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Phase structure of cement pastes with antifreeze agents

E.A. Vdovin ✉ , ***V.F. Stroganov***

Kazan State University of Architecture and Engineering, Kazan, Russian Federation

✉ *vdovin007@mail.ru*

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Abstract. This paper is concerned with changes in the phase structure of cement paste modified by complex antifreeze agents based on sodium formate, calcium chloride and S-3 superplasticizer. Complex modifiers were developed for cement-crushed mixtures hardening at low temperatures (down to –15.0 °C) used in pavement structures. In countries where construction and operation of highways occur at low air temperatures (below 0 °C), it is promising to use the method of modifying cement-crushed mixtures with complex antifreeze agents. The structural studies of cement paste with these additives are poorly described in scientific literature. Therefore, the aim of this work was to consider the impact of complex antifreeze agents in cement paste on the peculiarities of phase structure formation and the relationship between the structure and the properties of the obtained materials. The cement paste was tested for compressive strength using the standard technique; then after preparation, the samples were tested by X-ray, differential thermal and thermogravimetric analyses. It was established that the modification provides the possibility to increase the content of the crystalline phase compared with the amorphous one in the form of new formations (portlandite and dicalcium hydrosilicates). The developed complex modifiers contribute to activation of hydration processes in cement paste, which is confirmed by the level of the hydration degree up to 0.6 and the integral value of weight loss up to 20.5 %. The relationships between the increase in the compressive strength of cement paste and the increase in the hydration degree of calcium silicates and the integral value of weight loss were established. It was shown that the combined use of components of the complex three-component additive provided synergism of processes of structure formation and, as a consequence, an increase in the strength of cement paste. The use of the developed compositions of antifreeze agents in the technology of construction of cement-crushed bases at subzero temperatures (up to –15 °C) prolongs the road construction season and improves the operational indicators of road pavement materials.

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1. Introduction

The priority tasks in the development of building materials science include the creation of materials with improved physical and mechanical characteristics by modifying them with complex multifunctional additives [1, 2].

In countries where construction and operation of highways occur at low air temperatures (below 0 °C) [3–5], these tasks can be solved using technologies for constructing structural layers of road pavements made of low-strength stone materials and soils, reinforced with cement and modified with functional additives [6–9].

For example, the effect of combined use of hydromechanical activation of cement and antifreeze agents on the physical and technical properties of fine-grained materials, hardening at low temperatures,

was studied in [10]. The proposed approach made it possible to increase the effectiveness of the studied additives and opened up additional possibilities for their application in winter concreting.

The admixtures for winter concreting were studied in [11, 12]. It was shown that calcium chloride was effective, but its use as an antifreeze agent was not recommended due to the serious danger of corrosiveness. The impact of chloride-containing antifreeze additives with two types of chloride-containing components (NaCl and $CaCl_2$) on the rheological properties of cement concrete at negative temperatures was studied [13] the modification with two types of chlorides provides a decrease in the yield strength and an increase in viscosity. Increase in antifreeze concentration and cement content, decrease in sub-zero curing temperature, and addition of slag were found to have significant effects on the rheological properties of cement-mineral mixtures. In addition, chlorides promote early cement hydration, reduce the freezing temperature and prevent early freezing of cement-mineral materials. The authors [14] additionally found that chloride-based accelerators adversely affect the strength of concrete, while non-chloride-based accelerators provide an alternative use if mixed with the appropriate type and amount of cement.

Accelerators are used at low temperatures for patching the road surface using fast-hardening concrete mixtures of high strength and construction of cement-mineral road pavement bases [12, 15, 16]. It is noted that at subzero temperatures the accelerator promotes cement hydration, shortening the setting time and increasing the strength gain at an early age.

It should be noted that one-component antifreeze agents in cement-mineral materials do not provide the required level of cement paste (CP) hydration at subzero temperatures, especially at air temperatures below –5 °C [12]. It was found that in some cases the chloride antifreeze deteriorates the physical and mechanical properties of materials [12, 17].

A chemical mechanism of concrete destruction under the action of magnesium chlorides was discussed in [12, 18]. The authors explain it by the formation of multiphase nanosized crystals in the material, including $CaCl_2$, $Mg(OH)_2$ and $Mg_3(OH)_5Cl(H_2O)_4$. Additionally, the destruction of concrete by the proposed mechanism is indirectly confirmed by testing concrete samples taken from several selected concrete bridge decks. It is shown that the cumulative effect of $MgCl_2$ antifreeze caused a significant decrease in splitting tensile strength (up to 50 %), as well as a decrease in microhardness (up to 60 %), even at a depth of 25 to 50 mm.

