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Properties of cement-bound mixes depending on technological factors

E.A. Vdovin*, V.F. Stroganov

Kazan State University of Architecture and Engineering, Kazan, Russia * E-mail: vdovin007@mail.ru

Keywords: cement-bound mixes, sodium formate, technological factors, workability, density, humidity, mixture manufacturability time

Abstract. The influence of technological factors on the properties of cement-bound mixes, hardening at positive and negative temperatures in the construction of pavements, is studied. The relationships between density and strength of cement-bound mixes and the content of cement and water are established. The optimal moisture contents of mixes (10.5-11.5 %) were determined, which ensure the maximum material density from 2000 to 2300 kg/m3 with a cement content of 6 to 12 % by weight of the crushed stone mix. The influence of complex antifreeze additives on the mix technological properties (density, workability, constructability time) was studied. It was shown that sodium formate additives contribute to increasing the mix density and reducing the mix technological hardness (workability) under positive and negative temperatures. The influence of temperature and the amount of functional additives on the constructability time of cement-bound mixes is considered. It was established that additives contribute to preservation of the required workability of mixes at negative temperatures (down to -15 °C) for 1-2 hours and provide the necessary conditions for efficient work performance without reducing their quality and reducing the technological cycle period.

1. Introduction

The importance of influence of technological factors on the properties of cement-mineral materials (cement primers, cement-bound mixes (CBM), concrete, etc.) is noted in many works [1-17]. CBM preparation for road construction is associated with the need to determine the optimal moisture and maximum density. Their relationship with the properties and the forming material structure is considered in [18, 19], especially under the conditions of paving at low and subzero temperatures down to -15 °C. The relevance of this problem is shown in works [25-23]. The literature analysis showed that CBM have significant porosity and, when exposed to negative temperatures, the number of pores and capillaries in which water passes into ice increases with the occurrence of stresses that cause material destruction. Thus, work at low temperatures requires the development of technology for the construction of cement-bound layers of pavement, providing the maximum material density. To achieve the greatest degree of compaction of CBM, placed in road pavements at low and negative temperatures, antifreeze additives can be used, which reduce the CBM open porosity and preserve the liquid phase in mixes [24-31]. However, the higher efficiency of antifreeze additives is provided by the use of additives with multifunctional effect. In this regard, we have developed complex antifreeze additives based on sodium formate (FN) using a hardening accelerator - calcium chloride (CC) and C-3 superplasticizer, which is a polycondensation product of naphthalenesulfonic acid and formaldehyde (SP). It should be noted that the superplasticizer included in the complex composition is designed to reduce moisture, improve technological properties and increase the CBM density. Calcium chloride, in addition to accelerating hardening, enhances the anti-frost effect of sodium formate, and its low content in the complex additive prevents the destruction development during hardening of cement-mineral material. The development of work technology at low temperatures is based on the results of studies of the influence of technological factors on the properties of materials using new modifiers. Based on the properties of the developed functional additives and the relevance of their application, the following work aim is formulated: to study the influence of

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technological factors on the properties of cement-bound mixes with functional additives based on sodium formate, hardening at low temperatures in the construction of pavements.

2. Methods

The studies were carried out using crushed stone mixes of limestone and dolomite rocks, including substandard crushed stone of stone quarries of (0–40) mm fractions. The grain size distribution and physicomechanical properties of mixes are given in Tables 1 and 2.

Table 1. The grain size distribution of the crushed stone mixture.

Maximal grain size, mm	The total residue on the sieves with hole sizes, mm								
	40	20	10	5	2.5	1.25	0.63	0.315	0.14
40	5	37	56	70	80	85	86	88.5	91

Table 2. Physico-mechanical properties of the crushed stone mixes.

Fraction size, mm	Bulk density, kg/m ³	Water absorption,%	Attrition grade	Strength grade	Frost- resistance indicator
0-40	1600	9.1	IV	200	10

The Portland cement of CEM I 42.5N grade of the following mineral and chemical compositions (Tables 3 and 4) was used in the studies.

Table 3. Mineral composition of the cement.

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

Table 4. Chemical composition of cement.

Name	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO ₃	R ₂ O (Na ₂ O+0.65 K ₂ O)	CaO _{sv}
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 additives:

- Sodium formate (FN) sodium salt of formic acid HCOONa, a water-soluble product of the "chemically pure" grade;
- Crystalline calcium chloride CaCl₂ (CC), a water-soluble product of the "chemically pure" grade;
- Superplasticizer C-3 (SP) sodium salt of the condensation product of β -naphthalenesulfonic acid and formaldehyde. It was used in the form of a 2.5% aqueous solution with pH in the range of 7–9.
- Batched water water that complies with the requirements of EN 1008: 2002.

