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PHYSICO-CHEMICAL METHODS FOR INVESTIGATING THE EFFECT OF THE «MADOR» MODIFIER ON THE CHARACTERISTICS OF CEMENT REINFORCED MATERIAL

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Problem statement. When performing road construction works using cold recycling technology, the construction of foundations from cement-crushed stone-gravel-sand mixtures or reinforced soils, the question arises about the use of various modifiers or stabilizers. A large number of various modifications and stabilizers are produced serially on the territory of the Russian Federation, which are additives used together with binders to improve the quality of reinforced materials - structural layers of road clothes. Determining the effect of modifiers and stabilizers (in particular, the MADOR modifier) on the structure of the binder-reinforced material requires research by physico-chemical methods.
Results. The review of the results of physico-chemical studies of the effect of the MADOR modification on the structure of non-cohesive soils reinforced with cement and used for the construction of structural layers of pavement is given. The results of studies of the structure of the material reinforced with cement together with the MADOR modifier are presented.
Conclusions. A positive effect from the use of the MADOR modifier for strengthening the material under study has been established due to the predominance of the active phase, which provides a higher uniformity of the structure and increased physical and mechanical properties. The studies carried out allow us to conclude that the durability and reliability of the structural layers of road clothes arranged by the method of cold regeneration using the MADOR modifier are increased.

Keywords: highways, soil reinforcement, cement, MADOR modifier, X-ray phase analysis, cold recycling technology.

Introduction. Currently, in the practice of road construction, when strengthening soils or crushed stone-sand-gravel mixes with cements, various modifiers and stabilizers are broadly used for improving their technological as well as physical and mechanical properties [2, 6, 7, 15—21]. A large number of studies have been dedicated to the efficiency of modifiers and stabilizers in soil stabilization using various methods [3, 4, 11, 12], positive experience has been obtained in the field of construction and road repairs [1, 5, 9, 10, 13, 14].

In order to improve the technological properties, enhance the strength and frost resistance, as well as to increase the deformation and load-bearing capacity of the structural layer [8], chemical additives should be utilized meeting the requirements of the relevant regulatory documents. The use of cement additives in soil stabilization should be justified for a specific type of roadwork conditions.

Various manufacturers are offering a lot of various additives to cement used in strengthening materials used as a road base. At the same time, in the overwhelming majority of cases, there is no information available on the effect of the modifier on the physical and chemical properties of the material to be strengthened, according to which it is possible to make an objective assessment of the possibility of its application for specific conditions of road repair or construction. This circumstance has caused a need to investigate the preparations for strengthening soils with cement.

In order to assess the effect of the additive on the physicochemical properties of the cement-reinforced material, studies of the modifier MADOR (STO 16308651-001-2022) were performed. According to the manufacturer, this additive improves the quality of the cultivated soil or crushed stone-sand-gravel mix reinforced with cement for increasing the durability and service life of a road base. The study of the influence of the MADOR modifier on the change in the structure of the dispersed material strengthened by cement was performed in three following ways:

1) by investigating the microstructure of materials by means of a JSM-6380LV scanning electron microscope;

2) X-ray phase analysis on a PANalytical EMPYREAN automatic diffractometer;

3) analysis of the chemical composition of the average material sample on an X-ray fluorescence spectrometer S8 Tiger (Bruker AXS GmbH).

For the study, the following samples of the material reinforced with cement and MADOR modifier of the following composition were taken:

— soil (sandy) in accordance with GOST 25100-2020 — 50 %, sand from screenings of crushed stone of the Obukhov quarry (fr. < 0.315 mm) — 50 %, cement 42.5 — 10 % of the mass of the mineral part (soil + screenings), water — 11.43 % (optimum soil moisture);

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1. Study of the microstructure of cement-reinforced materials using electron microscopy. The study of the microstructure of materials reinforced with cement (C) and MADOR modifier (M) was performed by means of a JSM-6380LV scanning electron microscope. Through the course of the research, images of objects were obtained in the secondary electron emission mode at an accelerating voltage of 20 kV and magnification from ×350 to ×10000. The images show the microstructure of the cleavage surface of the samples. The micron marker present in the images makes it possible to estimate grain sizes, layer thicknesses, and scales of other features. In order to investigate the surfaces by means of a scanning microscope, fresh fractures (chips) of structures were made. Flat cleavage fragments sized 5—10 mm were fixed on sample holders using double-sided adhesive electrically conductive tape. The samples prepared in this way on holders were placed on a goniometric table in the working chamber of the SEM and, after the chamber was evacuated, were examined. The conducted studies allow us to obtain images of the surface of an object with a high (up to 0.4 nanometers) spatial resolution. The resulting images are shown in Fig. 1 and 2.

