

Modification by Zeolite-Containing Additive the Road-Building Materials Based on Carbonate Crushed Stone-Sand Mixtures and Cements

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Abstract. Carbonate stone materials are one of the most widespread rocks. Due to insufficient strength and frost resistance, their usage in road construction is limited. This problem can be solved by treatment of carbonate stone materials and their mixtures with soils by binders and modifiers. A promising direction for expanding the application field of carbonate crushed stone-sand mixtures in road construction is treatment by cement modified by zeolite-containing additive. The zeolite-containing additive usage leads to increase the compressive strength, flexural tensile strength and frost resistance coefficient of strengthened materials. The usage of crushed stone-sand mixture treated by cement and modified zeolitecontaining additive in upper layer of road pavement base and the soil strengthened by cement in lower layer leads to achieve the greatest economic effect.

Keywords: Crushed stone-sand mixture · Carbonate crushed stone · Soils · Portland cement · Zeolite-containing additive · Physical and mechanical properties · Economic efficiency

1 Introduction

One of the promising directions in road building materials development is the modification of local mineral raw materials by different additives [\[1–](#page-7-0)[5\]](#page-8-0). This work is devoted to the study of zeolite-containing additives effect on physical and mechanical properties of carbonate crushed stone-sand mixtures treated by cement, and its economic efficiency assessment. In road construction industry, the transporting materials take a large proportion of financial costs. It is possible to abandon the imported stone materials usage by local mineral raw materials strengthened and treated by cement in road pavements construction [\[6](#page-8-1)[–8\]](#page-8-2). In many countries there are crushed carbonate deposits, the demand of which is constantly decreasing due to low strength and frost resistance [\[9\]](#page-8-3). Today various ways of its usage have been proposed $[10-12]$ $[10-12]$, including in road construction [\[13\]](#page-8-6). In this regard, imparting the required physical and mechanical properties to carbonate crushed stone is the actual task.

Many scientific works are devoted to increasing of strength and frost resistance of carbonate crushed stone-sand mixtures. The method of preparing mixtures treated by

organic binder [\[14\]](#page-8-7), sulfur-containing aqueous solution of calcium polysulfide [\[15\]](#page-8-8), phosphogypsum [\[16\]](#page-8-9) and others is known. These methods of increasing the physical and mechanical characteristics of crushed stone-sand mixtures are characterized by high energy consumption of impregnation technological process, as well as the fragility of obtained modified material. The particular interest is the treatment of carbonate stone material by cement mortar, due to the low cost and technology simplicity [\[17](#page-8-10)[–19\]](#page-8-11).

It should be noted that one of the most promising way to improve the cement quality is the various additives introduction into its composition, which actively affect the cement stone structure formation and properties [\[20\]](#page-9-0). Natural zeolite rocks occupy a special place among numerous additives for cements. [\[21](#page-9-1)[–26\]](#page-9-2). Zeolites are referred to as pozzolanic additives due to $SiO₂$ and $Al₂O₃$ presence, which react with Portlandite during the Portland cement hydration, form hydrosilicates and calcium aluminates. It improves the cement stone microstructure. It is noted that the cement content increase in mixture increases the using zeolite efficiency $[27]$. In this regard, their usage as modifiers can be effective in cement-soil mixtures, because they usually have higher cement content. In cement-soil mixtures, the cement addition leads to increase the maximum density and optimal moisture content, however, the zeolite content increase acts in opposite way [\[28\]](#page-9-4). Only the optimal additives dosage including zeolite additives at processing and strengthening local mineral raw materials by cement, has the most effect on physical and mechanical characteristics of materials obtained.

The aim of the work is the modification by zeolite-containing additives the carbonate crushed stone-sand mixtures treated by cement, for the road building materials production.

2 Materials and Methods

Carbonate crushed stone was used as a starting material in the study, from which a crushed stone-sand mixture of optimal granulometric composition was prepared.

For the preparation of crushed stone-sand mixture, treated by an inorganic binder, Portland cement CEM I 42,5N was used. The mineralogical composition of Portland cement is represented by the following minerals, %: C₃S – 56.8 \pm 3.0; C₂S – 19.0 \pm 2.0; $C_3A - 7.0 \pm 0.5$; $C_4AF - 12.9 \pm 1.0$. The specific surface area was in the range of 320,0–360,0 m²/kg. The content of Portland cement was 4.00; 6.00; and 8.00% of total mass.

The modification was carried out by a natural active mineral pozzolanic additive – a zeolite-containing rock. It is a ground rock, in the form of a light-colored powder. The rock mineral composition is represented by clinoptilolite – 14–28%, calcite – 18– 23%, free silica – 24–30% and clay minerals – 24–30%. Density is 2.2–2.3 g/cm³. The pH value is 6.8–7.2. Ion exchange capacity is not less than 1.23 mg-eq/g. The additive content was 1.25%, 2.50%, 3.75%, 5.00% of total weight.

The compressive strength of crushed stone-sand mixture treated by cement was determined on samples of $10.0 \times 10.0 \times 10.0$ cm water-saturated for 2 days.

