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Compatibility of portland cement and polycarboxylate-based superplasticizers in high-strength concrete for precast constructions

Совместимость портландцемента и суперпластификаторов на поликарбоксилатной основе для получения высокопрочного бетона сборных конструкций

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Key words: building materials; construction; precast concrete; heat-steaming treatment; polycarboxylate-based superplasticizer; stiff fresh concrete

Ключевые слова: строительство; строительные материалы; сборный бетон; тепловлажностная обработка; суперпластификатор на поликарбоксилатной основе; жесткая бетонная смесь

Abstract. Application of polycarboxylate-based superplasticizers can contribute to the increase of concrete early strength. It makes possible to obtain the concrete of the required strength after heat-steaming treatment with decreasing the isothermal temperature and the Portland cement quantity compared to the concrete without admixtures. Reducing of water-cement ratio and lack of accelerated high-temperature of heat-steaming treatment raises the durability of precast concrete. The use of low heat-steaming treatment must not lead to an increase of the duration of treatment and reduction of productivity of plant with double turnover of moulds per day. It is necessary to take into account the compatibility of Portland cement and polycarboxylate-based superplasticizers to obtain the high concrete strength after heat-steaming treatment. The problem of the compatibility of Portland cement and polycarboxylate-based superplasticizers in precast concrete production contains the following items: the influence of chemical and mineralogical compositions of Portland cement on the water-reducing effect of polycarboxylate-based superplasticizers, on the retention of workability of fresh concrete as well as on the growth of early concrete strength. Most of the published papers contain the results received when investigating the cement paste. However, the effect of polycarboxylate-based superplasticizers in stiff fresh concrete has not yet been fully investigated. The optimal dosages of polycarboxylate-based superplasticizers, requirements to the granulometric and chemical-mineralogical compositions of Portland cements with the purpose of reducing the cement consumption and providing the required concrete strength after the heat-steaming treatment at 40 °C have been defined.

Аннотация. Применение поликарбоксилатных суперпластификаторов позволяет получать высокопрочный бетон и может способствовать повышению ранней прочности бетона. Это дает возможность получать бетон с требуемой прочностью после тепловлажностной обработки (ТВО) при снижении температуры изотермической выдержки и расхода портландцемента по сравнению с бетоном без добавок. При этом необходимо учитывать совместимость портландцемента и поликарбоксилатного суперпластификатора. В области производства сборного бетона и железобетона под вопросом совместимости портландцементов с суперпластификаторами следует понимать влияние химико-минералогического состава портландцемента на водоредуцирующее действие добавок, исключение быстрой потери подвижности бетонной смеси, почасовую кинетику набора ранней прочности бетона с суперпластификатором. Большая часть работ отражает результаты, полученные на цементном тесте. Однако эти вопросы не исследованы для жестких бетонных смесей. Установлены оптимальные расходы суперпластификаторов, требования к гранулометрическому и химико-минералогическому составу портландцементов с целью снижения расхода цемента и обеспечения требуемой прочности бетонов после ТВО продолжительностью 12 часов при температуре изотермической выдержки 40 °С. Получены зависимости прочности бетона после ТВО от расхода портландцемента и поликарбоксилатных суперпластификаторов.

Introduction

Application of polycarboxylate-based superplasticizers can contribute to the increase of concrete early strength. It makes possible to obtain the concrete of the required strength after heat-steaming treatment with decreasing the isothermal temperature and the Portland cement quantity compared to the concrete without admixtures. Steaming at high temperatures reduces a number of technical characteristics of concrete such as strength at age of 28 days and frost resistance [1]. Reducing of water-cement ratio and the lack of accelerated high-temperature of heat-steaming treatment raises durability of precast concrete due to the improvement of the concrete structure [2–6]. The use of low heat-steaming treatment must not lead to an increase of the duration of treatment and reduction of productivity of plant.

It is necessary to take into account the incompatibility of Portland cement and polycarboxylate-based superplasticizers to obtain the high concrete strength after heat-steaming treatment. Such concrete should provide the required transfer strength (strength at the moment of release tension bars) in a relatively short time 10–12 hours. For example, with double turnover moulds per day at the plant the concrete strength of class B40 should be not less than 35 MPa at the age of 10–12 hours and 44 MPa – for concrete strength of class B50.