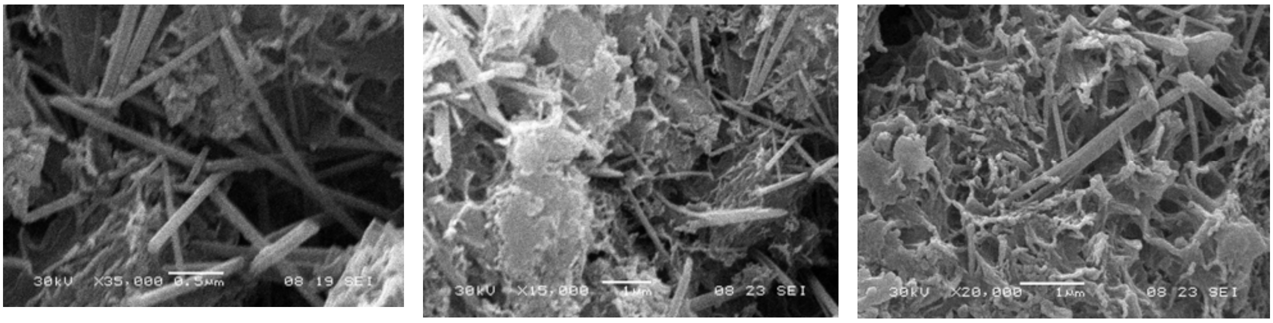


Fig. 1. Image of the material samples reinforced with cement

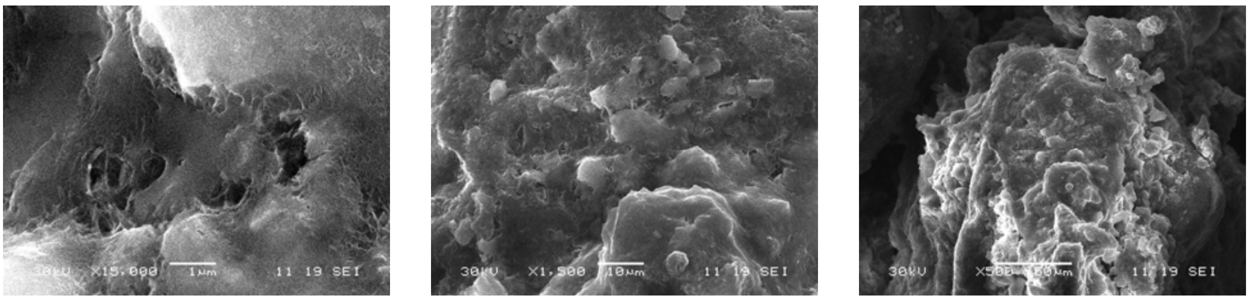


Fig. 2. Image of the material samples reinforced with cement and the MADOR modifier

According to the results of studies performed by electron microscopy, it can be concluded that:

— the samples of material treated with cement without a modifier are dominated by a framework crystal structure with the presence of acicular crystals which are typical of those of neoplasms of cement stone which cause brittleness of the material while an external load is being applied;

— the material samples treated with cement and MADOR modifier are dominated by a monolithic amorphous structure with a microporous crystalline network of aluminosilicates with pore sizes less than 50—500 nm, which ensures the homogeneity of the material structure as well as its stable physical and mechanical properties. The joint action of cement and the MADOR modifier is associated with a complex of interrelated mechanisms: the catalytic role of nanosized (up to

100 nm) particles as crystallization centers where the energy barrier of chemical and physicochemical interactions decreases; mechanism associated with a higher probability of chemical transformations occurring in heterogeneous processes of phase formation of hydrated compounds with the corresponding chemical and mineral composition and high values of the specific surface area of the particles of the MADOR modifier and nanosized particles of the reacting phases.

