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## Research of influence of polymer additives-stabilizers on physical-mechanical indicators and microstructure of cement ground

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Abstract. The article describes the positive effect of cement ground modification by polymer stabilizers. The influence of the latex polymer stabilizer Nanoterrasoil, manufactured by NanoSky (Germany), and the polymer acryl-based stabilizer (SAP) on the physico-mechanical parameters of a light sandy loam exposed by Portland cement stabilization has been investigated. The effect of acrylic polymer on the microstructure of the cement ground based on light sandy loam has been studied. It has been established that when introducing the polymer stabilizer Nanoterrasoil (NTS) (1-1.5 wt. %) into the cement-ground mixture with a simultaneous decrease in the cement consumption, the final product - cement ground acquires the increased compression strength (28 days) in water-saturated state and saturation coefficient. Significant increase of physico-mechanical parameters has been established even in case of loam stabilization by acrylic polymer (SAP), even without cement introduction. The cement ground modified with acrylic polymer is characterized by a solid fusion microstructure. This proves that the individual organic ions of the acrylic polymer, when introduced into the cement ground, are adsorbed on the surface of the solid particles of clay minerals, enveloping and bonding them during polymerization, forming a complex organo-mineral system.

#### 1. Introduction

One of the most effective ways to reduce the cost of road construction and the consumption of resources is to use stabilized ground made of available local materials in the structural layers of the road surface dressing. Technical and economic calculations, taking into account the actual production costs, have shown that the use of layers of fortified local grounds instead of equivalent in strength bases of imported stone materials leads to a decrease in the total cost of construction by 20-60 %. Therefore, the use of local consolidated grounds is a promising area for road network development.

Many years of research by the State Research Institute of Ukraine have shown that the strength of road surf with layers of hardened ground is not lower, and in many cases higher, the strength of road surface dressing with bases of gravel and gravel [1]. In this case, the evenness of the coating, as a rule, is much higher than on the bases of stone granular materials. At the same time, one of the causes of poor road condition is wetting of ground due to excessive moistening. The creation of a monolithic cement-based slab in the basis of road construction has a positive effect on the water-thermal conditions of the ground and reduces the gauge of the surface. Cement ground, as a result of the interaction of inorganic binders and colloid-clay ground components, is characterized by increased

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mechanical strength, frost resistance and durability, which allows to reduce the number of additional layers of road surface dressing for roads of categories II-III and replace with only one layer for roads of categories IV-V.

All this testifies to the practical necessity and economic benefit of the widespread use of various types of hardened grounds in the construction of the road network.

It is known that in the consolidation of ground, the cement acts as a structure-forming agent and is the main component of the mixture, which provides the creation of a crystallization rigid framework, which actually strengthens the ground [2]. The introduction of cement into the ground leads to a significant reduction in the number of macropores by filling the space between the ground aggregates with products of hydration, which in turn provides a decrease in the permeability to water of the material. It is known that during the hardening of the cement-ground mixture calcium ions released during the cement hydration are actively absorbed by clay ground particles [3]. The basic minerals of clay grounds (feldspars, quartz, calcite) show maximum adsorption capacity for calcium hydroxide in the first 4-8 days, which contributes to the active set of strength, afterwards this process is slowed down. The presence of a clay fraction plasticizes the cement-based mixture and light laying. However, the presence of a clay colloidal fraction causes difficulties in the treatment of ground binder, since the clay particles are carriers of coagulation bonds, which requires significant dosages of binder to change the construction and technical properties of grounds. At the same time, the high dispersion of the clay component makes it difficult to obtain a homogeneous (uniform) structure of the cement ground due to the formation of floccules - loose aggregates with a shell of cement and a core of ground. Therefore, cement grounds containing a large number of dusty and clay particles have anisotropy, which is a prerequisite for low fracture toughness and as a consequence of low water, frost resistance and durability [4].

At the same time, under the influence of dynamic loading, compression and tensile stresses occur in the cement-base layer, which are smaller than the limit values and, therefore, cannot be the main cause of its destruction [2]. The seasonal temperature fluctuation, namely the change of the water phase, has a stronger damaging effect on the cement ground. Repeated cycles of freezing and defrosting of the cement ground in the water-saturated state contribute to the accumulation of residual deformations, which leads to the formation of crack pattern that destroys the monolithic structure of the cement ground. It has been established that the introduction of less than 10 % of Portland cement into the ground composition does not provide the material with the necessary long-term resistance to the influence of natural climatic factors.