The use of advanced composite materials with magnesium oxychloride cement and mineral aggregates was discussed in [19]. It was found that the problem of magnesia composites hardening under freezing temperatures hadn’t been solved yet.

The studies on replacing chlorides or reducing their negative effects in antifreeze agents are of high versatility. For example, in [20], urea was discussed as an antifreeze agent instead of chlorides for concreting in cold weather. However, its effectiveness as an antifreeze agent has been confirmed only at temperatures down to –5 °C. The use of calcium nitrate as an additive in antifreeze was considered in [20]. The negative effect of corrosion processes on the physical and mechanical characteristics of concrete was shown in [21], where calcium nitrate was studied as an antifreeze agent. The authors [22] believe that sodium nitrite ($NaNO_2$) and potassium carbonate (K_2CO_3) are the most common antifreeze additives that ensure the required level of properties of concrete (compressive strength, tensile strength, flexural strength, modulus of elasticity and Poisson's ratio) at negative temperatures. The effect of chloride-free antifreeze additives (calcium nitrite ($Ca(NO_2)_2$), calcium nitrate ($Ca(NO_3)_2$) and urea ($CO(NH_2)_2$)) on the rheological properties of cement-mineral materials with different types and content of binders (Portland cement, ground blast furnace slag) at negative temperatures were also studied [23–25].

High-strength calcium sulfoaluminate was also used as a mineral accelerator in winter construction [26–28].

The process of cement hydration acceleration during winter concreting can be performed through the use of accelerating additives of various chemical structures: calcium formate and nitrate, CSH crystals, and triethanolamine [29–31]. It was shown that additives based on calcium nitrate, calcium formate, and CSH crystals were the most efficient for Portland cement mortars, and triethanolamine was the most efficient for cement with the addition of ground granulated blast furnace slag.

The positive effect of sodium formate (SF) on the process of concrete hardening at subzero temperatures and its effective anti-icing properties was experimentally confirmed in works [32, 33]. This work presented a regression equation, which predicted the strength of concrete with the addition of sodium formate used in winter works. The effect of an antifreeze additive on the flexural strength of road concrete was also studied in [34]. Here the authors used the method of orthogonal planning of the experiment and took into account water-cement ratio, the content of antifreeze modifier, fly ash and technological factors of the works.

It is important to take into account that cement-crushed stone mixtures (CCSMs) have significant porosity. When CCSMs are exposed to subzero temperatures, the number of pores and capillaries increases, in which stresses are formed during the transition of water into ice, causing material destruction [2]. To solve this problem, it is necessary to develop multifunctional antifreeze additives that provide the greatest compaction of the material to reduce open porosity and determine their effect on the formation of a frost-resistant and durable phase structure of the material.

It is recommended to develop complex antifreeze additives using mixtures of nitrate and thiocyanate, and in some cases using alkanolamines, carboxylic acids, or their salts [11, 35]. These studies also confirm that chemical combinations can provide synergistic effects when combined antifreeze additives are used.

The effective implementation of multifunctional additives is exampled by the development of a nano-modified high-tech additive [36], applied in concreting at outside air temperatures up to –5 °C. The multifunctionality of this additive consists in the combined use of four components (sulfonaphthalene-formaldehyde, amorphous nano-silica, saponified wood resin, and sodium nitrite). The proposed ratio of plasticizing, stabilizing, air-entraining, and antifreeze components made it possible to provide optimal conditions for the cement hydration during winter concreting and, as a consequence, the required strength and workability.

O. Tene carried out similar studies on the development of a multifunctional antifreeze additive for modifying cement-based pavements during work under subzero temperatures [37]. As components of complex additives, he proposed a combination of plasticizing (solutions of melamine-formaldehyde polymers, technical lignosulfonates), antifreeze (sodium and calcium formates), and hydrophobizing substances (sodium liquid glass, ethyl silicones, and sodium methylsiliconates) with hardening accelerators (sodium, ammonium and iron sulfates), and the introduction of mineral fillers and stabilizers (fly ash, active microsilica, dolomite flour, slaked lime).

The authors [38, 39] point out that when developing complex antifreeze additives, it is necessary to consider the nature of the effect of the components of antifreeze modifiers on the composition of hydration products, processes and features of the formation of structure and hardening of concrete.