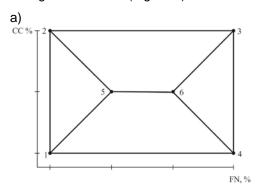
The composition of the cement-crushed stone mixes was selected according to the Russian State Standard GOST 23558. The cement content in CBM varied from 6 to 12 % by weight of the dry crushed stone mixture, and the moisture content varied from 7 to 15 % by weight of the dry CBM.

The density of the finished CBM was determined according to the Russian State Standard GOST 10181, the compressive strength of the samples was determined according to the Russian State Standard GOST 10180 after hardening them for 28 days under normal conditions (temperature (20 ± 2) °C, moisture not less than 90 %). The dimensions of the samples were adopted taking into account the maximum size of the aggregate in accordance with the Russian State Standard GOST 10180. Cement-bound mixes were compacted using the laboratory vibratory platform of the S-I35-A type, providing vertical vibrations of the filled form with a frequency of 2900 \pm 100 vibrations per minute and an amplitude of 0.5 \pm 0.05 mm.

Technological hardness (workability) of CBM was determined in 200×200×200 mm molds for formation of concrete samples according to the method of B. Skramtaev using a metal cone according to the Russian State Standard GOST 10181.

The influence of FN and CC additives on the hardness and density of mixes with a constant SP content was studied using the experiment-planning method according to V. Kleiman's contour-graphic scheme [43]. The tests were carried out on mixes of optimal moisture with addition of 9% cement. The content of anti-frost components of additives (FN, CC) was changed in accordance with the plan of the two-factor experiment (Figure 1). The test results were used to construct dependencies with isolines of equal density and technological hardness (Figure 5).

b)



D)					
№ of experiment	Additives	•	Experimental results		
	FN	CC	ρ	TH	
1	0	0	ρ1	TH ₁	
2	0	4	ρ_2	TH ₂	
3	15	4	ρ_3	TH ₃	
4	5	0	ρ4	TH ₄	
5	5	2	ρ_5	TH ₅	
6	10	2	ρ_6	TH ₆	

Figure 1. Experiment planning: a) contour-graphic scheme of experiment planning; b) experiment plan.

When studying the influence of aging time and temperature on workability of mixes in additives, the FN content was changed at a constant content of CC and SP.

In all experiments CBM after preparation was placed in chambers with the required temperature and moisture conditions (Figures 2–5, Table 5): for normal storage (temperature (20 \pm 2) °C, moisture not less than 90 %) and with temperatures -5 °C, -15 °C. After exposure in chambers, the properties of CBM were determined.

3. Results and Discussion

The influence of the amount of the introduced cement and water on the indicators determining the optimum moisture, maximum density, and strength of the material is preliminary examined.

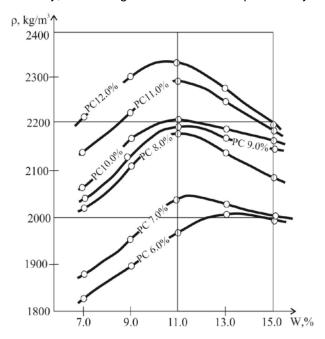


Figure 2. Relationship between CBM density and the mix moisture.

For all CBM studied with a cement content from 6 to 12 % by weight of the crushed stone mixture, the optimal moisture content of mixes were determined. These optimal moistures are in the range of 10.5–11.5 %, ensuring the maximum density of the material from 2000 to 2300 kg/m³ (Figure 2). The compressive strength of samples obtained from optimally moistened mixes at the age of 28 days increased from 3.5 to 14.5 MPa (Figure 3). It was established that a twofold increase in the cement content in the mixture provided a more than fourfold increase in the strength of the material. The addition of one percent of cement is equivalent to a strength increment of 1.8 MPa.

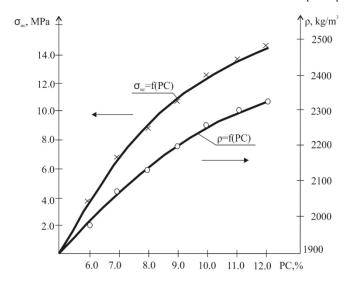


Figure 3. Relationship between density and strength of CBM and the cement content at optimum moisture.

