), the aggregate content is (siftings with density $\rho_A = 2.7 \text{ g/cm}^3$)

$$A = \left(1000 - \left(\frac{503}{3.1} + 170 \right) \right) \cdot 2.7 = 1802 \text{ kg/m}^3$$

The calculated concrete mix composition: cement – 503 kg/m³, water – 170 l/m³, aggregate (granite siftings) – 1802 kg/m³. Superplasticizer SP-1 – 1.5 kg/m³.

8. Conclusions

1. Results, obtained in the frame of this research demonstrate possibility of producing low clinker slag Portland cement that has strength higher than 40 MPa using bi-component modifying admixtures: superplasticizer of naftalene-formaldehyde type and hardening activator-sodium silicofluoride (Na₂SiF₆). The binder specific surface is 400-450 m²/kg, superplasticizer content – 1%, content of hardening activator (Na₂SiF₆) – 1% of the total binder weight.

2. Complex sulphate-fluoride-alkaline activation of LCSPC significantly shortens the binder setting duration, increases the pH of the concrete and LCSPC strength at 7 and 28 days.

3. The study demonstrates possibility of fine-grained concrete obtaining with rather high strength using as binder LCSPC including less than 20% of clinker. Concrete strength after 28 days of curing in normal conditions is above 50 MPa. Higher effect of applying fine milled LCSPC is observed at using heat curing. Using polycaroxilate type hyperplasticizers SikaVC allows using LCSPC for producing concrete that after heat curing at 80°C has compressive strength of about 80 MPa.

4. The obtained design equations enable to calculate compositions of fine-grained concrete mixtures based on LCSPC with given strength and workability in cases of normal and heat curing.

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