Structure and mineral composition of soil-cement with complex additive

Структура и минеральный состав цементогрунта с комплексной добавкой

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Key words: soil-cement; polycarboxylate ether; octyltriethoxysilane; X-ray diffraction pattern; differential scanning calorimetry; ettringite; low-basic hydrated calcium silicate; structure

Ключевые слова: цементогрунт; эфир поликарбоксилата; октилтриэтоксисилан; рентгенофазовый анализ; сканирующая дифференциальная калориметрия; эттрингит; низкоосновные гидросиликаты кальция; структура

Abstract. The effect of the polycarboxylate ether and the complex hydrophobic-plasticizing additive on the structure, phase and mineral composition of cement based on polymineral clay with content of relict minerals more than 85 % (52.49 % of quartz) was studied. As research methods chosen X-ray diffraction pattern, differential scanning calorimetry and scanning electron microscopy. The regularities of the effect of the complex hydrophobic-plasticizing additive based on polycarboxylate ether and octyltriethoxysilane on the formation of cement hydration products in a strengthened clayey soil are established. Changes in structure and composition include the following: the formation of a strong skeleton of the crystallization phase due to the increase in the number of hydrated new formation in the form of low-basic hydrated calcium silicate and ettringite, decrease in portlandite content, as well as an increase in the amount of amorphous phase (up to 16 %) in the form of tobermorite gel filling intercrystalline spaces. In soil-cement hydrated silicate calcium are formed in an amount of more than 4 % and ettringite in an amount of more than 7 %, the amount of portlandite reduced by 46 %. The result of modification of the complex hydrophobic-plasticizing admixture of soil-cement, a denser and homogeneous structure with a pronounced "overgrowth" of the pores formed by gel-like hydrated calcium silicate is formed, which are deposited in a large amount on the minerals of the strengthened soil.

Аннотация. Проведены исследования влияния эфира поликарбоксилата и комплексной гидрофобно-пластифицирующей добавки на структуру, фазовый и минеральный состав цементогрунта на основе полиминеральной глины содержанием реликтовых минералов более 85 % (52,49 % кварца). В качестве методов исследования выбраны рентгенофазовый анализ, дифференциально-сканирующая калориметрии и электронно-растровая микроскопия. Установлены закономерности влияния комплексной гидрофобно-пластифицирующей добавки на основе эфира поликарбоксилата и октилтриэтоксисилана на процессы образования продуктов гидратации цемента в укрепленном глинистом грунте, заключающиеся в следующих структурных изменениях: создание прочного каркаса кристаллизационной фазы за счет повышения количества гидратных новообразований в виде низкоосновных гидросиликатов кальция и эттрингита, уменьшения содержания портландита, а также увеличение количества аморфной фазы (до 16 %) в виде тоберморитового геля, заполняющего межкристаллическое пространство. В цементогрунте происходит образование гидросиликатов кальция в количестве более 4 % и эттрингита в количестве более 7 %, уменьшается количество портландита на 46 %. В результате модификации комплексной гидрофобно-пластифицирующей добавкой цементогрунта формируется более плотная и однородная структура с ярко выраженным «зарастанием» пор, образованными гелевидными

гидросиликатами кальция, которые в большом количестве осаждаются (плотно формируются) на минералах укрепляемого грунта.

1. Introduction

Clay minerals are class of phyllosilicates, which are usually formed as a result of chemical weathering of other silicate minerals on the crustal surface [1, 2].

Since the time of prehistoric civilization, mankind has used layered clay minerals in various fields of activity because of their wide distribution and diversity in nature [2–4]. Depending on the structure and properties, such as high specific surface area, ion exchange capacity or hydration of clays are widely used in ceramics, paper industry, in oil drilling, in pharmaceutical preparations, as adsorbents, etc. [1, 5, 6].

Clay soils, strengthened by Portland cement (soil-cement), are used in the construction of road clothes as bases and road surfaces [7]. However, the use of clay soils strengthened by Portland cement is ineffective due to the high costs of binder (more than 12 % of the mass of the soil) to achieve the required grades in strength and frost resistance. The solution to this problem is the modification of soil-cement with various chemical additives [8].