Therefore, it is advisable to study the effect of stabilizers on the structure, crystallization and, as a consequence, the physical-mechanical properties of the cement ground. This will provide the differentiation of ground types (plastic clays, acidic, humic, saline) suitable for strengthening, extension of the construction season due to the possibility of cultivation of wetted grounds and performance of works at unfavourable temperatures, improvement of technological properties of cement-ground mixtures, stability of physical and mechanical properties of the ground cement regardless of seasonal fluctuation of weather and climatic factors, creation of optimal conditions for hardening and saving of cement, increase of water and frost spine, strength and durability of the ground cement.

To increase the physical-mechanical properties of the cement ground, the polymer additives are widely used in the world practice. Manufacturing and introduction into the road industry of polymer additives for domestic cement ground has not yet become widespread. And, foreign polymer additives have a fairly high cost, but their use on the technical and economic indicators of cement is fully justified. The mechanism of influence of polymers (in particular latex) on the structure formation in cement ground is reflected in details in the research papers [5; 6]. The formation and development of the crystallization structure of the cement ground stabilized with cement polymer is similar to ordinary cement stone. When mixing an aqueous dispersion of latex polymer with Portland cement, the latter selects water from the latex. When the processes of crystallization end in the cement, the coagulation of the polymer particles of the latex takes place as a result of its dehydration. In the process of further

structure formation there is an increase of polymer particles on the binder crystals. Thus, two phases are formed, representing a spatial mesh of rubber (latex polymer), which is located in a threedimensional mesh of crystallized binder. The additional introduction of cellulose to latex-based polymeric stabilizers provides a powerful synergistic effect on the physical and mechanical properties of the cement ground, due to the creation of branched polymeric filaments that penetrate the cement ground structure from the cellulose. In this case, there is an increase in the strength of the material for compression and tensile flexure, frost resistance and crack resistance [7].

Liquid polymeric acrylic based emulsions are relatively innovative additives-stabilizers for mineral binder grounds [8]. A typical polymer emulsion contains about 40-60 % polymer, 1-2 % emulsifier, and the rest is water. Studies [8] have shown that acrylic-based polymer emulsions provide significant strength gains. The process of hardening of such an emulsion is accompanied by its delamination and gradual water evaporation. The demulsification occurs when its individual organic ions, which are in the suspension state, are interconnected and adsorbed on the surface of the solid ground particles, forming complex organo-mineral complexes. Such liquid acrylic-based polymeric emulsions are equated with binder materials. Some manufacturers of polymeric acryl-based stabilizers note that when using SAP to strengthen the clay grounds - cement can not be used.

Therefore, cement ground is an effective and cost-efficient material for the construction of highways. However, as studies have shown, clay grounds, even with the strengthening of Portland cement, significantly lose their strength in the cycles of freezing and defrosting. This is due to the heterogeneity of the structure and the high tendency to crack formation. Therefore, for clay grounds that are amenable to cement consolidation, research in the field of modification of such a material by polimer stabilizing additives to improve the physical and mechanical properties is promising.

#### 2. Materials and methods

The main component of the cement is a clayed ground. According to DSTU B V.2.1-17:2009 "Grounds. Methods of laboratory determination of physical properties" it has been found that the clay ground is represented by a loamy sandy loam with humidity at the boundary of rolling Wp = 22 % and humidity at the boundary of fluidity WL = 29.2 %. The granularity of the loam was determined by the hydrometer test (DSTU B V.2.1-19:2009 "Grounds. Methods of laboratory determination of particle size (grain) and microaggregate composition". The granularity of the loam is represented by particles of the following sizes: 0.1-0.05 mm. - 10.33 %; 0.05-0.01 mm. - 42.98 %; 0.01-0.005 mm. - 32.29 %; less than 0.005 mm - 14.4 %. The organic matter content of the dry weight is 9.2 wt. % (DSTU B V.2.1-16: 2009. Change No. 1. Grounds. Methods of laboratory determination of organic matter content) and ground pH - 8.34 (ISO 10390:2005, IDT)

The loam was strengthened by Portland cement of the PC II/A-W-400-N (DSTU B.V. 2.7-46: 2010) of PJSC Ivano-Frankivskcement. Latex Nanoterrasoil (NTS) and acrylic (SAP) polymer stabilizers were used as stabilizing additives.

The maximum density of the ground skeleton at optimum humidity was determined by the Proctor compaction test (ASTM D 698-91). The compressive strength of hardened ground samples was determined according to DSTU B V. 2.1-309:2016 "Grounds strengthened with binder. Test methods", DSTU B V.2.1-4:96 "Grounds. Methods of laboratory determination of strength and deformation characteristics ", DSTU B V.2.7-214:2009 "Building materials. Concretes. Methods for determining the strength of companion specimen".