While developing a method for modifying CCSMs hardening at low temperatures, we took into account the positive experience and previous results on the complex antifreeze additives. We used the multifunctional antifreeze compositions, including sodium formate, calcium chloride, and superplasticizer S-3. It should be noted that superplasticizer S-3 as part of a complex multifunctional modifier, is intended to reduce moisture, improve technological properties and increase the density of the central chemical mixture [2]. In addition to accelerating the hardening process, calcium chloride enhances the antifreeze effect of sodium formate, and its reduced content in the complex additive should prevent the development of destructive processes during hardening of cement-mineral materials. Modification of cement-crushed mixtures with the developed additives makes it possible to increase the material compressive strength by 3.6, splitting tensile strength by 4.3, frost-resistance by 7.0, crack-resistance by 1.5, elasticity modulus by 1.9 times as compared to unmodified compositions (at a hardening temperature of –15 °C). The use of the developed compositions of antifreeze agents in the technology of construction of cement-crushed bases at subzero temperatures (up to –15 °C) prolongs the road construction season and improves the operational indicators of road pavement materials.

The performed analysis shows the prospects of CCSMs modification with complex antifreeze additives in countries where construction and operation of highways occur at low air temperatures (below 0 °C). It also indicates the need for research on the cumulative positive effect of antifreeze additives, plasticizers, and hardening accelerators in cement pastes on the formation of the phase structure and the identification of the relationship between the structure and the properties of the materials obtained.

Given the lack of structural surveys of cement pastes with antifreeze additives, this work aims to study the effect of multifunctional antifreeze compositions, including sodium formate, calcium chloride, and superplasticizer S-3, on the formation of the phase structure of cement pastes.

To achieve this aim, the following tasks were solved:

1. Determination of the phase compositions of cement paste and the ratio of amorphous and crystallization phases in the material.

2. Investigation of the impact of the components of antifreeze multifunctional additives on the degree of cement hydration, the qualitative and quantitative composition of the hardening products.

3. Determination of the relationship between CP strength and the degree of cement hydration in the presence of antifreeze agents used.

2. Materials and Methods

The research was carried out in the laboratories of the Scientific and Educational Center "Roads" of the Institute of Transport Structures of the Kazan State University of Architecture and Civil Engineering. The studied materials were CP without additives, with one-, two- and three-component antifreeze compositions and with each component of complex additives after hardening for 28 days at a temperature of –15 °C.

The studies used CEM I 42.5N Portland cement of the following mineral and chemical compositions (Tables 1 and 2).

Table 1. Mineral composition of cement.

Material	C 3 S	C 2 S	C 3 A	C 4 AF
Content, %	58	17	8	13

Table 2. Chemical composition of cement.

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O (Na_2O+ +0.65 K_2O)	CaO_{free}
Content, %	21.1	5.85	4.2	65.4	1.13	1.03	1.07	0.16

The following substances were used as components of complex antifreeze agents (Table 3), by analogy to [2]:

- sodium formate is the sodium salt of formic acid (HCOONa), a chemically pure water-soluble product;
- crystalline calcium chloride (CC) ($CaCl_2$), a chemically pure water-soluble product;
- superplasticizer S-3 is the sodium salt of the condensation product of naphthalenesulfonic acid and formaldehyde. It was used as a 2.5 % aqueous solution, pH 7-9.
- tempering water, according to EN 1008:2002.

The CP samples after 28 days of curing were tested for compressive strength, according to EN 1 96-1: 2005. The prepared samples were examined by X-ray, differential thermal and thermogravimetric analyzes.

The X-ray diffraction of samples was studied using the DRON-3 X-ray diffractometer. The following operation mode was used: CuK_α with a wavelength of 1.54178 Å, exposure 10 sec., step 0.05°, interval from 2° to 78°.

Differential thermal analysis (DTA) and differential thermogravimetry (DTG) of samples were carried out on the 3425-1500-OD optical derivatograph of the F. Paulik, J. Paulik and L. Erdey system (MOM, Hungary). The sample weighed portions varied from 400 to 1700 mg, with a thermal balance sensitivity of 100 mg. The recording modes were DTA, DTG – 1/5, heating rate was 15 deg./min up to 1000 °C. Air was used as a comparison standard (empty crucible on the T-junction).

Diagnostics of each crystalline phase was carried out by identifying the corresponding characteristic reflections with specific interplanar distances (d) and relative intensities (l) on the obtained diffractograms. The identification procedure was carried out by comparing the obtained diffraction patterns with the international database of powder diffractometric data (JCPDS database), which contains the l and d values of reference minerals.

The relative contents of the amorphous and crystalline components in the studied CP were calculated using the XRYTOOL interactive computer program (Russia).

The hydration degree (HD) of cement pastes was determined by two independent methods.