The history of the development binders using for improving the exploitative properties of soil in construction goes back to the distant past. Strengthened soil roads existed in Ancient Mesopotamia, Egypt, Greece and Rome [9].

Lime and cement were widely spread in road construction. A significant contribution to the development of strengthened soils, inorganic binders, in particular cement and lime, in construction was made by V.M. Bezruk, V.M. Mogilevich, Yu. M. Vasiliev, L.V. Goncharova, O.V. Tyumentseva, G.A. Levchanovsky, L.A. Markov, V.M. Knatko, V.A. Kelman, V.V. Okhotin, M.M. Filatov, C.W. Correns, C.S. Dunn, J. Hashimoto, J.K. Mitchell, A. Herzod, G.H. Hilt, D.T. Davidson, J.G. Laguros, T.W. Lambe, R.C. Mainfort and others.

Increasing the strength of soil-cement occurs as a result of physical and chemical reactions between the soil and the binder, i.e. in the interaction of substances present in ground minerals and products of hydration of Portland cement [10]. At the same time, a higher density and strength are achieved by reducing the voids, binding the ground particles and aggregating them, preserving the flocculation structure and soil swelling [11, 12].

According to D.T. Bergado, L.R. Anderson, N. Miura, A.S. Balasubramaniam [13], there are two main chemical reactions that regulate the physical and mechanical properties of soil-cement. Primary hydration reaction between cement and water, and the secondary – pozzolanic reaction between portlandite, resulting from the cement hydration and clay minerals. The hydration reaction leads to the formation of primary products of cement hydration, which proves the relatively high strength and frost resistance of soil-cement. A secondary pozzolanic reaction occurs when the $Ca(OH)_2$ concentration reaches a certain limit in the pore water. According to the data [13–15], the pozzolanic reaction occurs between the silicon and aluminum oxides present in the clay with calcium ions in the cement with the formation of calcium aluminate hydrates, calcium silicate hydrates and calcium aluminosilicate hydrates.

It was established earlier that in order to increase the soil-cement and soil strength, it is expedient to use polycarboxylate superplasticizers [16, 17], and for increasing the freeze-thaw resistance – organosilicon compound octyltriethoxysilane [8]. Earlier, we found the influence of a complex hydrophobic-plasticizing additive based on the polycarboxylate ether and octyltriethoxysilane on the basic physical and technical properties of soil-cement [18]. However, the influence of polycarboxylate superplasticizers and complex hydrophobic-plasticizing additive on the structure, phase and mineral composition of the soil-cement remains uninvestigated.

In this connection, the aim of the work was to determine the effect of a complex hydrophobic-plasticizing additive on the composition and structure of soil-cement based on polymineral clay to identify the reasons for increasing its physical and technical properties.

To achieve this aim, the following tasks are formulated:

1. to study the effect of the complex hydrophobic-plasticizing additive on the phase and mineral composition of soil-cement;

2. to investigate the structure of the soil-cement modified with the complex hydrophobic-plasticizing additive.

2. Materials and methods of research

For research, clay soil was used with the mineral composition (Table 1) in accordance with Russian State Standard GOST 9169-75 refers to polymineral clay, and according to Russian State Standard GOST 25100-2011 in accordance with the number of ductility and the content of sand particles to loam light silty. The content of relict minerals is more than 85 % (52.49 % quartz). The selected clayey soil satisfies the requirements of Russian State Standard GOST 23558-94 in terms of the plasticity number, according to which for strengthening of inorganic binders in the construction of bases and road surfaces, it should not exceed 12. This soil is the most widespread polymineral clayey soil in the Republic of Tatarstan and the Volga Region, according to the granulometric composition.

The mineral composition of the investigated clay soil is presented in Table 1, the X-ray diffraction pattern in Figure 1. The particle-size distribution, physical and technical properties of clay soil are presented in Tables 2 and 3.

For the batching of cement mortars, portland cement CEM I 42.5N was used. To obtain more clear results on the determination of the mineral composition of the hardening products, the dosage of cement in the samples of the cement mortar was 50 %.