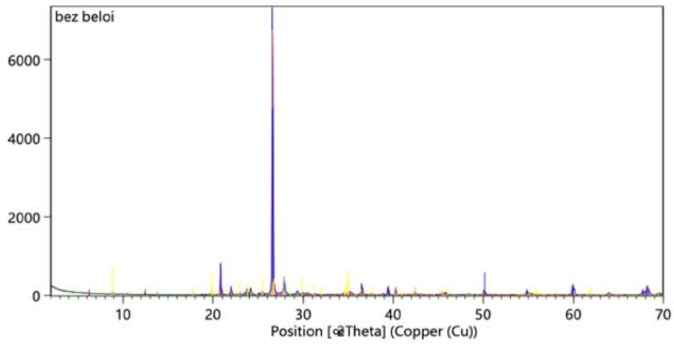
2. Study of the microstructure of cement-reinforced materials using X-ray phase analysis. X-ray phase analysis was conducted on a PANalytical EMPYREAN automatic diffractometer (Fig. 3) using Cu Kα1 radiation (hybrid Ge{111} monochromator on the primary beam) and a PIXcel1D position-sensitive detector. The measurement was carried out in reflection mode, $\theta/2\theta$ scanning with a step of 0.026° over 2θ. Measurement range – 15…80° 2θ. The calculation of interplanar spacings and integrated intensities used to refine the cell parameters was carried out according to the profile analysis of experimental diffraction patterns (Pauli method). Phase analysis (semi-quantitative) was carried out using a "powder" database.

PDF-2 ICDD (International Center for Diffraction Data). All of the calculations for refinement of diffraction patterns, determination and refinement of cell parameters, determination of the phase composition were performed using the HighScore Plus, Version: 3.0.t (3.0.5) software package (developed by PANalytical B.V., the Netherlands).

Fig. 3. Equipment for the study of microstructure by means of X-ray phase analysis

Through the course of the studies of the material reinforced with C and CM, the x-ray diffraction patterns shown in Fig. 1 were obtained by means of X-ray phase analysis (Fig. 4 and 5).

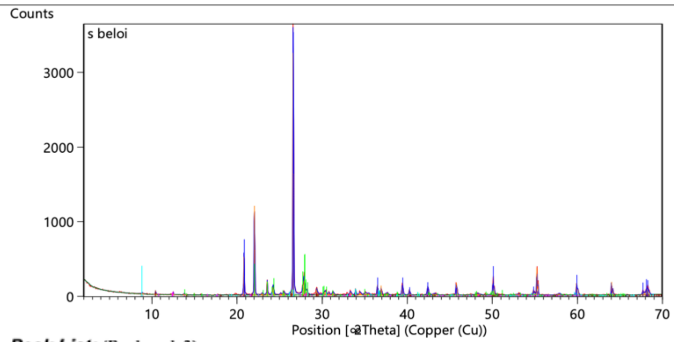
According to the results of the studies conducted by means of the method of X-ray phase analysis, it was found that 39% of silica particles participate in the structure formation of the material treated with cement without a modifier, and 50% of silica particles in the material treated with cement and the MADOR modifier, which is 1.28 times higher. Silica particles provide an amorphous (active) part of the structure for adsorption processes on their surface. Apart from the appearance of mechanical contacts between the particles of the composite, new chemical bonds with amorphous silica are formed, which provides higher physical and mechanical characteristics of the material.



Peak List: (Bookmark 3)

Visible	Ref. Code	Compound Name	Chemical Formula	SemiQuant [%]
*	03-065-0466	Silicon Oxide	Si O2	39
*	00-009-0466	Sodium Aluminum Silicate	Na Al Si3 O8	5
*	01-079-1270	Magnesium Iron Aluminum Silicate Hydrate	(Mg2.96 Fe1.55 Fe.136 Al1.275) (Si2.622 Al1.376 O10) (O H)8	4
*	01-072-1937	Calcium Carbonate	Ca C O3	1
*	01-076-0827	Potassium Aluminum Silicate	K.904 Na.085 Ca.005 Ba.006 Al0.95 Si3.05 O8	4
*	01-080-0742	Potassium Sodium Iron Aluminum Silicate Hydroxide	(K0.82 Na0.18) (Fe0.03 Al1.97) (Al Si3) O10 (O H)2	47

Fig. 4. Radiograph of the samples of the cement-reinforced material



Peak List: (Bookmark 3)

Visible	Ref. Code	Compound Name	Chemical Formula	SemiQuant [%]
*	01-086-1560	Silicon Oxide	Si O2	50
*	01-076-1819	Sodium Aluminum Silicate	Na (Al Si3 O8)	37
*	01-072-1214	Calcium Carbonate	Ca C O3	1
*	01-084-0984	Sodium Magnesium Iron Aluminum Beryllium Silicate Hydrate	Na.25 (Mg1.4 Fe.6) (Al3.84 Be.16) Si5 O18 (H2 O).6	2
*	01-079-1667	Potassium Iron Aluminum Silicate Hydroxide Fluoride	K.99 (Fe1.92 Al1.08) (Al1.05 Si2.71 O10) (O H F)	7
*	01-070-4800	Sodium Ammonium Silicate Hydrate	Na0.1 (N H4)1.01 (Si4 O8) (H2 O)2.37	3

Fig. 5. X-ray pattern of the samples of the material reinforced with cement and the MADOR modifier

3. Study of the microstructure of cement-reinforced materials by means of the method of chemical composition analysis. The chemical composition of an averaged sample of materials reinforced with Z and ZM was determined on an X-ray fluorescence spectrometer S8 Tiger (Bruker AXS GmbH). The results were processed using the developed methods in the Spectra Plus program (Bruker AXS GmbH). X-ray phase analysis was conducted on a Panalytical Empyrean automatic diffractometer on oriented preparations with a fraction of less than 0.002 mm. Quantitative determinations of mineral phases were performed by means of the method of integral intensities over the height of reflections.