The bending tensile strength was determined on samples with a size of 10.0×10.0 \times 40.0 cm water-saturated for 2 days.

Frost resistance was studied on cubes with an edge of 10.0 cm after 28 days of normal hardening storage. Freezing time was at least 2.5 h at temperature (−18 \pm 2) °C,

thawing time for 2.0 ± 0.5 h in water at a temperature of (20 ± 2) °C. The frost resistance coefficient was determined as the ratio of the sample strength after 15 freeze-thaw cycles to the sample strength before testing.

The cement and zeolite-containing additive effect on the strength and frost resistance of cement-crushed stone mixtures was studied using the method of experiment planning according to V. Kleiman contour-graphic scheme, which we used in our research earlier [\[29\]](#page-9-5). The content of cement and zeolite-containing additives (cement, zeolite) was changed in accordance with the plan of two-factor experiment (Fig. [1\)](#page-2-0). Based on test results on contour-graphic models of response function, isolines of equal values of strength and frost resistance coefficient were constructed (Fig. [2,](#page-3-0) [3](#page-4-0) and [4\)](#page-4-1).

a)		b					
C		No.	Additives content, $\%$		Test results		
$\%$		experiment	Cement	Zeolite	R_c	R_f	K_f
cement, 5	6		4.00	1.25	R_{c1}	R_{f1}	$K_{\rm fl}$
		2	8.00	1.25	R_{c2}	R_{f2}	K_{f2}
			8.00	5.00	R_{c3}	R_{f3}	K_{f3}
4			4.00	5.00	R_{c4}	R_{f4}	K_{f4}
	zeolite, %		6.00	2.50	R_{c5}	R_{f5}	K_{f5}
		6	6.00	3.75	R_{c6}	R_{f6}	K_{f6}

Fig. 1. Experiment planning: a) contour-graphic scheme of experiment planning; b) experimental design.

The design of pavement structures was carried out according to permissible elastic deflection, shear resistance, bending resistance, static load, frost resistance and drainage layer. The reliability factor for the IV category is 0.80, for the V category is 0.70. The elastic modulus for IV category is 150.0 MPa, for V category is 50.0 MPa.

The device cost of road pavements designed structures was determined by a local resource estimate. Economic efficiency was determined by comparing the estimated cost of cheapest pavement construction with the rest options, separately for IV and V roads categories.

3 Results and Discussion

Taking into account the work purpose and the experiment plan, the results of indicators changes of physical and mechanical characteristics of crushed stone-sand mixtures treated by Portland cement with a content of 4.00 were obtained; 6.00; 8.00% by mixture weight, which are the control material parameters without modifier (Table [1\)](#page-3-1).

The cement content increase from 4.00% to 6.00% and 8.00% at processing a crushed stone-sand mixture leads to increase the compressive strength by 31.74–90.25%, the bending tensile strength by 38.04–101.09% and the coefficient of frost resistance by 60.0–92.0%.

Portland cement	Characteristics					
content, $%$	Compressive strength, MPa	Flexural tensile strength, MPa	Frost resistance coefficient			
4.00	4.41	0.92	0.50			
6.00	5.81	1.27	0.80			
8.00	8.39	1.85	0.96			

Table 1. Physical and mechanical characteristics of crushed stone-sand mixtures treated by Portland cement.

Fig. 2. The effect of zeolite-containing additive on compressive strength of crushed stone-sand mixture treated by Portland cement: included isolines the ultimate compressive strength (MPa).

When the Portland cement content is 4.00% and a zeolite-containing additive is 1.25%, the compressive strength does not increase (Table [1,](#page-3-1) Fig. [2\)](#page-3-0). However, the further increase of the Portland cement and zeolite-containing additive content leads to increase of compressive strength. In comparison with the control compositions of the material with the Portland cement content of 6.00% and a zeolite-containing additive of 2.50%, 3.75%, there is an increase of compressive strength by 6.54% and 17.38%, respectively. With a Portland cement content of 8.00% and a zeolite-containing additive of 5.00%, the indicator increases by 22.17%.

Fig. 3. The effect of zeolite-containing additive on tensile strength of crushed stone-sand mixture treated by Portland cement: —————————— isolines the ultimate compressive strength (MPa).

Fig. 4. The effect of zeolite-containing additive on frost resistance of crushed stone-sand mixture treated by Portland cement: ———————————— isolines the ultimate compressive strength (MPa).

It was found that with the Portland cement content of 4.00% and zeolite-containing additive of 1.25%, the tensile strength also does not change (Table [1,](#page-3-1) Fig. [3\)](#page-4-0). With the Portland cement content of 6.00% and zeolite-containing additive of 2.50%, 3.75%, the strength increase is observed by 20.47% and 23.62%. With the Portland cement content of 8.00% and zeolite-containing additive of 5.00%, the indicator increases by 38.38%.