Table 1. Mineral composition of polymineral clay

No.	The name of the mineral	Content,%
1	Quartz	52.49
2	Montmorillonite	2.44
3	Kaolinite	1.00
4	Hydromica	8.80
5	Potash feldspar	15.05
6	Peach-stone	1.86
7	Albite	16.03
8	Pyrite	0.33
9	Dolomite	0.66
10	Calcite	1.34

Table 2. Particle-size distribution of clay soil

Size of fraction, mm	1.00	0.50	0.25	0.10	0.05	<0.05
Partial remains, %	-	0.01	0.11	0.76	8.26	90.86
Full remains, %	-	0.01	0.12	0.88	9.14	100.00

Table 3. Physical and technical properties of clay soil

No	The name of properties	Values of properties
1	Liquid limit, %	30.04
2	Plastic limit, %	18.42
3	Plasticity index, %	11.62
4	pH aqueous extract	8.70
5	Organic matter contents, in mass, %	-

The following additives as surface-active agent are used: polycarboxylate ether and octyltriethoxysilane.

Polycarboxylate ether – polycarboxylate superplasticizer Pantarhit PC 160 Plv is a light gray powder obtained by spray drying from a polymer solution. The active substance is polyacrylic acid.

1. Octyltriethoxysilane ($C_8H_{17}Si(OC_2H_5)_3$) is a colorless, low-viscosity, low-volatile liquid with a density of 0.875 g/cm³.

2. The additives were introduced in the following dosages from the weight of the soil-cement: ether polycarboxylate 0.1 %; octyltriethoxysilane – 0.02 %.

To research and identify the processes of hydration hardening soil-cement at the age of 28 days was used and the method of X-ray diffraction pattern of the combined thermogravimetry, differential thermogravimetry and differential scanning calorimetry.
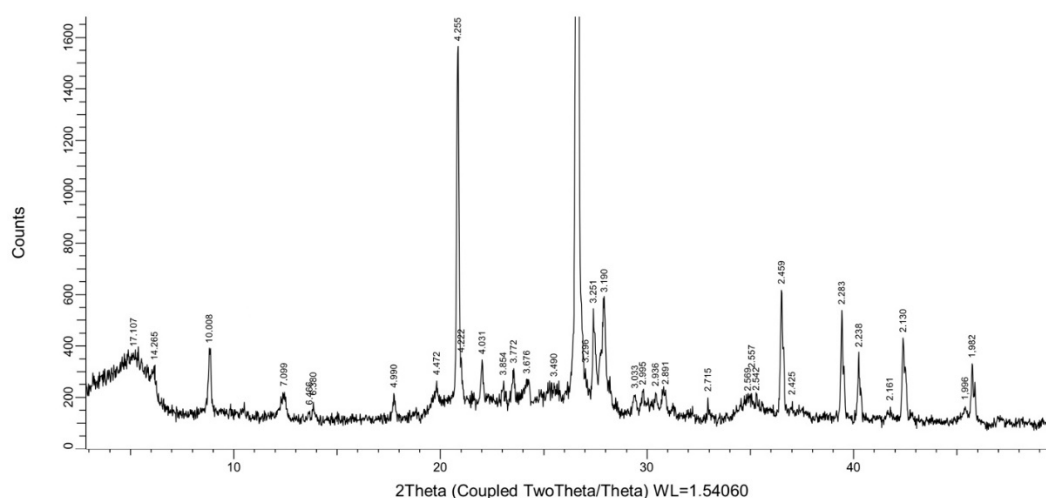

Figure 1. X-ray diffraction pattern polymineral clay

A study of the structure and composition was carried out on the following samples, soil-cement at the age of 28 days hardening of the following compositions.

Composition No 1 is a soil-cement.

Composition No 2 is a soil-cement modified by polycarboxylate ether.

Composition No 3 is a soil-cement modified by complex hydrophobic-plasticizing additive based on polycarboxylate ether and octyltriethoxysilane.