The research of microstructure and qualitative phase composition was performed by scanning electron microscopy and X-ray microanalysis using the REMMA-102-02 scanning electron microscope.

#### 3. Results of investigation

The degree of compaction of the mixture significantly affects the processes of structure formation in the cement ground, its porosity, water and frost resistance, mechanical strength, and, ultimately, its durability. With the maximum compaction of the mixture from its volume, excess air is displaced, the

thickness of the water films decreases, the liquid phase and solids are redistributed, resulting in a denser packing, the number and contact area between the cement and the ground increases. [9]. It is known that in order to improve the compaction process and ensure the readiness of the ground cement, it is necessary to increase the water content. And to ensure long-lasting strength and frost resistance, it is necessary that the ground compaction (cement-ground mixture) approaches the values of the maximum skeletal density at the values of optimal humidity close to the percentage of bound water. Since, when the water content is above the norm required for the chemical reaction between the cement and the ground, a high amount of pores is formed in the material, and at its curing deformation shrinkage, which leads to low values of physical and mechanical parameters. This inconsistency in the technology of creating cement ground is solved by the introduction of polymeric stabilizers.

At the first stage of testing, studies were conducted to determine the effect of polymer additives Nanoterrasoil (NTS) and SAP on the value of maximum density of dry ground (cement-ground) mixture at values of optimal humidity (table 1). Determination of the maximum density of the ground skeleton at optimum humidity was performed according to the Proctor compaction test (ASTM D 698-91). The inner diameter and height of the mold are 101.6 mm and 116.4 mm, respectively. The number of layers in the mold is 5, the number of strokes for each ground layer is 25. The weight of the sealing load is 4.5 kg and the height of the fall is 457.2 mm.

	Name of the cement- ground mixture	Composition of the cement-ground mixture					Maximum
No.		Light sandy loam (LSL), wt.%	Portland cement PC II/A- Sh-400- N (C), wt.%	Nanoterrasoil (NTS) additive, wt.%	Additive acrylic polymer, SAP wt.%	Optimal humidity ground (cement ground) Wopt (%)	density dry ground (cement ground) $\rho_{d max}$ (g/cm <sup>3</sup> ) at Wopt (%)
1	LSL100%	100	-	-	-	18.0	1.82
2	LSL95% +C5%	95	5	-	-	17.6	1.84
3	LSL94%+C6%	94	6	-	-	16.8	1.86
4	LSL94%+C5%+NTS1%	94	5	1	-	16.5	1.88
5	LSL93%+C6%+NTS1%	93	6	1	-	16.2	1.89
6	LSL92.5% +C6% +NTS1.5%	92.5	6	1.5	-	16.1	1.89
7	LSL92%+ C7% +NTS1%	92	7	1	-	16.0	1.92
8	LSL97% +SAP3%	97	-	-	3	17.3	1.86
9	LSL94.5% +C4%	94.5	4	-	1.5	16.5	1.90
	+SAP1.5%						

**Table 1.** The value of optimal humidity and maximum density of the dry ground (cement ground) with polymer additives Nanoterrasoil (NTS) and SAP.

According to table 1, with the introduction of additives Nanoterrasoil (NTS) and SAP is a positive dynamics of increasing the maximum density of dry ground (cement ground) while reducing the values of optimal humidity.

To establish the effect of polymer stabilizers Nanoterrasoil (NTS) and SAP on compression strengths and frost resistance (table 2) were formed samples cylinders with a diameter of 50 mm, by applying a sealing load of 15.0 MPa for 3 minutes using hydraulic press. Formed specimens were stored under normal conditions according to DSTU B V.2.1-309:2016 "Grounds stabilized with binder. Test Methods" and were tested for compressive strength at 7, 28 days of age. Frost resistance was evaluated by the compression strength after a certain number of freeze-defrosting cycles and frost resistance.

In the case of stabilization of the light sandy loam by polymer stabilizer Nanoterrasoil (NTS), it has been established that according to the coefficient of frost resistance of compositions No. 2-4 correspond to the M40 mark and the composition No. 5 - M60, i.e. to the strength class [10, 11]. According to the experimental data (Table 2), cement consumption for cement ground with the composition No. 2-5 decreases on average by 2-6 %, according to clause 3 of standards [10]. This positive effect of the Nanoterrasoil (NTS) stabilizer is due to the fact that the ratio of the individual structural elements, their physico-mechanical properties, as well as the nature of the relationships between them, determine the qualitative differences of the cement ground stabilized with polymer.