Considering the problem of the incompatibility of Portland cement and polycarboxylate-based superplasticizers in precast concrete production it is necessary to take into account the influence of chemical and mineralogical compositions of Portland cement on the water-reducing effect of polycarboxylate-based superplasticizers, on the retention of workability of fresh concrete as well as on the growth of early concrete strength.

Considerable decrease of water quantity in fresh concrete mixes of equal workability by means of introducting small dosages of polycarboxylate-based superplasticizer accelerates the Portland cement hydration. On the other hand, the increased dosages of polycarboxylate-based superplasticizer slow down the Portland cement hydration in spite of their high water-reducing effect.

The authors [7, 8] highlight the role of a soluble alkali and C_3A in the retention of workability of fresh cement paste.

The papers published on incompatibility theme can be classified into the following subjects depending on the factor studied: chemical and mineralogical compositions of Portland cement (quantity of C_3A, Na_2O_{equiv}, SO_3) and its fineness [9–10]; fineness and quantity of mineral fillers [11–15]; quantity of admixture [12, 16]; chemical base of admixture, structure of its molecule [17], speed of polycarboxylate-based superplasticizer adsorption on the cement particles being hydrated [18–23].

The mineral additions in Portland cement impact rheology of cement paste and affect the interaction between superplasticizers and cements. The results of paper [11] show that cement-superplasticizers compatibility is altered by the physical (specific surface) and chemical (surface charge) characteristics of the mineral additions (limestone, fly ash and silica fume). In paper [14] it has investigated the incompatibility of Blended cement and polycarboxylate-based superplasticizers in range from 0.7 to 1.2 %. The delay of admixtures on cement hydration intensifies with rising PCE dosage. This admixture-mediated retarding effect was also observed to vary depending on the nature of the addition, and was most intense in slag-blended cement.

Most of the published papers contain the results received when investigating the cement paste. However, the effect of polycarboxylate-based superplasticizer in stiff fresh concrete has not yet been fully investigated. It is necessary to specify to what changes in admixture dosage or water quantity as well as in concrete strength development the changing Portland cement properties can lead to. The results of the research can be used in the production of precast prestressed reinforced concrete with polycarboxylate-based superplasticizers on the existing technological lines of plants with double turnover of moulds per 24 hours.

Materials and methods of research

For research it was selected the domestic Portland cements PC500-D0-N of six manufacturers corresponding to Russian Standard GOST 30515-97 “Cements. General technical conditions” and CEM I 42.5N from two factories corresponding to Russian Standard GOST 31108-2003 “Cements. Technical conditions”. Chemical and mineralogical compositions of Portland cements are presented in

Tables 1 and 2. Most of Portland cements had the content of C_3S within 60 % and the content of C_3A – 6–9 %. Such Portland cements are the most effective in the precast concrete production under conditions of heat-steaming treatment at temperature 80 °C. As polycarboxylate-based superplasticizers it was selected those, which due to their certain molecule structure are able to increase the concrete early strength. These are: Glenium ACE 430, Sika Viscocrete 20 Gold. The sand and crushed stone aggregates were according to Russian Standards GOST 8736-93 and GOST 8267-93. The control sample was prepared from the concrete mix (Portland cement 470 kg/m^3) used in the production of precast prestressed reinforced concrete with the double turnover of moulds every 24 hours and heat-steaming treatment at the isothermal temperature of 80 °C. The workability of fresh concrete was 18–20 seconds.

Table 1. Chemical compositions of Portland cements

No of sample	Cement	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	Na_2O_{eqv}	$CaO_{св}$	L.O.I.
1	CEM I 42.5N	63.80	21.20	4.90	3.90	1.00	2.80	0.60	0.13	0.52	0.30	1.10
2	PC500-D0-N	63.90	21.00	4.88	4.12	0.92	2.77	0.58	0.17	0.55	0.25	1.00
3	CEM I 42.5N	66.20	21.60	5.77	4.12	1.09	2.50	0.57	0.30	0.68	-	1.06
4	PC500-D0-N	65.97	21.41	5.67	5.12	0.80	2.57	0.68	0.31	0.76	-	0.86
5	PC500-D0-N	63.79	21.26	3.67	3.54	1.75	2.76	0.59	0.76	1.15	-	1.17
6	PC500-D0-N	65.74	21.50	4.96	5.32	1.32	2.60	0.57	0.32	0.69	0.07	0.33
7	PC500-D0-N	63.56	20.56	5.21	4.13	1.41	2.82	0.65	0.36	0.79	-	0.94
8	PC500-D0-N	61.90	19.70	4.92	3.30	3.90	3.12	0.67	0.71	1.15	-	-