X-ray diffraction pattern analysis was chosen to determine the mineralogical composition, change and identification of products of new formation during hardening of strengthened soils with polycarboxylate ether. The experiment was carried out on an automatic X-ray diffractometer Bruker D8 Advance, equipped with a Vario attachment and a linear coordinate detector Vantec. CuKα radiation monochromatized (λ(Cu-K) = 1.54184 Å) is used with a germanium curved monochromator of Johanson, the operating mode of the X-ray tube is 40 kV, 40 mA. The experiments were performed at room temperature in the Bragg-Brentano geometry with a flat sample. The construction and analysis of the diffractograms were performed using the Bruker Diffrac Eva program. This method is one of the most effective way of determining the mineral composition in cement and clay soils.

The thermal analysis of the samples was carried out by the method of combined thermogravimetry and differential scanning calorimetry using a NETZSCH STA 449C thermal analyzer under continuous heating (40 to 1000 °C) of samples weighing 35–40 mg at a flow rate of 10 °C/min (50 ml/min) of air in crucibles from alundum with mass-spectrometric control of the gas phase. This method was chosen to identify the features of cement hydration products in strengthened soils with polycarboxylate ether and complex hydrophobic-plasticizing additive at the 28-day age.

To study the structure of clay soils strengthened with cement, the morphology of the hydrate new formation and the surface of the investigated soil-cement compositions, electron microscopic studies of the samples were carried out using a scanning electron microscope REM-100U.
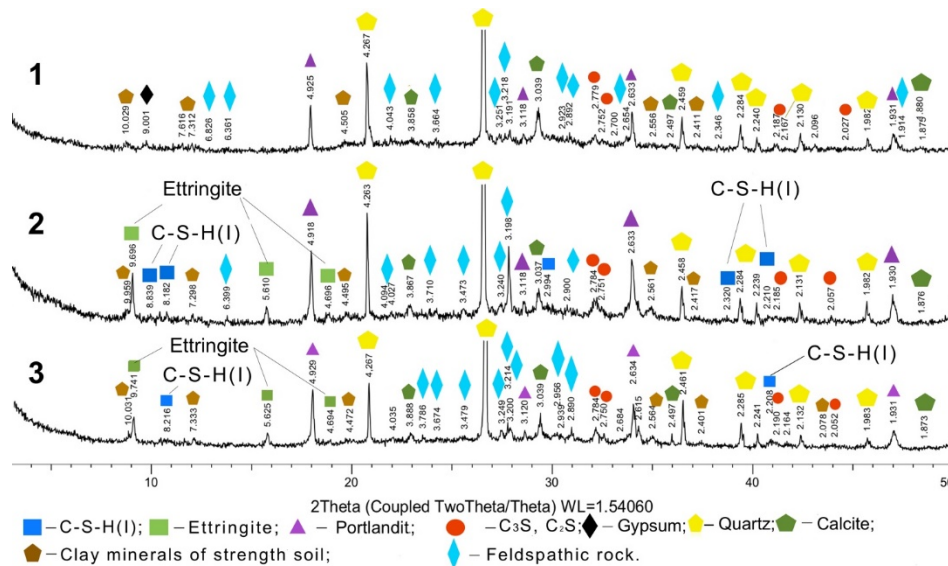
3. Results and Discussion

Figure 2 – X-ray diffraction pattern of soil-cement:
1 – control composition; 2 – composition modified by polycarboxylate ether;
3 – composition modified with a complex hydrophobic-plasticizing additive

Figure 2 is shows an X-ray diffraction pattern control composition (composition No 1), which is characterized by large peaks unreacted clinker minerals – alite and belite (d = (2.779; 2.752; 2.700; 2.187; 2.027)·Å). Diffraction peaks with basal spacings d = (4.925; 3.118; 2.633; 1.931)·Å correspond to reflections new formation portlandite and unreacted gypsum d = (9.002)·Å. The remaining peaks in the X-ray diffraction pattern correspond diffraction maxima with basal spacings relict d = (6.826; 6.361; 4.267; 4.043; 3.858; 3.664; 3.347; 3.251; 3.218; 3.191; 3.039; 2.972; 2.923; 2.892; 2.654; 2.497; 2.459; 2.346; 2.284; 2.240; 2.167; 2.130; 2.096; 1.982; 1.914; 1.880; 1.875)·Å clay and d = (10.029; 7.616; 7.312; 4.505; 2.556; 2.411)·Å minerals present in strengthens clayey soil. The content of the amorphous phase is 38.1 % of the sample weight.