It was shown that with increasing content of water and binder, the technological hardness (workability) of mixes decreases (Figure 4). This can be explained by the fact that crushed stone mixes of low-strength carbonate rocks are characterized by significant hydrophilicity and water absorption, due to the developed specific surface and high porosity. As a result of the liquid phase absorption by aggregate a sharp loss of workability of mixture occurs after preparation of CBM. The minimum mixture hardness is achieved at a level of 5–6 s with a 15 % water content and a 11–12 % cement content. The highest value of technological hardness (200–210 s) is typical for mixes with a minimum content of water of 7 % and cement of 6–7 %. Increasing the water content in CBM for achieving the required workability helps to reduce the density and strength of material, and increasing the cement content reduces the deformability and crack resistance.

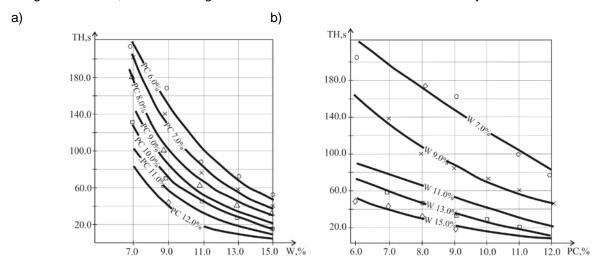


Figure 4. Relationship between technological hardness and content of water (a) and cement (b)

To solve these problems, especially at low and subzero temperatures, CBM was modified with complex functional additives based on sodium formate, calcium chloride and C-3 superplasticizer.

The influence of complex additives on the hardness and density of mixes was studied. It was found that for various moistures of mixes with a constant content of C-3 additive (2 %), the density significantly depends on the FN content and is practically not associated with a change in CC additives (Figure 5). The contours of technological hardness repeat the shape of the density contours. FN additives promote density increase and improve the CBM workability. In particular, with FN introduction, the hardness decreased for three times from 42 s to 14 s. The influence of calcium chloride on workability was not significant. Consequently, the presence of FN in antifreeze compositions increases the constructability of mixes, and density increase provides an improvement in the structural and mechanical characteristics of the material.

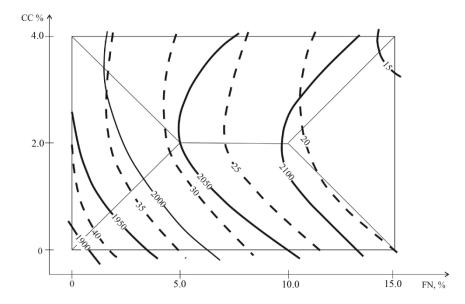


Figure 5. Relationship between FN and CC content on the technological hardness (-----) and density (______) of CBM at SP = const.

Workability of CBM is associated with duration and temperature aging of mixes (Table 5). When the air temperature drops to -15 °C, a decrease in workability indicators begins earlier after preparation and occurs more intensively than at temperature of -5 °C. Three-hour aging of mixes until the moment of compaction increases the hardness of mixes by 5–6 times, which limits the constructability time of mixes and shortens the technological cycle period. Preservation of the required indicators of mix workability in time we call the constructability.

Table 5. Relationship between temperature and FN content and the CBM technological hardness change in time.

Additives content, % of cement mass			Temperature, °C	Technological hardness of CBM, s, after preparation of mixes, min							
FN	CC	SP		0	20	40	60	90	120	150	180
-	-	-	+20	45	54	66	85	98	114	130	>200
7	2	2	-5	13	20	25	31	38	46	55	64
5	2	2	-5	15	22	29	36	45	56	68	79
3	2	2	-5	17	24	30	38	47	58	73	86
7	2	2	-15	13	21	30	41	50	67	80	85
5	2	2	-15	15	24	36	52	60	70	83	90
3	2	2	-15	17	25	40	55	66	73	84	91
3	2	2	+20	17	24	36	44	60	70	98	136

Exploration of the influence of complex additives on preserving the CBM constructability time showed that FN additives contribute to the stability of this process (Table 5). The hardness of mixes without additives is 1.5 times higher than that for mixes with additives, and is 2–3 times higher than that of mixes aged at subzero temperatures. Thus, antifreeze components contribute to the extension of the CBM constructability time at low and subzero temperatures. This ensures performing high-quality work on the construction of pavement layers and achieving the required construction and technical properties of road construction materials.