The following methods were used: analysis of the particle size distribution (the laser particle size distribution analyzer – MicroSizer 201), termokinetic analysis (Calvet-type calorimeter), scanning electron microscopy (Supra55VP-3249 Zeiss). The kinetics of the plastic strength growth of the cement paste was investigated using a cone plastometer following the methodology of academician P.A. Rebinder [24]. The tests were conducted at intervals of cone immersing, equal to 30 minutes. As the criterion were used the value of the plastic strength in MPa, which was determined from the expression:

$$P_m = K \cdot \frac{F \cdot g}{100000 \cdot h^2},$$

where F – the load in g;

h – depth of cone immersion in cm, h = 1 cm;

K – coefficient depending on the angle of the cone at the top, at 45° K = 0.656.

The results of defining the plastic strength are expressed graphically in the form of plastograms, on which one can distinguish specific periods: the initial period (induction period) and that of rapid growth plastic strength.

Table 2. Mineralogical compositions of Portland cements

No of sample	C_3S	C_2S	C_3A	C_4AF
1	63.0	14.7	6.5	13.0
2	63.1	14.6	6.3	13.5
3	64.4	14.3	9.9	11.0
4	59.1	17.0	6.2	15.5
5	66.4	14.6	4.2	10.7
6	63.9	13.0	4.1	16.0
7	65.0	9.4	6.4	12.4
8	62.1	10.4	6.9	11.3

Results and discussion

Comparison of particle size distribution of the selected Portland cements showed that there are fewer particles having the grains size less than 2, 3, 5 and 10 µm in Portland cements No. 1, 2, 3, 4 than in the other Portland cements (Table 3).

Table 3. The particle size distribution of Portland cements

No of sample	Содержание зерен размером менее, %					
	2 мкм	3 мкм	5 мкм	10 мкм	16 мкм	32 мкм
1	7.2	9.9	15.9	25.7	37.8	59.6
2	6.3	8.6	14.1	23.7	48.8	68.9
3	9.7	13.6	20.2	33.8	44.2	71.6
4	9.0	12.5	19.8	36.7	47.1	72.6
5	14.8	20.8	28.7	42.9	51.3	70.7
6	11.6	16.6	23.7	38.6	49.2	75.2
7	6.6	11.5	24.0	38.9	45.8	71.0
8	13.9	19.7	27.4	42.2	51.8	73.8

Setting time can be estimated on cement pastes through the Vicat needle method. A recent study [25, 26] suggested improving the Vicat test by using a static method that allows monitoring of the evolution of the setting starting immediately from the mixing time. Based on ultrasound techniques, a new testing device is suggested to analyze setting and hardening of concrete materials. In this paper the cone plastometer of academician P.A. Rebinder are proposed. This method allows also monitoring of the evolution of the setting starting immediately from the mixing time [27].

By comparing the kinetics of the plastic strength development it was found out that Portland cements, which have a shorter initial period (induction period) of hardening and more intensive plastic strength development in the second period of hardening, contained the increased number of grains of size less than 10 µm, which was 36–42 % (Figure 1). The application of such Portland cements allows reducing the duration of curing before heat-steaming treatment of concrete.

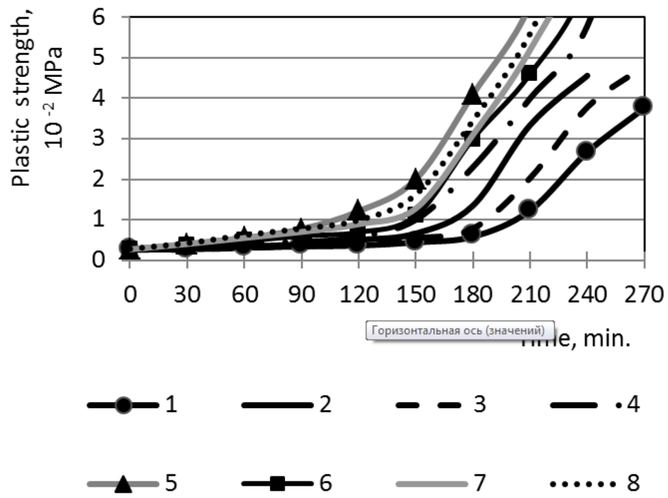


Figure 1. Influence of Portland cements on plastic strength development cement paste of equal fluidity

It was stated that the required strength of concrete of class B40 (34.9 MPa) after the heat-steaming treatment duration of 12 hours at isothermal temperature of 40 °C, can be obtained on Portland cements with the content of grains of size less than 3 µm within 17–21 % (Figure 2).