The composition No 2 is an appearance of new formations in the form of ettringite (d = (9.696; 5.610; 4.696)·Å) and low-basic hydrated calcium silicate of the type C–S–H(I) (d = (8.839; 8.182; 2.994 2.320; 2.210)·Å. Diffraction maxima with interplanar distances d = (4.918; 3.118; 2.633; 1.930)·Å correspond to new formations of portlandite. The addition of polycarboxylate ether leds to decrease the formed portlandite in comparison with the composition No 1. In comparison with the composition No 1 decreases the amount of unhydrated remaining clinker minerals, as evidenced by diffraction peaks with interplanar spacings d = (2.784; 2.751; 2.185; 2.057) · Å, characteristic of the alite and belite. The intensity of peaks characterizing the presence of relict (d = (6.399; 4.263; 4.094; 4.027; 3.867; 3.710; 3.473; 3.348; 3.240; 3.198; 3.037; 2.900; 2.458; 2.284;2.239; 2.131; 1.982; 1.876)·Å) and clay (d = (9.959; 7.298; 4.495; 3.474; 2.561; 2.417; 2.210)·Å) minerals present in clay soil. Most of the new formations are in the form of amorphous compounds, which is confirmed by an increase in the amorphous phase to 46.0 %, which is 7.9 % higher in comparison with the composition No 1.

Composition No 3 shows slightly more unreacted clinker minerals d = (2.784; 2.750; 2.190; 2.052)·Å in comparison with composition No 2, but less with composition No 1. There are traces of formed ettringite (d = (9.741; 5.625; 4.694)·Å), low-basic hydrated calcium silicate of type C–S–H(I) (d = (8.216; 2.208)·Å and portlandite (d = (4.929; 3.120; 2.634; 1..931)·Å, in a smaller amount in comparison with composition No 2. However, the diagram shows the presence of relict (d = (4.267; 4.035; 3.888; 3.786; 3.674; 3.479; 3.353; 3.249; 3.200; 3.039; 2.956; 2.939; 2.890; 2.497; 2.461; 2.285; 2.241; 2.164;2.132; 1.983; 1.931; 1.873)·Å) and clay (d = (10.031; 7.333; 4.472; 2.564; 2.401; 2.078)·Å) minerals of the clay soil to be consolidated. The amorphous phase of composition No 3 amounted to 44.2 %, which is 6.1 % higher than for composition No 1, and 1.8 % lower than for No 2.

Figure 3 shows the thermogram of the control composition (composition No 1) sample. It can be seen from figure 3 that when the sample is heated, a continuous mass decrease is observed, reaching up to 13.27 % at 1000 °C. In this case, the rate of change in the mass of differential thermogravimetry has three expressed maxima at temperatures of 110, 448 and 693 °C, coinciding with peaks of endothermic effects on the differential scanning calorimetry heat flux line.
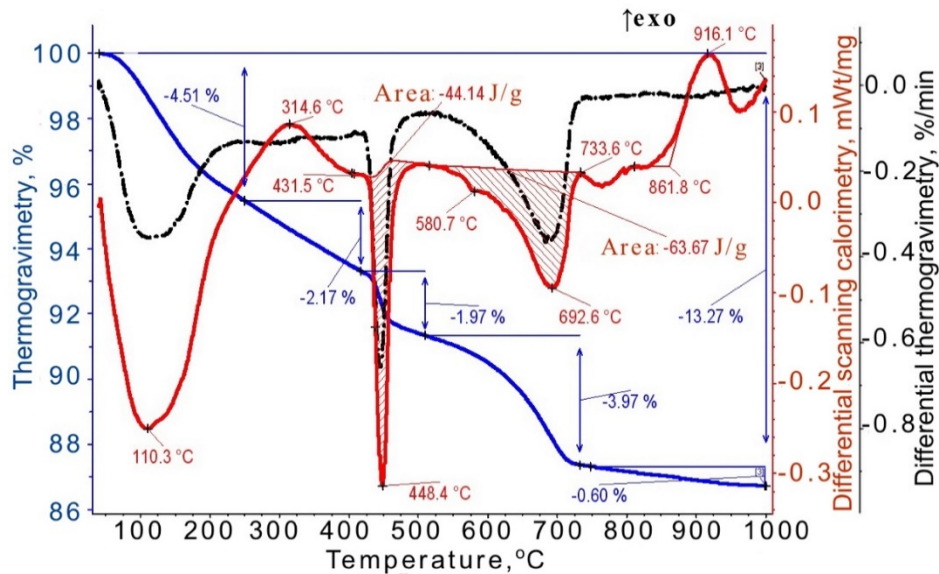
Figure 3. Curves of thermogravimetry, differential thermogravimetry and differential scanning calorimetry upon heating of a control sample (composition No 1)

