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Optimization of complex frost-resisting additives in line with operational requirements towards freezing temperature in road dressing constructions

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Optimization of complex frost-resisting additives in line with operational requirements towards freezing temperature in road dressing constructions

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Abstract. The subject of the study is to optimize the compositions containing frost-resisting complex organic and inorganic additives (FRA) that provide the required level towards freezing temperature when constructing cement-mineral layers (CML) of road dressing (pavement). As a prerequisite to carry out these studies is the necessity to preserve the liquid phase in CML during asphalt laying at low (subzero) air temperatures, as well as ensuring a given level stated to the performance criteria and durability of road dressing layers. In our studies, we applied the comprehensive approach to the experiment, concluding in a choice of FRA components and in the use of experiment planning. The influence of functional additives and their quantitative composition on the freezing temperature (T_z) during the experiment optimization in line with the D-optimal second-order plan has been considered. A mathematical model of the process has been obtained. We have found that the most significant mixture is the content of sodium formate (SF), compared to calcium chloride ($CaCl_2$) and a superplasticizer based on the polycondensation product of naphthaleisulfonic acid and formaldehyde (C-3), the amount of which varies in the series 3>1>0.3. The obtained results on optimization allow to choose FRA compositions that provide the ability to perform construction works in conditions of subzero temperatures up to –15.6 °C.

1. Introduction

The importance of the transport system development is much disscussed in [1–4] and one of the limiting factors for increasing a number of constructions is the necessity to carry out works in adverse conditions – at low air temperatures. The other way in development of the country's transport strategy is the use of CML modified with functional additives (stone materials and soils reinforced with cement) for road dressing [5–27]. Construction works conducted at subzero air temperatures (up to –15 °C) allows to use CML for road dressing, chloride compounds, sodium and calcium nitrite, potash and other additives that ensure the presence of a liquid phase in mixtures and the process of cement hydration [28–36]. However, these substances do not increase frost resistance of cement-reinforced materials and impair the mixture workability. Frost-resisting additives, in addition to lowering the ice point of hardening water and accelerating the hardening processes and CML plasticization, should improve the material performance and their durability. It is known that the most widespread compounds are sodium formate (SF) – the sodium salt of formic acid, as frost-resisting additive to cement concrete and CML [37–40]. However, the high efficiency of FRA is provided by the use of additives, having polyfunctional characteristics. We have developed the complex FRA based on SF using a hardening accelerator — calcium chloride ($CaCl_2$) and C-3 superplasticizer — the product of the polycondensation of naphthalenesulfonic acid and formaldehyde. It should be noted that the superplasticizer included in the complex composition is intended to reduce humidity, improve technological properties and increase CML density. Calcium chloride, in addition to accelerating the process of hardening, enhances the anti-frost effect of SF, and its reduced dosage prevents some destruction development at hardening processes of cement-mineral material. Strength gain at CML hardening in the condition of subzero temperatures, providing the operational requirements, significantly depends on T_z water solutions of frost-resisting additives. Thus, the aim of our work is to optimize the compositions of frost-resisting complex additives, taking into account the operational requirements for freezing temperature at road dressing constructions.

2. Materials and methods

2.1. Materials

Components of complex frost-resisting additives:

- sodium formate – sodium salt of formic acid (HCOONa), a water-soluble product under "ChP" (chemically pure) brand;
- crystalline calcium chloride ($CaCl_2$), a water-soluble product under 'ChP' (chemically pure) brand;
- superplasticizer C-3 – sodium salt of the condensation product β-naphthalenesulfonic acid and formaldehyde. Used as 2.5 % water solution with pH in a range of 7–9.
- hardening water – water that complies with the requirements of EN 1008: 2002.

2.2. Methods

- optimization towards the composition of complex FRA was carried out by the method of experiment planning according to the second order D-optimal plan. The levels of variation and conventional concrete signs are presented in table 1. According to the results of digital processing, a regression dependence of T_z on the components dose in FRA was obtained. The significance of the coefficients to be calculated for regression model equations was estimated with the critical values by the Duncan's test, and the adequacy of the models was tested on the basis of Fisher's variance ratio. Then, according to the obtained regression equations, there was built the dependences of T_z on the components dose in FRA with isolines of the equal values of the water-ice transition temperature, which was in water solutions of the complex additives (WSCA).
- preparation of WSCA: the components of complex additives (SF, $CaCl_2$ and C-3) were sequentially added into the required amount of hardening water (the figures are introduced in Table 2), mixing it for 2–5 minutes at the temperature of 20 ± 2 °C;
- determination of the freezing temperature (T_z): prepared WSCAs were placed in the TFPT apparatus (manufactured by PM Tamson Instruments) with Tamson TLC80-14 creamer, allowing to do measurements up to –70 °C according to ASTM D1177 – ASTM D852 – ASTM D1015 – ASTM D1493 – ASTM D6875 standards. For each WSCA with a different components dose, the values of T_z have been determined.