- in X-ray technique, HD was assessed using the ratio of the intensities of reflexes of non-hydrated components of cement (alite, belite) and reflections of hydrated new formations (portlandite and aqueous dicalcium hydrosilicates):

$$\mathbf{HD} = \\ = \left(\mathbf{I}_{\text{Ca2SiO4*nH2O}} + \mathbf{I}_{\text{Ca(OH)2}} \right) \Big/ \left(\mathbf{I}_{\text{Ca2SiO4*nH2O}} + \mathbf{I}_{\text{Ca(OH)2}} + \mathbf{I}_{\text{C2S+C3S}} \right), \quad (1)$$

where $\mathbf{I}_{\text{Ca2SiO4*nH2O}}$ is the intensity of dicalcium hydrosilicate reflection, d = 9.6 Å; $\mathbf{I}_{\text{Ca(OH)2}}$ is the intensity of portlandite reflection, d = 4.9 Å; $\mathbf{I}_{\text{C2S+C3S}}$ is the intensity of alite and belite reflection, d = 2.78 Å.

- in differential thermal analysis and differential thermogravimetry, HD was assessed using the mass loss (Δm) within the limits of the considered effect on thermoanalytical curves.

3. Results and Discussion

Phase composition of cement pastes hardened at subzero temperatures was determined using the X-ray, differential thermal and thermogravimetric analyzes.

The CP samples hardened for 28 days were tested for compressive strength R_{comp} (Table 3).

Table 3. Compressive strength of CP hardened at –15 °C.

Sample No.	Content of additives in cement pastes, % by weight of cement			W/C	R_{comp}, MPa, of CP samples hardened for 28 days at -15 °C
	CC	SF	SP		
1	-	-	-	0.26	4.7
2	-	6	-	0.23	20.2
3	3	-	-	0.26	33.3
4	3	6	-	0.23	25.9
5	3	6	2	0.20	48.4
6	-	-	2	0.21	7.5
7	-	6	2	0.20	22.6
8	3	-	2	0.21	35.4

The studied CPs have a similar composition of crystalline phases. The main predominant compound in them is unhydrated C_3S. Calcium aluminate and aluminoferrites remained at the same level in quantitative terms, i.e. they underwent insignificant hydration in contrast to alite. New hydration formations in cement pastes are represented by portlandite $Ca(OH)_2$ and dicalcium hydrosilicate ($Ca_2SiO_4 \cdot nH_2O$). Along with the crystalline phases, CP also contains an amorphous component, which consists of new hydration formations of colloidal dimension, with a probable composition of $Ca_2SiO_4 \cdot nH_2O$ (Table 4).

Analysis of X-ray diffraction patterns for CPs without additives shows that in Portland cement the most hydrated were alite and belite, while calcium aluminates and alumoferrites were hydrated to a much lesser extent.

Table 4. Relative phase content and hydration degree for alite and belite in CP.

Sample No	Sample composition	Relative phase content,%		Relative HD, r.u.
		Crystalline	Amorphous	
1	Cement paste without additives	49.5	50.5	0.45
2	Cement paste with 6% SF	53.6	46.4	0.58
3	Cement paste with 3% $CaCl_2$	62.0	38.0	0.7
4	Cement paste with 3% $CaCl_2$; 6% SF	61.4	38.6	0.51
5	Cement paste with 3% $CaCl_2$; 6% SF; 2% S-3	62.6	37.4	0.6
6	Cement paste with 2% S-3	64.4	35.6	0.37
7	Cement paste with 6% SF; 2% S-3	67.2	32.8	0.31
8	Cement paste with 3% $CaCl_2$; 2% S-3	61.5	38.5	0.56

The scheme of hydration transformation that took place in CPs can be described by two main reactions:

$$Ca_3SiO_5 + nH_2O \rightarrow Ca_2SiO_4 * nH_2O + Ca(OH)_2, \quad (2)$$

$$Ca_2SiO_4 + nH_2O \rightarrow Ca_2SiO_4 * nH_2O, \quad (3)$$

These equations show that both compounds (alite and belite) are converted into dicalcium hydrosilicate, which in the initial period of Portland cement hardening exists in the form of colloidal particles. The appearance of $Ca_2SiO_4*nH_2O$ results in the presence of a significant amount of amorphous component in CPs (Table 4), when the main part of the new formations is in colloidal form and the process of Portland cement hydration is fixed at the initial stage. Only a small part of the colloid crystallizes into portlandite $Ca(OH)_2$ and calcium hydrosilicate $2CaO*SiO_2*nH_2O$. The number of water molecules in its structure is from 3 to 4 and it belongs to the group of highly basic hydrosilicates of the CSH (II) type by H. Taylor or C_2SH_2 by R. Bogg.