The differential scanning calorimetry curve shows the most pronounced endothermic effects with the temperature at the beginning of the maximum at 40/110, 432/448 and 500/693 °C, as well as the exothermic effect at 862/916 °C. In the low-temperature region (up to 250 °C), a combined endothermic effect with a temperature maximum at 110.3 °C is observed, which is related to the loss of free and adsorption water present in the control sample. Also on the differential scanning calorimetry curve, two more endothermic peaks are seen in the temperature range at 140 and 170 °C, related to the presence of unreacted gypsum. The total weight loss in the temperature range 0–250 ºC is 4.51 %. The loss of mass in the temperature range of 250–430 ºC is equal to 2.17 %.

The endothermic effect with the maximum at 448 °C, followed in the temperature range 431–505 °C by a mass loss of 1.97 %, is associated with the decomposition of portlandite. The magnitude of the thermal effect is 44.14 J/g. In the temperature interval 505–734 °C the high temperature endotherm maximum at 692.6 °C is observed with characterized decompounding of calcium carbonate. Also, the following endothermic effects are seen on differential scanning calorimetry: at 548 °C, associated with the removal of hydroxyl water from hydromica, at 580.7 °C – with removal of hydroxyl water from kaolinite and at 624 °C – destruction of the brucite chlorite layer and loss of water from the montmorillonite lattice. The total mass loss in the temperature range 505.0–733.6 ºC is 3.97 %, and the magnitude of the thermal effect is 63.67 J/g.
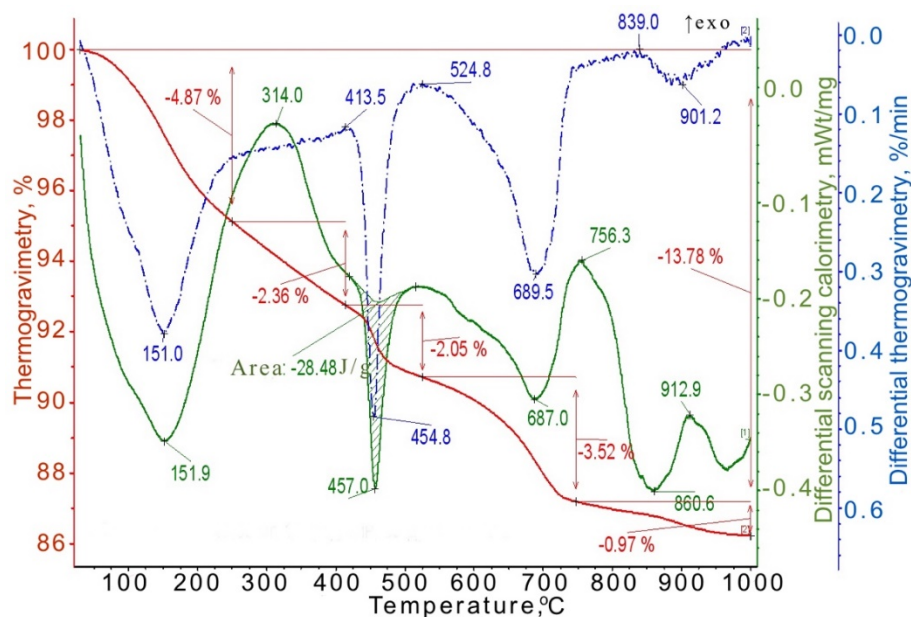