The frost resistance coefficient increases with the Portland cement content of 4.00% and zeolite-containing additives 1.25% is 28.00% in comparison with the control samples (Table [1,](#page-3-1) Fig. [4\)](#page-4-1). However, with the content of Portland cement increase from 4.00% up to 8.00% and zeolite-containing additive from 2.50% up to 5.00%, significant changes in frost resistance coefficient are not observed.

The economic efficiency of crushed stone-sand mixture treated by cement and modified zeolite-containing additive is assessed on four designed constructions option under equal conditions and loads (Fig. [5\)](#page-5-0).

Fig. 5. Pavement constructions with different base layer options: $a - IV$ category; $b - V$ category.

I option of pavement construction (IV category) consists of:

1 – Dense asphalt concrete, grade II, type B, bitumen grade BND-50/70, 5.0 cm;

2 – Coarse porous asphalt concrete, grade II, bitumen grade BND-50/70, 6.0 cm;

3 – Crushed stone-sand mixture, treated by cement, M40 and modified by zeolitecontaining additive, 24.0 cm;

4 – Sand and gravel mixture, 30.0 cm.

Option II (IV category):

1 – Dense asphalt concrete, grade II, type B, bitumen grade BND-50/70, 5.0 cm;

2 – Coarse porous asphalt concrete, grade II, bitumen grade BND-50/70, 6.0 cm;

3 – Crushed stone-sand mixture, treated by cement, M40 and modified by zeolitecontaining additive, 23.0 cm;

5 – Soil-cement, M20, 30.0 cm.

III option (IV category):

1 – Dense asphalt concrete, grade II, type B, bitumen grade BND-50/70, 5.0 cm;

- 2 Coarse porous asphalt concrete, grade II, bitumen grade BND-50/70, 6.0 cm;
- 3 Crushed stone M400, fr. 40–70, 24.0 cm;
- 4 Sand and gravel mixture, 30.0 cm.

IV option (V category):

1 – Dense asphalt concrete, grade II, type B, bitumen grade BND-50/70, 4.0 cm; 3 – Crushed stone-sand mixture, treated by cement, M40 and modified by zeolitecontaining additive, 21.0 cm;

4 – Sand and gravel mixture, 29.0 cm.

V option (V category):

1 – Dense asphalt concrete, grade II, type B, bitumen grade BND-50/70, 4 cm; 3 – Crushed stone-sand mixture, treated by cement, M40 and modified by zeolitecontaining additive, 20.0 cm; 5 – Soil-cement, M20, 29.0 cm.

VI option (V category):

1 – Dense asphalt concrete, grade II, type B, bitumen grade BND-50/70, 4.0 cm;

3 – Crushed stone M400, fr. 40–70, 21.0 cm;

4 – Sand and gravel mixture, 29.0 cm.

The comparison cost of developed pavements construction options is shown in Fig. [5](#page-5-0) (Fig. [6\)](#page-6-0).

Fig. 6. Cost comparison of road pavements device (I-III option for the IV road category, IV-VI for the V road category).

The cost calculation of designed road pavements structures device showed that the greatest economic effect is achieved for IV road category with the II option of road pavement construction with usage of processed crushed stone-sand mixture and strengthened soil (cost reduction is 2.2–22.5%), for V category with the V option with similar materials (cost reduction is 0.7–29.4%).

In accordance with the scientific works results $[20-23, 25-28]$ $[20-23, 25-28]$ $[20-23, 25-28]$ $[20-23, 25-28]$, the zeolite-containing additive introduction improves the physical and mechanical characteristics of carbonate crushed stone-sand mixture treated by Portland cement due to silica ($SiO₂$) and aluminum oxide $(A₁₂O₃)$ active centers in zeolites.

4 Conclusions

- 1. The effect of zeolite-containing additive on physical and mechanical properties of crushed stone-sand mixture treated by Portland cement was investigated. The zeolitecontaining modifier in content of 2.50 to 5.00% is effectively used and increases the strength when the Portland cement content was more than 6.00%. When cement content is lower (4.00%), the positive modification result was insignificant and the resulting material did not match the requirements for pavement materials.
- 2. It was established that the modification of crushed stone-sand mixture provided the maximum increase of compressive strength by 29.78% when the Portland cement content was 6.00% and zeolite-containing additive was 5.00%. Flexural tensile strength is maximally increased by 38.38% when the Portland cement content was 8.00% and zeolite-containing modifier was 5.00%.
- 3. It was found that the zeolite-containing additive introduction significantly affects the frost resistance coefficient. When the Portland cement content is 4.00%, the increase was up to 38.00%. When the Portland cement content is 6.00% and 8.00%, the frost resistance coefficient was not increased significant.
- 4. The greatest economic effect for IV and V road categories is achieved at option of road pavement construction with usage of treated crushed stone-sand mixture and strengthened soil. The cost reduction amounted to 22.50% and to 29.40%, respectively.
- 5. The improvement of physical and mechanical characteristics of carbonate crushed stone-sand mixture treated by Portland cement and modified zeolite-containing additive may be associated with the action of silica $(SiO₂)$ and aluminum oxide $(Ai₂O₃)$ active centers in zeolites. In this regard, this is the urgent topic for further research.

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