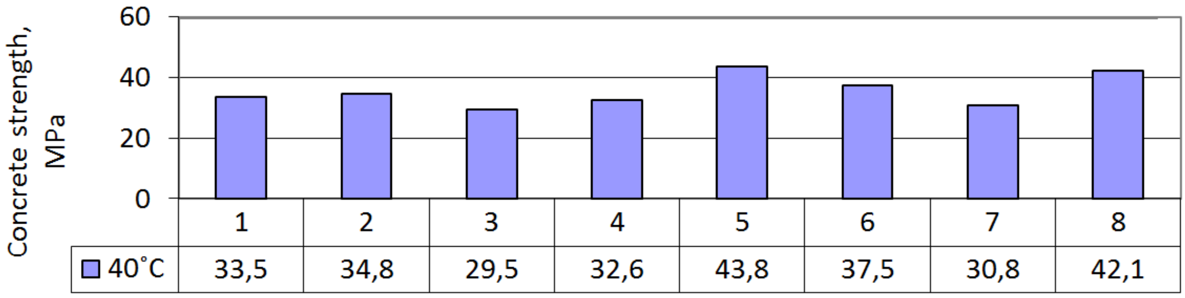


Figure 2. Concrete strength after the heat-steaming treatment duration of 12 hours at isothermal temperature of 40 °C

However, not always the high value of early concrete strength on Portland cements, containing the defined number of fine particles is a characteristic that guarantees the high early strength of concrete on these Portland cements with polycarboxylate-based superplasticizers.

The water-reducing effect of polycarboxylate-based superplasticizers depends on the chemical and mineralogical compositions of cement (Figures 3–4). It is established that the increasing of C_3A in Portland cement results in the decreasing of the water-reducing effect of polycarboxylate-based superplasticizers. This was also confirmed in fresh concrete mixes of equal workability when comparing the water-reducing effect of Sika Viscocrete 20 Gold and Glenium ACE 430 (Figure 5). The content of SO_3 and alkaline metals in Portland cement No. 1, 2, 3 was almost the same, so their influence on the plasticizing action of admixtures can be neglected. Reduction of water consumption within the limits of 16 % was received in concrete mixtures on Portland cement containing C_3A about 6.5 % with the introduction of 0.4 % of polycarboxylate-based superplasticizers and 0.8 % of polycarboxylate-based superplasticizers – on Portland cement containing C_3A about 9.9 %. With the increase of dosage of polycarboxylate-based superplasticizers the difference between their water-reducing effects in fresh concrete on these Portland cements is decreased.