		Co	mpressive				
No.	Name of the cement ground	R <sup>7</sup> st ( <sup>1</sup> n. c.)	R <sup>28</sup> st. ( <sup>1</sup> n. c.)	R <sup>28</sup> st.w. ( <sup>1</sup> n.c.+full water saturation)	R <sup>28</sup> st.w ( <sup>1</sup> n.c + <sup>2</sup> m freeze- defrosting cycles)	Coefficient of frost resistance K <sub>m</sub>	Mark of the cement ground
1	LSL95% +C5%	3.70	6.63	-	-	-	-
2	LSL94%+C5%	3.46	4.36	4.17	3.22	0.74	M40
	+NTS1%						
3	LSL93%+C6% +NTS1%	3.52	5.77	5.04	4.44	0.77	M40
4	SLP92.5% +C6% +NTS1.5%	3.84	6.78	5.92	5.15	0.77	M40
5	LSL92%+ C7% +NTS1%	3.96	7.14	7.03	5.36	0.75	M60
6	LSL97% +SAP3%	0.90	5.14	4.89	3.82	0.74	M40
7	LSL94.5% +C4% +SAP1.5%	4.10	8.29	6.68	6.46	0.78	M60

**Table 2.** The values of the compressive strength and frost resistance coefficient of cement ground with polymer additives Nanoterrasoil (NTS) and SAP.

<sup>1</sup>n.c. - normal curing conditions;

<sup>2</sup>For cement ground of the M40 brand m=15, and for the M 60 brand, m = 20, according to clause 6.2 of the State Construction Standards of Ukraine (SCSU) B.2.3-37641918-554:2013 «Highways. Layers of road surface dressing made of stone materials, industrial waste and cement grounds

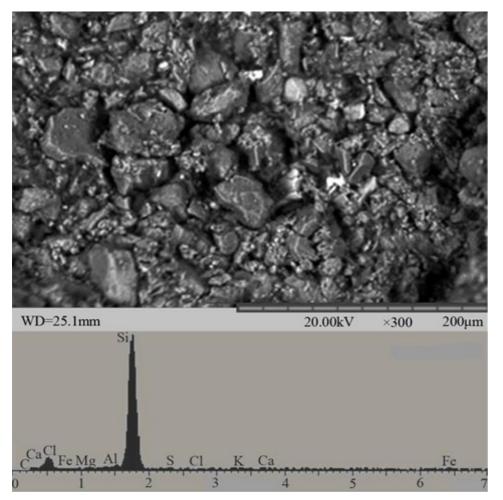
Due to the simultaneous content in the nanoterrasoil stabilizer (NTS) of latex and cellulose, which enhance the action of each other and in the decay of the emulsion "moisten" the surface of particles ofstone material with the subsequent formation of polymer filaments on them, which form sufficiently strong waterproof bonds and like a mesh penetrates the crystalline structure of the cement ground. In this case, there is an increase in the compressive strength of the material, frost resistance and durability.

The stabilization of loam with acrylic polymer (SAP) in the amount of 3 wt. % without the introduction of cement is accompanied by the achievement of the M40 mark [clause 6.2, 11]. With the introduction of SAP (1.5 wt. %) and Portland cement (4 wt. %) in the cement-ground mixture, the values of the compressive strength (28 days) in the water-saturated state and the coefficient of frost, which corresponds to the mark M60 [clause 6.2, 11], have been obtained. Significant savings of cement have been established, as the content of cement in the composition of No. 7 is only 4 wt. % opposed to the recommended 8-10 wt. % for loam, according to [clause 3, 10].

Therefore, by introducing an acrylic polymer stabilizer in the strengthening of clay grounds can significantly reduce or refuse the use of cement, without reducing the physico-mechanical properties of cement. One can state that a small amount of cement in such systems serves to enhance the processes of interaction of the clay particles with the acrylic polymer. The scientific article [8] studies

the processes of structure formation in the system of "clay ground-acrylic polymer-cement". It is commonly accepted that the cement content of the clayed ground should be greater than 10 wt. % by stabilization bonds, which actually increase the physico-mechanical properties. However, it was experimentally established that the introduction of cement in small quantities simultaneously with the development of crystallization bonds, increasing the strength of water-colloidal bonds, which are characteristic of clay grounds. The strengthening of water-colloidal coagulation bonds occurs more intensively in grounds with a higher specific surface area, which indicates their increased physicochemical activity, both for cement particles and polymer. It is known that in heavy loam with a cement content of 2 wt. %, and in sandy loam - 4 wt. %, the strength of coagulation bonds over rigid crystallizations will enhance physical and mechanical parameters. That is, the durability and resistance to cracking, in such systems with little introduction of cement, is determined by the strength of the coagulation bonds. However, the strength and stability of coagulation bonds increases with the introduction of a small amount of cement into the clay ground-acrylic polymer system.