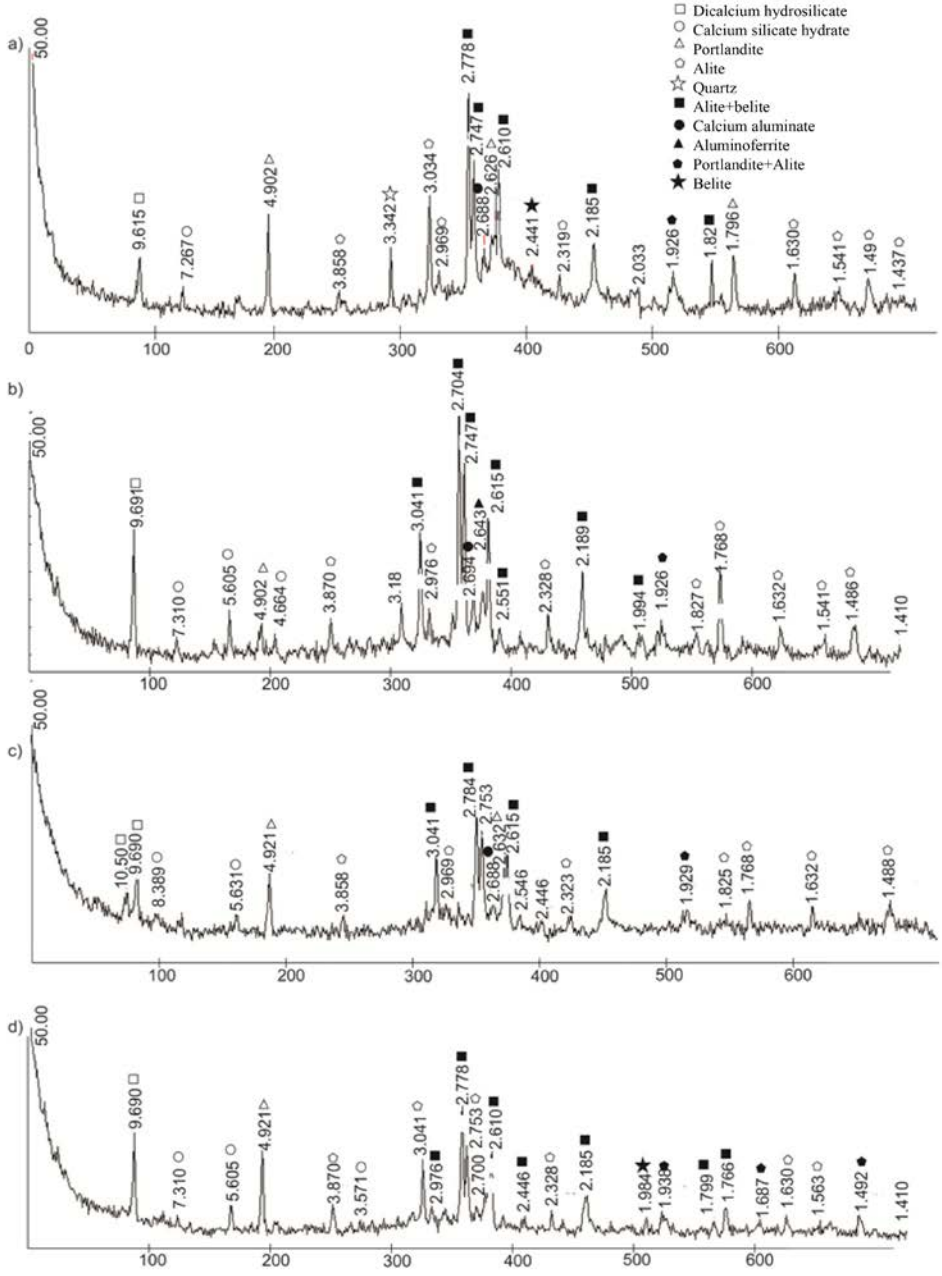

Figure 1. X-ray diffraction patterns of CP samples hardened for 28 days at –15 °C: a) without additives, b) with addition of 6 % SF, c) with addition of 3 % CC and 6 % SF, d) with addition of 3 % CC, 6 % SF, 2 % S-3.

It should be noted that CP with addition of 6 % SF shows a higher degree of hydration. It results in a larger crystallization of the amorphous component into portlandite $Ca(OH)_2$ and calcium hydrosilicate $2CaO*SiO_2*nH_2O$. The latter is represented by two varieties: one modification is characterized by reflection d = 10.5 Å, the other one has d = 9.69 Å (Fig. 1), their position is explained by the different content of water molecules. The deeper hydration process is explained by the fact that the addition of SF under the conditions of formation of cement paste at –15 °C has a multifunctional effect on the hydration of Portland cement. Firstly, SF helps to lower the freezing point of water, which ensures hydration in CP at subzero temperatures. Secondly, SF enhances the hydrolysis of compounds that make up Portland cement, i.e. increases the rate of hydration of the crystalline phases of the clinker. Thirdly, when SF dissolves in water, free sodium ions are formed in the solution, which, being activators of hardening, accelerate the hydration of Portland cement. The listed factors together determine the increase in CP strength.