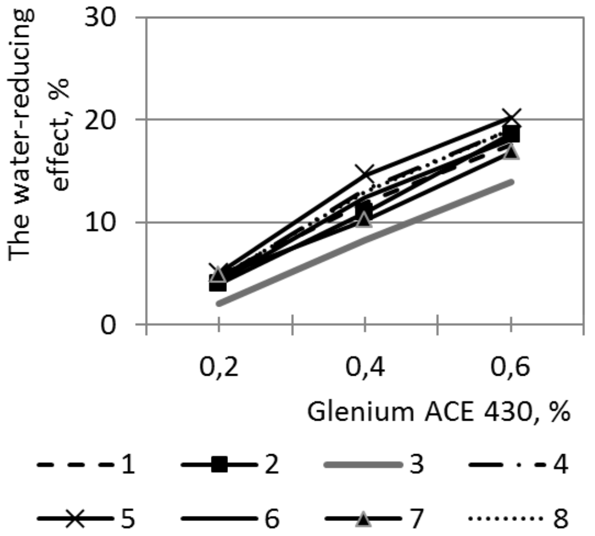


Figure 3. The water-reducing effect of Glenium ACE 430 depending on cement

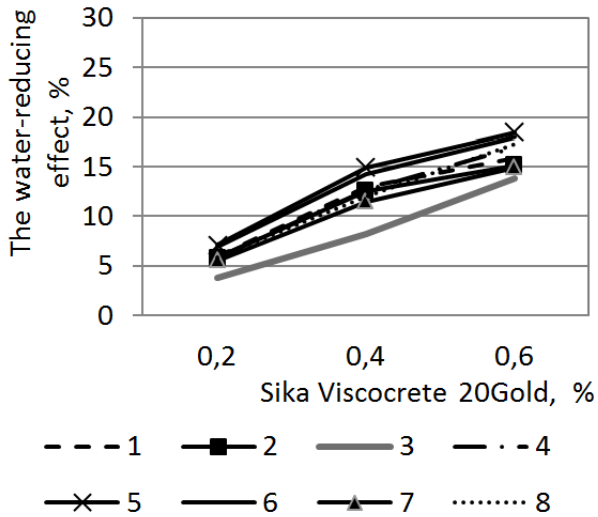


Figure 4. The water-reducing effect of Sika Viscocrete 20 Gold depending on cement

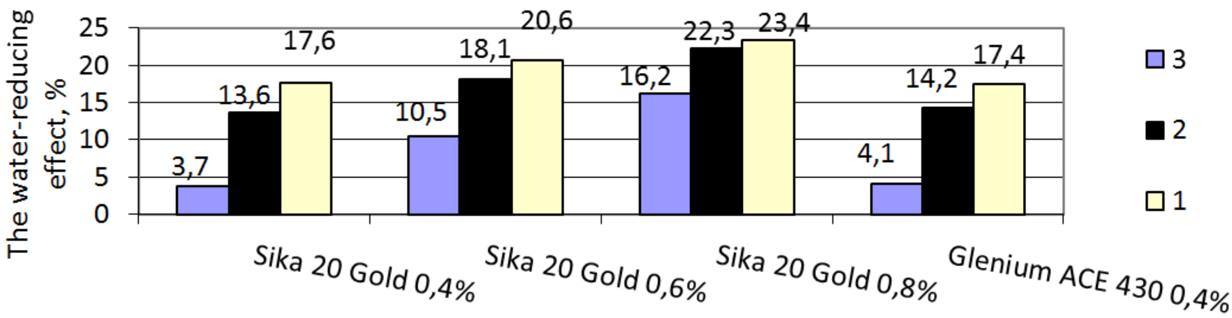


Figure 5. The water-reducing effect of polycarboxylate-based superplasticizers in the stiff fresh concrete mixes depending on cement

In fresh concrete containing polycarboxylate-based superplasticizers and Portland cements with a high content of alkali metals in 8–15 minutes from the moment of water addition there was observed the rapid loss of workability. This agrees with the data obtained by calorimetric measurements on cement pastes with polycarboxylate-based superplasticizers (Figures 6–9). The influence of alkali metal content in cement on the value of first peak of heat flow curve was shown. In the cement paste on Portland cement No. 2 ($Na_2O_{equiv} = 0.55$) the first peak appears in 3–5 minutes, i.e. actually in the period of preparation of fresh concrete mix. When increasing the alkali metal content in cement to $Na_2O_{equiv} = 1.15$ the first peak appears in 8–12 minutes. According to G. Verbek [28] the value of heat flow is proportional to the number of hydrate phases, therefore, in case of Portland cements with high content of alkali metals there occurs the intensive growth of hydrate phases and the fast loss of workability of fresh concrete mix. The second peak of heat flow curve was noted on Portland cements No. 5 and 8 earlier than on the others, which agrees with the data of more high strength concrete on these cements at the age of 12 hours.

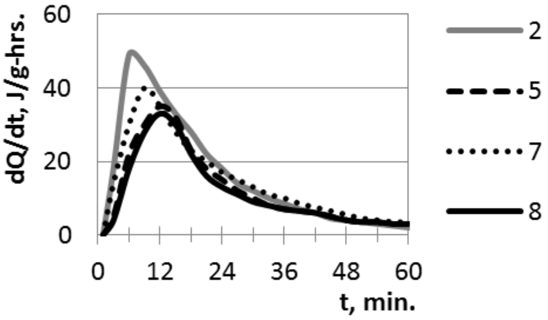


Figure 6. Heat rate of Portland cements with Sika Viscocrete 20 Gold 0.4 % during first hour of hydration