Using the method of scanning electron microscopy and X-ray microanalysis, the nature of the microstructure and the qualitative phase composition of the cement ground stabilized with acrylic polymer were obtained. According to the X-ray spectra, the phase composition of cement ground LSL95% +C5% (Figure 1) and LSL 94.5% +C4%+ SAP1.5% (Figure 2) is represented by a clay component: feldspars, muscovite, albite, chlorites and quartz . However, an intense carbon (C) line is present in the cement ground of LSL94.5% +C4% +SAP1.5% (Figure 2), which indicates a significant content of polymerized organic (-CH2-) inclusions corresponding to the acrylic polymer.



**Figure 1**. Microstructure and X-ray spectra of the cement ground LSL 95% + C5%.

Scanning electron microscopy was used for non-destructive testing of the solid cement microstructure. The image of the cement structure of the cement ground in the electron microscope was obtained using elastically reflected (backscattered BSE) electrons in the COMPO composite mode. In COMPO mode it is possible to observe not only the relief of the investigated surface, but also to set the elemental composition against the background of phase contrast. Each phase of the sample has a luminescence proportional to its averaged atomic number. That is, the heaviest elements are light in colour, and the lightest (or their full lacking) are darker. Microanalysis of the surface of cement grounds indicates that the composition of LSL95%+C5% (Figure 1) is characterized by a heterogeneous, slightly fractured microstructure, and individual grains of minerals are more separated. In the case of microanalysis of the composition of LSL94.5% +C4% +SAP1.5% (Figure 2), a solid fusion microstructure is clearly observed. Therefore, one can state that the individual organic ions of the acrylic polymer when introduced into the cement ground adsorbed on the surface of solid particles of clay minerals, envelop them, bonding during polymerization and forming a complex organomineral system. It has been established that the chemical composition of minor dark lines corresponds to carbon (C), namely to the cured polymerized (-CH<sub>2</sub>-) groups, which is confirmed by the X-ray spectrum.

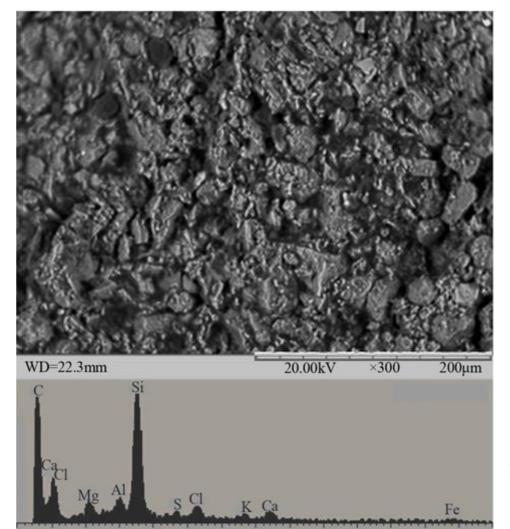


Figure 2. Microstructure and X-ray spectra of the cement ground of LSL94.5% +C4% +SAP1.5%.

#### 4. Conclusion

High efficiency of Portland cement loam stabilization with Nanoterrasoil polymer stabilizer (NTS) has been established. It has been proven that with the introduction of Nanoterrasoil (1-1.5 wt. %) in the cement ground it is possible to reduce the consumption of cement by 2-6 %, according to [clause 3, 10]. At the same time, this material satisfies the performance limit of compressive strength (28 days) in the water-saturated state and the coefficient of frost, which corresponds to the M40-M60 marks [clause 6.2, 11], that is, the first class of strength. The loam stabilization with acrylic polymer (SAP) in the amount of 3 wt. % without the introduction of cement is accompanied by the achievement of the M40 mark. With the introduction of SAP (1.5 wt. %) and Portland cement (4 wt. %) in the cement ground, the values of the compressive strength (28 days) in the water-saturated state and the frost resistance corresponding to the M60 mark were obtained. Significant cement saving is established, since the content in the cement ground is only 4 wt. % opposed to the recommended 8-10 wt. % for loam, according to [clause 3, 10]. Microanalysis of the structure of loam stabilized with acrylic polymer indicates a continuous fusion microstructure. This proves that the individual organic ions of the acrylic polymer, when introduced into the cement ground, are adsorbed on the surface of the solid particles of clay minerals, cover them, and during polymerization are bonded, forming a complex organ-mineral system.

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