The positive influence of the developed functional additives on the CBM technological properties at low and subzero temperatures occurs mainly due to the preservation of the liquid phase in the optimal amount from the point of view of gaining strength and ensuring the constructability time of mixture. The batched water for CBM pavement layers is a solution of complex functional additives. As it is known, when additives are dissolved, solvates are formed, which are compounds of particles of a dissolved substance with water molecules. In case of using the developed additives, along with lowering the freezing temperature, plasticization of mixes occurs. Lowering the freezing point and workability depends on the number of bound water molecules, i.e. the composition of the solvates, and the strength of this bond depends on the electrical properties of the particles, their size and concentration of solution, which is provided by the complexity and functionality of the used additives.

The practical significance of the obtained results is the possibility to regulate the CBM properties for road pavement, taking into account technological factors under various weather and climatic conditions of work, which is achieved by using optimal mixes with complex additives.

4. Conclusions

- 1. The optimum moistures of cement-bound mixes (10.5-11.5%) have been established, which ensure the maximum material densities from 2000 to 2300 kg/m³.
- 2. The recommended range of Portland cement content by weight of crushed stone mixture (6.0 %–9.0 %) was determined, which provides the necessary level of strength (from σ_{uc} = 4.0 MPa at ρ = 2000 kg/m³ to σ_{uc} = 10.0 MPa at ρ = 2200 kg/m³) for structural layers of pavement.
- 3. It was found that the presence of sodium formate in complex functional additives improves the constructability of mixes, and an increase in density provides an improvement in the structural and mechanical characteristics of material.
- 4. The influence of complex additives on preserving the constructability time of cement-bound mixes was studied. It was shown that sodium formate additives contribute to the stability of this process. The influence of temperature and the amount of functional additives on the constructability time of the use of cement-bound mixes is considered. It was established that additives contribute to maintaining the required workability of mixes at negative temperatures (up to -15 °C) for 1–2 hours and provide the necessary conditions for efficient work without reducing their quality and reducing the technological cycle period.
- 5. The positive influence of the developed functional additives on the technological properties of CBM at low and subzero temperatures occurs mainly due to the formation in the liquid phase of solvates, i.e. the compounds of solute particles with water molecules that lower its freezing temperature and plasticize the mixture.
- 6. The practical significance of the obtained results is the possibility of regulating the CBM properties for road pavement, taking into account technological factors under various weather and climatic conditions of work, which is achieved by using optimal mixes with complex additives.

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Contacts:

Evgenii Vdovin, +79196259171; vdovin007@mail.ru Victor Stroganov, +79872901642; svf08@mail.ru

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Влияние технологических факторов на свойства цементощебеночных смесей для дорожных одежд

Е.А. Вдовин, В.Ф. Строганов

Казанский государственный архитектурно-строительный университет, г. Казань, Россия, * E-mail: vdovin007@mail.ru

Ключевые слова: цементощебеночные смеси, формиат натрия, технологические факторы, удобоукладываемость, плотность, влажность, время технологичности смеси

Аннотация. Получены результаты исследований влияния технологических факторов на свойства цементощебеночных смесей, твердеющих при положительных и отрицательных температурах в конструкциях дорожных одежд. Установлены зависимости плотности и прочности цементощебеночных смесей от содержания цемента и воды. Определены значения оптимальной влажности смесей (10,5-11,5 %), обеспечивающие получение максимальных значений плотности материала от 2000 до 2300 кг/м3 при содержании цемента от 6 до 12 % от массы щебеночной смеси. Изучено влияние противоморозных добавок на технологические свойства: удобоукладываемость, время сохранения технологичности смеси. Показано, что добавки формиата натрия способствуют повышению плотности смеси и снижению технологической жесткости (удобоукладываемости) смеси в условиях положительных и отрицательных температур. Рассмотрено влияние температуры и количества функциональных добавок на время технологичности применения цементощебеночных смесей. Установлено, что добавки способствуют сохранению требуемой удобоукладываемости смесей при отрицательных температурах (до (-15)°C) в течение 1-2 часов и обеспечивают необходимые условия для эффективного производства работ без снижения их качества и уменьшения периода технологического цикла

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Контактные данные:

Евгений Анатольевич Вдовин, +79196259171; vdovin007@mail.ru Виктор Федорович Строганов, +79872901642; svf08@mail.ru

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