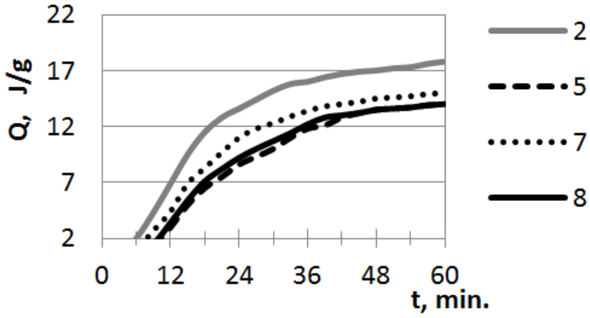


Figure 7. Cumulative heat of Portland cements with Sika Viscocrete 20 Gold 0.4 % during first hour of hydration

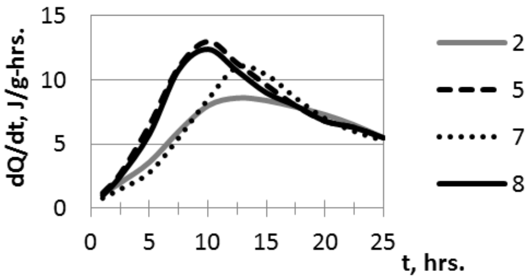


Figure 8. Heat rate of Portland cements with Sika Viscocrete 20 Gold 0.4 % during 25 hours of hydration

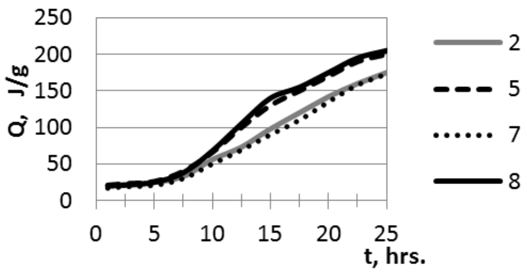
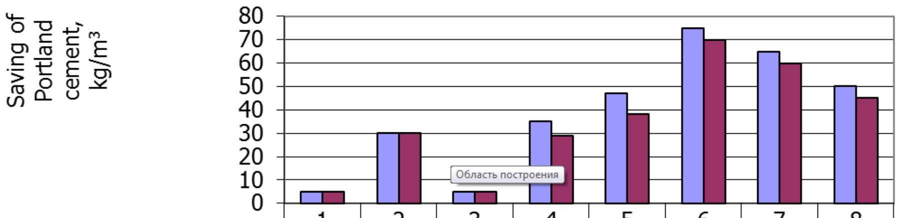


Figure 9. Cumulative heat of Portland cements with Sika Viscocrete 20 Gold 0.4 % during 25 hours of hydration

In order to avoid the loss of workability of fresh concrete with polycarboxylate-based superplasticizers on Portland cements, containing increased quantity of alkaline metals, it is necessary to add the mixing water in two stages. The polycarboxylate-based superplasticizers should be added with the second part of mixing water or it is necessary to increase the duration of mixing up to 1–2 minutes. In the absence of the possibility of adding the mixing water in the two stages it is necessary to increase the total quantity of the mixing water up to 5–7 %. However, the increase of mixing water leads to the reducing the early concrete strength and does not allow to receive the significant saving of Portland cement.

According to the results of studies of eight Portland cements it turned out that to ensure the high water-reducing effect of polycarboxylate-based superplasticizers and to eliminate the rapid loss of workability of fresh concrete, the recommended content of the C_3A, SO_3, Na_2O_{equiv} in Portland cements should be within 4.0–7.0 %; 2.57–2.82 %; 0.52–0.79 % respectively.

When comparing the effectiveness of admixtures such as Sika Viscocrete 20 Gold and Glenium ACE 430 in the studied Portland cements in order to ensure the necessary strength of concrete (class B40) after the heat-steaming treatment at the isothermal temperature of 40 °C and the duration of 12 hours, it was established that the maximum reduction of Portland cement consumption can be obtained with the Portland cement, with the content of cement grains of size less than 3 µm with 17 % and content of C_3A, SO_3, Na_2O_{equiv} within the limits mentioned above (Figure 10).