It was shown that the CC additive, being an accelerator of the hardening process, to a greater extent promotes the hydration transformation of di- and tricalcium silicates. It works like SF additive, lowers the freezing point of water, thereby increasing the hydration time of Portland cement. It should be noted that at this stage chloride does not form independent phases, since the concentration of chlorine ions in the solution is obviously insufficient for the formation of independent compounds.

In the considered variants of CP modification with the superplasticizer, a lower degree of hydration was noted than that obtained by joint addition of SF and CC. Such CPs are characterised by hydration degree similar to that of CPs without additives. The absence of a significant amount of amorphous phase in them is probably explained by the lower water-cement ratio (W/C) compared to that of CP without additives. It can be concluded that the SP additive is not a stimulator of the hydration transformation of Portland cement at subzero temperatures. Its effective impact is explained by a decrease in the water-cement ratio, which reduces the destructive effect of the liquid phase at subzero temperatures and affects improvement of the CP strength characteristics.

Cement paste with a complex additive of SF, CC and SP shows a fairly high degree of hydration of the cement silicate components. The X-ray diffraction pattern of this sample shows high intensities of reflections of calcium hydrosilicate d = 9.69 Å, portlandite d = 4.921 Å, d = 2.632 Å, and a significant decrease in the intensities of reflections of alite d = 3.041 Å and belite d = 2.778 Å. The combined use of SF and CC promotes the activation of hydrolysis and hydration of Portland cement, and addition of SP results in a decrease in the W/C ratio, which leads to acceleration of the hardening process and achievement of maximum CP strength at subzero temperatures.

It should be noted that each complex additive, especially a three-component one, maximally manifests its activity in hydration processes. This is confirmed by the strength characteristics of cement pastes.

The considered cases confirmed that the XRD method does not allow to unambiguously estimate the contribution of the X-ray amorphous component for assessing the hydration degree. In this regard, we carried out additional thermal studies to obtain more reliable information. The content of hydrated water in CP was used to assess the hydration degree of CP, the weight loss was used to determine the new formations (Fig. 2, Table 5).

It is shown that in the temperature range of 40–350 °C an endothermic effect is recorded, which characterizes the process of removing weakly bound, mainly adsorbed water (Fig. 2). The DTA curves for CP without additives in the range of 440–500 °C recorded the process of dehydration of calcium hydroxide $Ca(OH)_2$ (Fig. 2a). The endothermic effect is a consequence of two processes' superposition, it is observed on thermoanalytical curves with a maximum of 720–760 °C. The first process is dehydration of newly formed dicalcium hydrosilicates $2CaOSiO_2*nH_2O$ of the CSH (II) type. The second process is dissociation of calcium carbonate $CaCO_3$, formed as a result of calcium hydroxide carbonization.