The results obtained during the chemical analysis of the material reinforced with C and CM are shown in Table.

Table

Results of the element analysis

Index, %	Sample with the MADOR modifier	Sample without the MADOR modifier	Index, %	Sample with the MADOR modifier	Sample without the MADOR modifier
Na	0.377	0.302	Ca	8.982	7.741
Mg	0.538	0.446	Ti	0.272	0.249
Al	2.457	2.084	Cr	0.023	0.012
Si	12.483	11.104	Mn	0.123	0.095
P	0.038	0.036	Fe	4.283	3.635
S	0.15	0.132	Zn	0.03	0.02
K	1.056	0.925	Sr	0.104	0.098

Studies of the material reinforced with C and M by means of chemical analysis yielded the following results: the major structure-forming elements of these composites are calcium, silicon, aluminum, magnesium, and iron. In the samples treated with the MADOR modifier, their content is 15—20 % higher than in the samples without the modifier. The increased content of the major structure-forming elements makes it possible to obtain more coagulation and crystallization contacts during molding leading to an increase in the strength characteristics of the material.

Conclusions

1. Through the course of the studies of the influence of the MADOR modifier on the quality of cement-reinforced soils and mineral mixes, its positive effect on their physical and mechanical properties has been identified.
2. An increase in physical and mechanical characteristics is achieved due to the fact that while using the MADOR modifier, the active phase dominates in the cement-reinforced material roviding a higher uniformity of the structure and enhanced physical and mechanical characteristics.
3. 1.28 times more silica particles participate in the structure formation of the material treated with cement and the MADOR modifier. Silica particles provide an amorphous (active) part of the structure for the concentration of other solid particles on the surface. Apart from the appearance of mechanical contacts between the particles of the composite, new chemical bonds are formed providing higher physical and mechanical characteristics of the material.

4. The amount of calcium, silicon, aluminum, magnesium, iron present in the samples treated with the MADOR modifier is 15-20% more than in the samples not treated with the modifier. An increased content of such elements makes it possible to obtain a larger number of strong contacts in the crystal lattice during molding leading to an increase in the strength characteristics of the material.

5. The studies have enabled us to conclude that the durability and reliability of the structural layers of pavements arranged by the cold regeneration method using the MADOR modifier are increased.