	1	2	3	4	5	6	7	8
Sika 20 Gold 0.4%	5	30	5	35	47	75	65	50
Glenium ACE 430 0.4%	5	30	5	29	38	70	60	45

Figure 10. Saving of Portland cement after the heat-steaming treatment at 40 °C and the duration of 12 hours

The dependences of concrete strength after the heat-steaming treatment at temperature 40 °C and the duration of 12 hours on the Portland cement consumption and admixture dosage were obtained. Regression equations were calculated, which allows to choose the concrete compositions depending on the required concrete strength at the age of 12 hours. Variable factors were: admixture dosage – X1 (%) and Portland cement consumption – X2 (kg). The regression equations, obtained as a result of statistical data processing are the following:

1. $R = 38.837 + 3.158X1 + 13.1X2 + 0.303X1^2 + 6.428X2^2 - 2.150X1X2$,

where X1 – dosage of Sika 20 Gold.

2. $R = 40.676 + 0.713X1 + 3.970X2 - 3.098X1^2 - 2.048X2^2 - 2.070X1X2$,

where X1 – dosage of Glenium ACE 430.

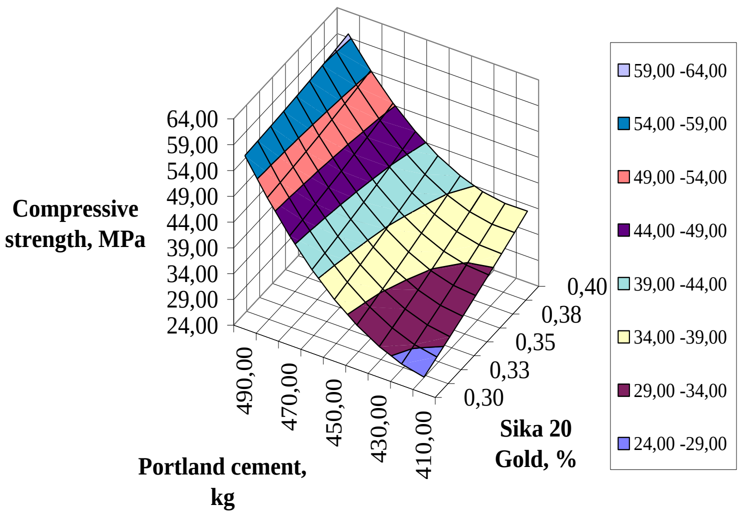


Figure 11. The dependence of concrete strength after the heat-steaming treatment at 40 °C and the duration of 12 hours on the cement consumption and admixture dosage

Checking adequacy according to the criterion of the Fisher in the level of reliability of 0.95 showed the suitability of mathematical models for the description of the investigated dependencies. In Figures 11 and 12 one can see the graphical representation of mathematical models. The use of admixtures in optimal quantity: Sika Viscocrete 20 Gold of 0.38 %, Glenium ACE 430 – 0.4 % made it possible to reduce Portland cement consumption by 15 % and the isothermal temperature of heat-steaming treatment from 80 °C to 40 °C. The concrete strength of samples with admixtures at the age of 28 and 360 days was actually equal to the samples without admixtures.

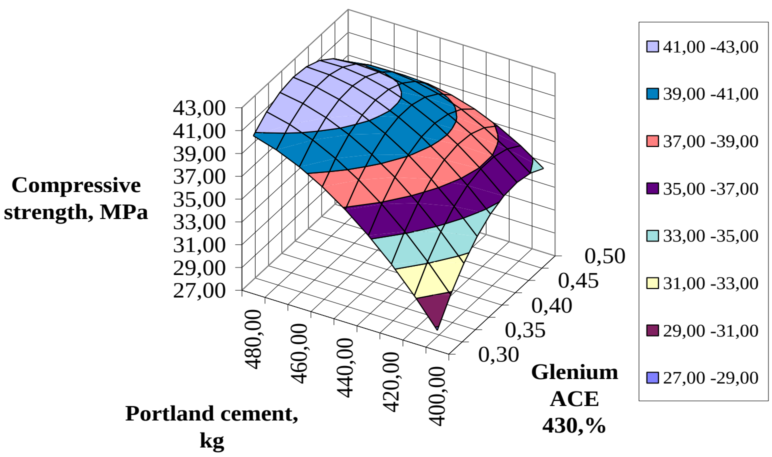


Figure 12. The dependence of concrete strength after the heat-steaming treatment at 40 °C and the duration of 12 hours on the cement consumption and admixture dosage

When comparing the shape and size of C-S-H phases by means of scanning electron microscopy it could be seen that the samples of the cement stone at the age of 12 hours with the admixture of Sika Viscocrete 20 Gold (0.4 %) are much finer and the structure of C-S-H phases is much denser (Figures 13–14), which increases the number of contacts between C-S-H phases and helps to increase the strength of cement stone.