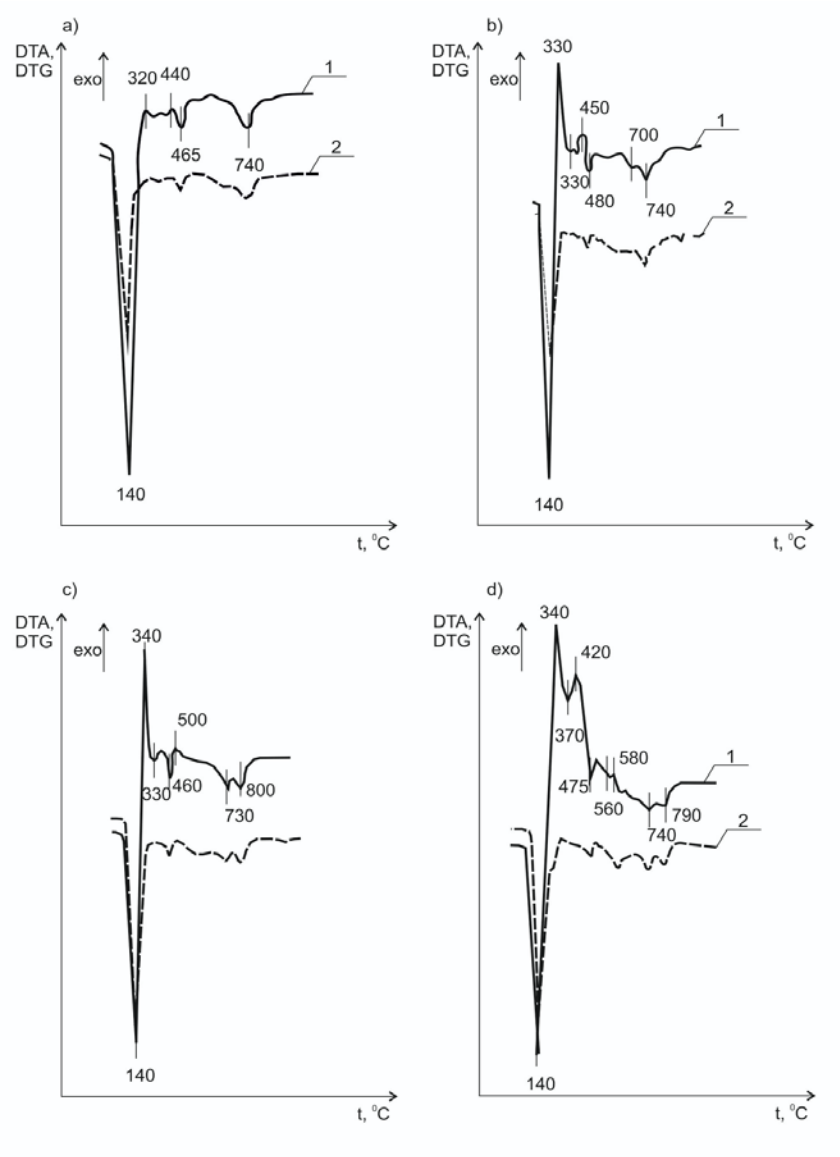

Figure 2. Thermoanalytical curves DTA (1) and DTG (2) of CP samples hardened for 28 days at –15 °C: a) without additives, b) with addition of 6 % SF, c) with addition of 3 % CC and 6 % SF, d) with addition of 3 % CC, 6 % SF, 2 % S-3.

It should be noted that a slight increase in total weight loss is observed in CP without additives (Table 5). This indicates a slow process of hydration of cement minerals and is confirmed by the minimum CP strength achieved.

A characteristic feature of the DTA curves of cement paste with SF (Fig. 2 b) is the appearance of peaks with maxima in the range of 330–450 °C, characterizing exothermic transformations. They are obviously associated with the destruction of organic substances of additive components. This indicates a deeper hydration process in CP with SF additive and provides an increase in the intensity of weight loss over the entire investigated temperature range (Table 5).

The positive impact of CC on the hydration process in CP was established. The active role of CC additive during the hydration transformation of alite and belite to CP is to increase the process of portlandite dehydration.

The SP additive has an insignificant impact on the hydration transformation of Portland cement in conditions of subzero temperatures.

When using a three-component additive from SF, CC and SP, the presence of thermal effects typical for each component is observed (Fig. 2d). However, each component of the additive is involved in the acceleration of the hydration of the clinker crystalline phases. The combination of additives provides an enhancement and deeper course of the hydration process, which is confirmed by the maximum total weight loss – 20.5 % (Table 5) and the highest CP strength – 48.4 MPa.

Table 5. Weight loss of CP with various additives and temperature modes.

Sample No	Material and content of additives in CP, %	Weight loss, % mass, In the temperature interval, ºC				
		20 -350	20 -500	20 -700	20 -800	20 -1000
1	Without additives	7.7	9.2	10.7	13.2	13.3
2	SF 6.0	10.0	11.3	17.4	18.6	19.1
3	CC 3.0	12.6	14.8	16.2	18.5	19.3
4	CC 3.0; SF 6.0	11.4	12.5	15.4	19.3	20.0
5	CC 3.0; SF 6.0 SP 2.0	11.6	13.0	16.3	20.0	20.5
6	SP 2.0	6.8	8.0	10.0	11.9	12.0
7	SF 6.0 SP 2.0	8.8	10.1	14.2	17.2	18.5
8	CC 3.0; SP 2.0	9.8	11.2	12.6	15.7	16.2

Data from Tables 3, 4, and 5 were used to build the relationships between the compressive strength of cement pastes (σ_{CS}), the hydration degree of calcium silicates in them (α) and the integral weight loss. Analysis of these curves confirmed an increase in the level of compressive strength of cement pastes with an increase in the hydration degree of alite and belite (Fig. 3). It is important to note that the nature of the obtained dependencies was confirmed by independent methods: X-ray and differential thermal analysis. The established dependences testify to the effectiveness of practical application of the developed antifreeze modifiers and explain the role of hydration processes in providing improved operational reliability of cement-mineral materials.