3. Results and Discussion

To achieve the goal we applied the integrated approach to conduct the experiment, which consisted in a choice of FRA components and in the use of experiment planning. The influence of functional additives and their quantitative composition on the freezing temperature was examined with the digital technologies. It enabled to optimize the experiment according to D-optimal second-order plan and design a mathematical model of the process.

As factors (X_1, X_2, X_3), when planning the experiment, we took the quantitative value of each FRA component ($CaCl_2$, SF, C-3) in % from the cement mass in CML (Table 1). $CaCl_2$ varied within 1.0–3.0 %, SF 5.0–9.0 %, C-3 0.5–2.0 %. The levels of variation and conventional concrete signs are presented in Table 1.

Based on the data presented in table 1, we designed the matrix on the experiment planning with coded and natural values of the factors and determined T_z for each complex FRA. The results are shown in Table 2.

Table 1. The levels of variation and conventional concrete signs

Factors	Name of factors	Level of variation low (–1)	medium (0)	upper (+1)
X_1	$CaCl_2$ consumption in % from the cement mass	1.0	2.0	3.0
X 2	SF consumption in % from the cement mass	5.0	7.0	9.0
X 3	C-3 consumption in % from the cement mass	0.5	1.25	2.0

Table 2. Ice point of WSCA solutions

Additives, % from the cement mass SF	$CaCl_2$	C-3	T_z WSCA, ºC
5.0	1.0	0.5	–8.0
5.0	1.0	1.25	–8.1
5.0	1.0	2.0	–8.5
7.0	1.0	0.5	–12.0
7.0	1.0	1.25	–12.1
7.0	1.0	2.0	–12.5
9.0	1.0	0.5	–13.6
9.0	1.0	1.25	–13.7
9.0	1.0	2.0	–14.0
5.0	2.0	0.5	–8.8
5.0	2.0	1.25	–8.9
5.0	2.0	2.0	–9.2
7.0	2.0	0.5	–12.8
7.0	2.0	1.25	–12.9
7.0	2.0	2.0	–13.2
9.0	2.0	0.5	–14.4
9.0	2.0	1.25	–14.5
9.0	2.0	2.0	–14.8
5.0	3.0	0.5	–9.6
5.0	3.0	1.25	–9.7
5.0	3.0	2.0	–10.0
7.0	3.0	0.5	–13.6
7.0	3.0	1.25	–13.7
7.0	3.0	2.0	–14.1
9.0	3.0	0.5	–15.1
9.0	3.0	1.25	–15.2
9.0	3.0	2.0	–15.6

The results have been processed with some statistical methods and due to this processing the mathematical model of the process has been designed. It has been described by the regression equation depicting the dependence between the freezing temperature T_z WSCA and the component dose in FRA:

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$$T_z = -12.9 - 0.78X_1 - 2.78X_2 - 0.22X_3 - 1.25X_2^2 - 0.15X_3^3 . \tag{1}$$

The significance of the coefficients to be calculated for regression models equations was estimated with the critical values by the Duncan's test, and the adequacy of the models was tested on the basis of Fisher's variance ratio.

Table 3. Calculated values of coefficients of regression equation

Type of dependency	Calculated values of coefficients of regression equation									
	B_0	B_1	B_2	B_3	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
$T_z = f(X_i)$	–12.9	–0.78	2.78	–0.22	0.00	1.25	–0.15	0.00	0.00	0.00

Table 4. Statistical evaluations of regression coefficients

Type of dependency	Statistical evaluation										
	S_y^2	$S^2 B_0$	$S^2 B_i$	$S^2 B_{ii}$	$S^2 B_{ij}$	ΔB_0	ΔB_{ij}	ΔB_i	ΔB_{ii}	$F_{calculation}$	F_{tab}
$T_z = f(X_i)$	0.023	0.004	0.002	0.009	0.003	0.131	0.097	0.187	0.108	2.10	2.7

We have found that the most significant element in FRA mixture is the content of sodium formate (SF), compared to calcium chloride and a superplasticizer C-3, the amount of which varies in the series 3>1>0.

With the regression equation (1), the experimental results were digitally optimized and the dependence between the freezing temperature of WSCA from FRA components in the form of isolines in the range from –9 °C to –15 °C in increments of 1 °C has been depicted (Fig. 1). The obtained results on optimization allow to choose FRA compositions that provide the ability to perform construction works in conditions of subzero temperatures up to –15.6 °C.

4. Conclusion

1. In line with the purpose stated for this work we conducted optimization on the compositions of complex frost-resisting additives based on sodium formate (SF), calcium chloride and C-3 superplasticizer. The operational requirements for freezing temperature when constructing road dressing with CML were taken into account. The obtained results on optimization allow to choose FRA compositions that provide the ability to perform construction works in conditions of subzero temperatures up to –15.6 °C.