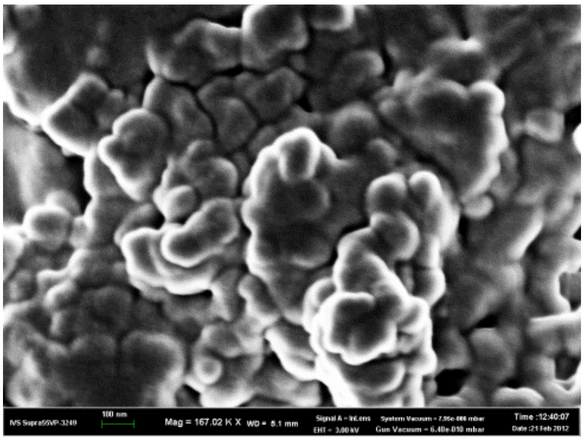


Figure 13. The structure of C-S-H phases in sample without admixture after the heat-steaming treatment at 40 °C and the duration of 12 hours

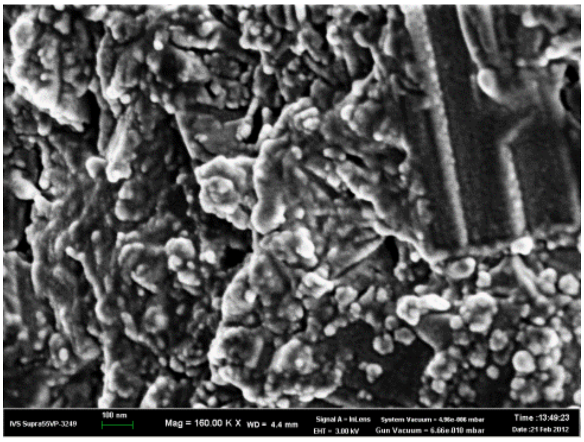


Figure 14. The structure of C-S-H phases in sample with admixture after the heat-steaming treatment at 40 °C and the duration of 12 hours

The C–S–H that forms in the hydration of Portland cement has variable stoichiometry depending on the water to cement ratio, curing conditions and use of supplementary cementitious materials [29, 30]. According [31] there are two types of C–S–H in hydrated Portland cement: low density and high density. The low-density C–S–H phase has a mean stiffness of about 22 GPa while the mean stiffness is about 29 GPa for high-density C–S–H.

Conclusions

1. The results of the research can be used in the production of precast prestressed reinforced concrete with polycarboxylate-based superplasticizers on the existing technological lines of plants with double turnover of moulds per day. The influence of chemical and mineralogical compositions of Portland cements should be taken into account to ensure the high water-reducing effect of these admixtures with their small dosage.

2. The optimal dosages of polycarboxylate-based superplasticizers, requirements to the granulometric and chemical-mineralogical compositions of Portland cements with the purpose of reducing the cement consumption and providing the required concrete strength after the heat-steaming treatment at 40 °C have been defined.

3. According to the results of studies of eight Portland cements it turned out that to ensure the high water-reducing effect of polycarboxylate-based superplasticizers and to eliminate the rapid loss of workability of fresh concrete, the recommended content of the C_3A, SO_3, Na_2O_{equiv} in Portland cements should be within 4.0–7.0 %; 2.57–2.82 %; 0.52–0.79 % respectively.

4. It was stated that the required strength of concrete of class B40 (34.9 MPa) after the heat-steaming treatment duration of 12 hours at isothermal temperature of 40 °C, can be obtained on Portland cements with the content of grains of size less than 3 μm within 17–21 %.

5. The use of admixtures in quantity: Sika Viscocrete 20 Gold of 0.38 %, Glenium ACE 430 – 0.4 % made it possible to reduce Portland cement consumption by 15 % and the isothermal temperature of heat-steaming treatment from 80 °C to 40 °C with providing the required concrete strength after the heat-steaming treatment.

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