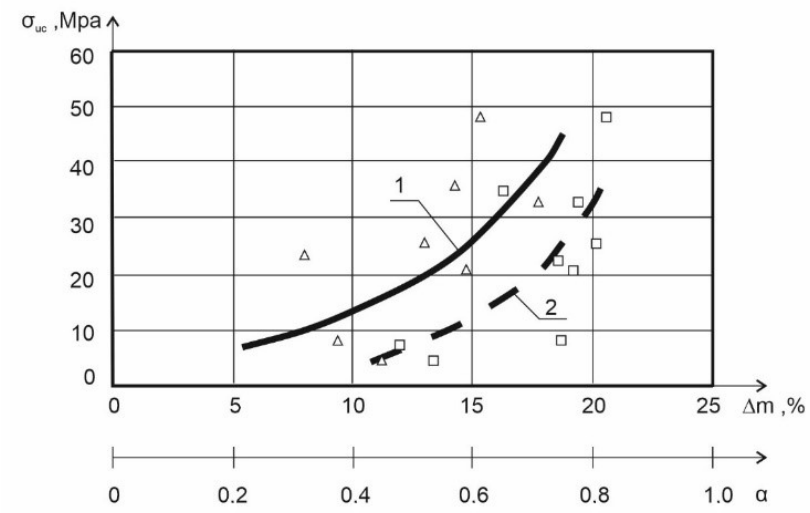

Figure 3. Relationships between the compressive strength of cement pastes (σ_{CS}) and the hydration degree (α) – 1 and the integral weight loss (∆m) – 2.

Thus, the combined use of the components of the complex three-component additive provides synergism of processes of structure formation and, as a consequence, an increase in the CP strength. It is recommended to use the developed antifreeze additives in the technologies of construction of cement concrete bases of pavements at temperatures up to –15 °C. The composition of additives is determined depending on the hardening temperature to ensure a given level of operational indicators and durability of pavement layers based on the results of previous research [40].

The results obtained are relevant as evidenced by the existing literature [11, 41]. As noted by the authors [11], action mechanisms of new non-chloride modifiers for cement paste have not been fully studied. The novelty of the present research consists in the establishment of synergistic effect of combinations of chemicals on the rate of hydration.

The effect of three-component modifiers on acceleration of cement hydration and increase in early strength [42, 43] in conditions of positive temperatures has been previously described. In contrast to [42, 43], it is shown that the modification with complex additives developed by us makes it possible to provide acceleration of cement hydration processes and increase the strength level of cement paste, not only at positive but also at subzero temperatures, during both fast and prolonged hardening. It should be noted that the modification provides an opportunity to increase the content of new formations [41, 42, 43] in the form of hydrosilicates. When using the developed compositions of additives, the new formations can be formed even at subzero temperatures, which increases the strength of the modified cement paste.

The authors [11, 41, 42] note the prospects of continuation and development of structural studies and examination of mechanisms of cement paste modification by complex modifiers of synergistic action in connection with insufficient information on this subject of research.

4. Conclusions

1. The features of formation of the phase structure of cement pastes hardened at subzero temperatures were established. They depend on the qualitative and quantitative compositions of the hardening products and the ratio of amorphous and crystallization phases in them, the rate and depth of the processes of cement hydration. These features determine the level of the achieved material strength.

2. The phase compositions of cement pastes and the ratio of amorphous and crystallization phases in them were determined. Hydrated new formations in cement pastes are represented by portlandite and dicalcium hydrosilicate. Along with crystalline phases, cement paste also contains an amorphous component, which comprises hydrated new formations of colloidal dimension, with a probable composition of $Ca_2SiO_4 \cdot nH_2O$.

3. The influence of complex additives and their components on the degree of cement hydration, the qualitative and quantitative composition of the hardening products was investigated. It is noted that the developed complex additives, especially the three-component ones, ensure the maximum manifestation of their activity in hydration processes.

4. It was confirmed that compressive strength of cement pastes increased with an increase in the degree of cement hydration and the integral weight loss in the presence of the used antifreeze agents. The combined use of the components of the complex three-component additive provides synergism of processes of structure formation and, as a consequence, an increase in the CP strength. The established dependences testify to the effectiveness of practical application of the developed antifreeze modifiers and explain the role of hydration processes in providing improved operational reliability of cement-mineral materials.

5. Modification of cement-crushed mixtures with the developed additives makes it possible to improve the construction and technical indicators of materials in road pavements of highways. Application of the developed polyfunctional compositions of antifreeze additives in technologies of cement concrete bases at subzero temperatures (up to –15 °C) extends of road construction season and improves the operational indicators of road pavement materials. The composition of additives is determined depending on the hardening temperature to ensure a given level of operational indicators and durability of pavement layers based on the results of the previous research.

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Information about authors:

Evgenii Vdovin, *PhD in Technical Sciences*
ORCID: https://orcid.org/0000-0002-0649-4342
E-mail: vdovin007@mail.ru

Victor Stroganov, *Doctor of Technical Sciences*
ORCID: https://orcid.org/0000-0001-9680-6698
E-mail: svf08@mail.ru

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