2. The influence of functional additives of sodium formate, calcium chloride and C-3 superplasticizer and their quantitative composition on the ice point of WSCA has been considered. The results have been processed with some statistical methods and due to this processing we gained the math model of the process, which is described by the regression equation depicting the dependence between the freezing temperature T_z WSCA and the component dose in FRA. We have found that the most significant element in FRA mixture is the content of sodium formate (SF), compared to calcium chloride and a superplasticizer C-3 the amount of which varies in the series 3>1>0.3.

3. With the regression equation (1), the experimental results were digitally optimized and the dependence between the freezing temperature of WSCA from FRA components in the form of isolines in the range from –9 °C to –15 °C in increments of 1 °C has been depicted (Fig. 1).

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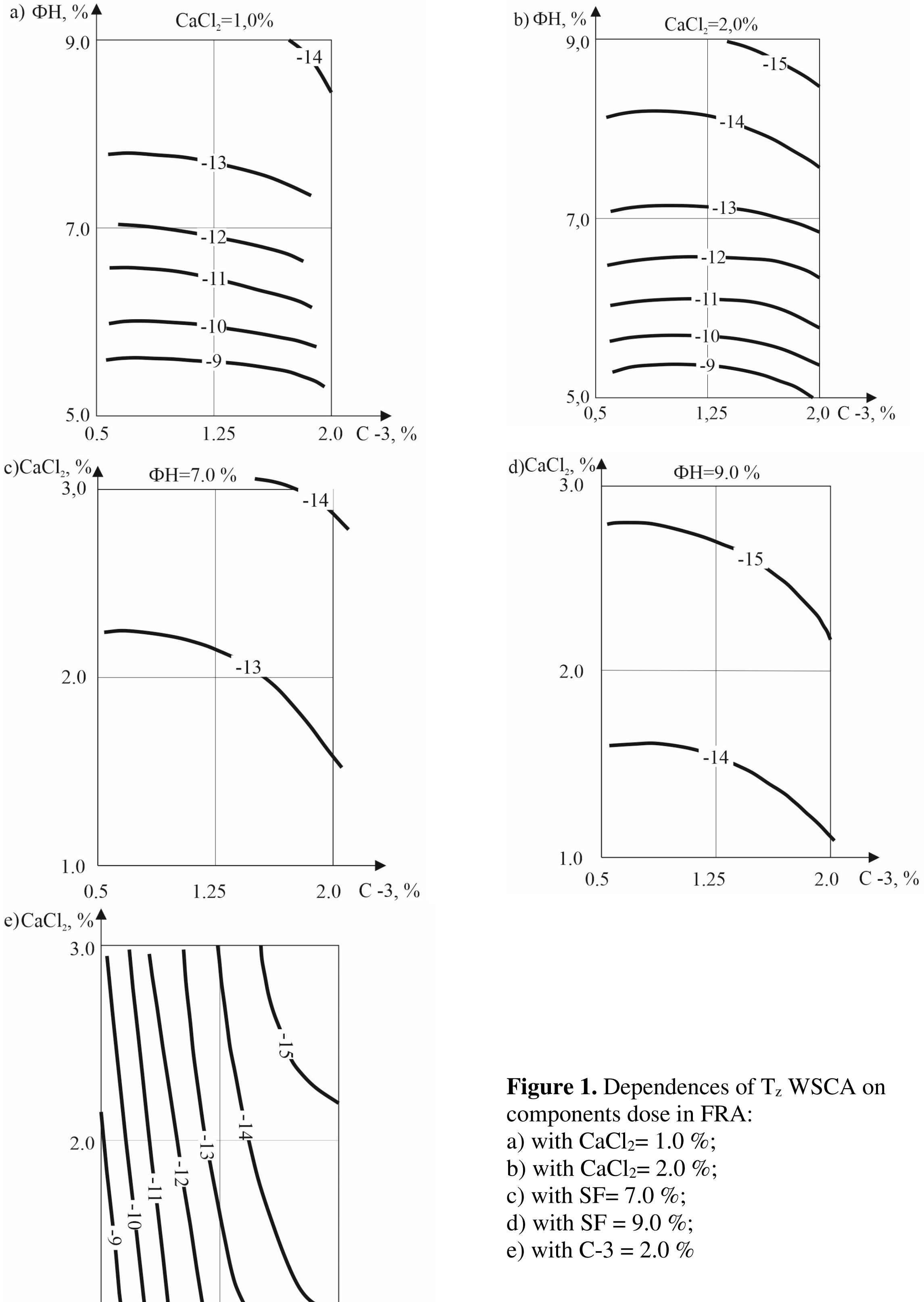

Figure 1. Dependences of T_z WSCA on components dose in FRA:
a) with $CaCl_2$= 1.0 %;
b) with $CaCl_2$= 2.0 %;
c) with SF= 7.0 %;
d) with SF = 9.0 %;
e) with C-3 = 2.0 %

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