References

1. Bezruk V. M., Guryachkov I. L., Lukanina T. M. *Ukreplennye grunty (svoistva i primenenie v dorozhnom i aerodromnom stroitel'stve)* [Fortified soils (properties and application in road and airfield construction)]. Moscow, Transport publ., 1982. 231 p.
2. Vasil'ev Yu. M. [Requirements for the deformative ability of reinforced soils]. *Primenenie ukreplennykh gruntov pri stroitel'stve dorozhnykh odezhd s ispol'zovaniem otkhodov promyshlennosti v kachestve vyazhushchikh i dobavok khimicheskikh veshchestv* [Demands on the deformation ability of reinforced soil reinforced soil Application in the construction of road clothes with use of industrial wastes as binders and additives chemicals]. Moscow, 1981., pp. 145—151.
3. Velichko E. G., Belyakova Zh. S Nekotorye aspekty fiziko - khimii i mekhaniki kompozitov mnogokomponentnykh tsementnykh sistem [Some aspects of physico-chemistry and mechanics of composites component cement systems]. *Stroitel'nye materialy*, 1997, no. 2, pp. 21—25.
4. Vernigorova V. M. *Sovremennye metody issledovaniya svoistv stroitel'nykh materialov* [Modern methods of research of properties of building materials]. Moscow, ASV publ., 2003. 239 p.
5. Gorelyshev N. V., Polosin-Nikitin S. M., Koganzon M. S. *Tekhnologiya i organizatsiya stroitel'stva avtomobil'nykh dorog* [Technology and organization of construction of roads]. Moscow, Transport publ., 1992. 551 p.
6. Kochetkova R. G. Uluchshenie svoistv glinistykh gruntov stabilizatorami [The Improvement of the properties of clay soil stabilizers]. *Avtomobil'nye dorogi*, 2006, no.3, pp. 25—28.
7. Lanko A. V. Gidrofobizirovannye lessovye tsementogrunty v dorozhnom stroitel'stve [Gidrogenizirovannye loess cementoplasty in road construction]. *Stroitel'nye materialy*, 2008, no. 4, pp. 27—30.
8. Matvienko F. V., Kanishchev A. N., Mel'kumov V. N., Volkov V. V. Prognozirovanie velichiny neobratimoi deformatsii dorozhnoi konstruktsii ot vozdeistviya transportnogo potoka [Forecasting the magnitude of irreversible deformation of road structure from the impact of traffic flow]. *Nauchnyi vestnik VGASU. Stroitel'stvo i arkhitektura*, 2010, no. 3 (19), pp. 81—92.
9. Nikerov N. S. *Dorozhnye odezhdy avtomobil'nykh dorog obshchego pol'zovaniya. Ch. 2. Konstruirovanie i raschet* [The pavement of public roads. Part 2. Designing and calculation]. St. Petersburg, Peterburgskii gos. un-t putei soobshcheniya publ., 2001. 84 p.
10. Petkyavichus K., Podagelis I., Laurinavichus A. Vozmozhnosti ispol'zovaniya mestnykh nerudnykh materialov pri stroitel'stve i remonte avtomobil'nykh i zheleznykh dorog [Possible use of non-metallic local materials for construction and repair of roads and Railways]. *Stroitel'nye materialy*, 2006, no. 3, pp. 32—35.
11. Pichugin A. P., Grishina V. A., Yazikov I. K. [Deformation processes in the fortified soils]. *Ekologiya i novye tekhnologii v stroitel'nom materialovedenii. Mezhdunarodnyi sbornik nauchnykh trudov* [Ecology and new technologies in building materials science. International collection of scientific papers]. Novosibirsk, 2010, pp. 74—75.
12. Pichugin A. P., Grishina V. A., Yazikov I. K. Fiziko-khimicheskie protsessy v ukreplennykh gruntakh [Physical-chemical processes in soils fortified]. *Stroitel'nye materialy*, 2009, no. 12, pp. 41—43.
13. Podol'skii Vl. P. et al. [Road Construction]. *Zemlyanoe polotno* [The roadbed]. Moscow, Akademiya publ., 2013. 304 p.
14. Podol'skii Vl. P., Gasilov V. V. Optimizatsiya ob"emov dobychi kamennykh materialov i transportnoi skhemy ikh dostavki potrebitelyu [Optimization of the volume of extraction of stone materials and the transport scheme of their delivery to the consumer]. *Stroitel'nye materialy*, 1992, no. 11, pp. 41—44.
15. Podol'skii Vl. P., Nguen Van Long, Nguen Dyk Shi. O vozmozhnosti rasshireniya resursnoi bazy dorozhnogo stroitel'stva za schet stabilizatsii i ukrepleniya gruntov [About the possibility of expanding the resource base of road construction by stabilizing and strengthening soil]. *Nauchnyi Vestnik Voronezhskogo GASU*, 2014, no. 1, pp. 102—111.
16. Fursov S. G. et al. Effekt modifikatora «DorTsem DS-1» [The Effect of the modifier "Dorcem DS-1"]. *Avtomobil'nye dorogi*, 2011, no. 5, pp. 136—139.

17. Sumio Horiuchi, Ka-waguchi Masato, Kazuya Yasuhara. Sumio Horiuchi Effective use of fly ash slurry as file material. *J. Hazardous Mater*, 2000, vol. 76, no. 2—3, pp. 301—337.
18. Xu A., Sarkar Sh.L. Potentials of high — volume fly ash utilization in concrete and cementations products. Proc. Amer. Power Conf. Vol. 58. 1 Pt. 59th Annu. Meet., Amer. Power Conf., Chicago, 111., 1996. Chicago (111), 1996, pp. 651—656.
19. Brendel Gary Tackling Indias coal ash problem. Mining Eng. (USA), 1999, vol. 51, no. 10, pp. 44—45.
20. Shao Jingbang. Fly ash utilisation in China. Proc. 20th Int. Miner Process. Congr., Aachen, 21—26 Sept., 1997. Vol. 5. Clausthal — Zellerfeld, 1997, pp. 109—111.
21. Cheriaf M., Rocha J. C. Pozzolanic properties of pulverized coal combustion asch. Cem. And Concr Stock, 1999, vol. 29, no. 9, pp. 1387—1391.