Figure 4. Curves of thermogravimetry, differential thermogravimetry and differential scanning calorimetry upon heating of a sample modified by polycarboxylate ether (composition No 2)
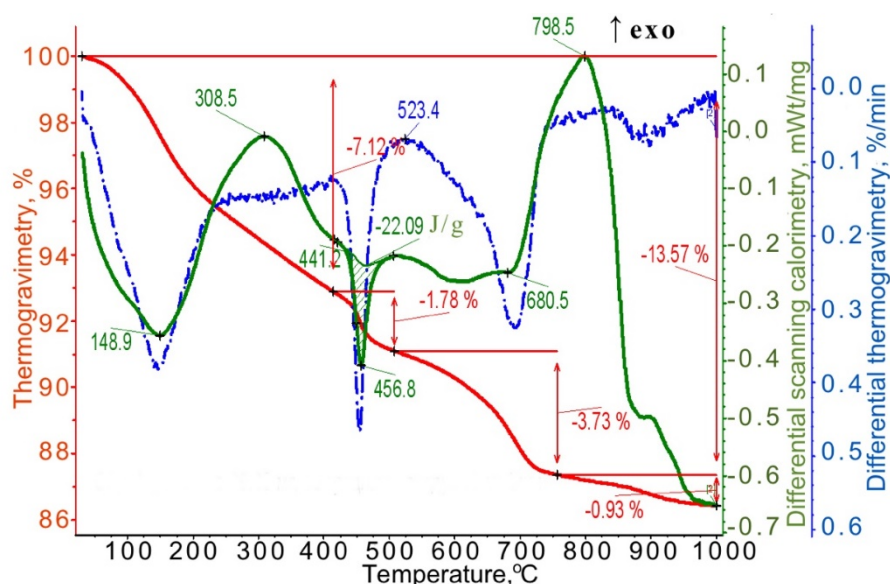
Figure 5. Curves of thermogravimetry, differential thermogravimetry and differential scanning calorimetry upon heating of a sample modified by complex hydrophobic-plasticizing additive (composition No 3)

In the temperature range 733.6–1000.0 ºC, in which the total weight loss was 0.60 %, there are small endothermic effects with the maximum at 769 ºC and 800 ºC, related to the decomposition of relict calcium carbonate and dehydration of the mica layer in chlorite, respectively. The exothermic effect at 916.1 ºC is due to the formation of spinel from the clay minerals present in the polymineral clay.

Thermal analysis of composition No 2 (figure 4) on the differential scanning calorimetry curve showed an endotherm at 151.9 °C, inherent dehydration of ettringite and low-basic hydrated calcium silicate. The total mass loss when sample No 2 is heated up to 250 °C is 4.87 %, and the mass loss in the temperature range 250–421 °C is 2.36 %. The endothermic effect on differential scanning calorimetry with the temperature maximum of 457.0 ºC and a loss of mass of 2.05 % in the temperature range 421–519 °C characterizes, basically, the decomposition of portlandite. The magnitude of the thermal effect is 28.48 J/g, which is 35.48 % less than the control composition No 1.

In the temperature range 519.0–756.3 ºC, the high endothermic effect with the maximum at 687 ºC is observed, characterized by the decomposition of calcium carbonate (composition No 2). Also on the differential scanning calorimetry with this temperature range, there are weak endothermic depressions associated with the removal of hydroxyl water from hydromica and hydroxyl water from kaolinite, the destruction of the brucite chlorite layer, and the loss of water from the montmorillonite lattice. The total weight loss in the temperature range 519.0–756.3 ºC was 3.5 %.

In the temperature range of 756.3–1000.0 ºC, in which the total weight loss was 0.97 %, an exothermic effect with the maximum at 847 ºC is observed, which is associated with the transition of a tobermorite gel of the type C-S-H(I) to ß-wollastonite. The exothermic effect at 916.1 ºC is associated with the formation of spinel. In general, when the sample is heated up to 1000 °C, the total weight loss is 13.78 %.

Figure 5 shows a thermogram of a sample modified by complex hydrophobic-plasticizing additive (composition No 3), the significant endothermic depression is observed at 148.9 °C, typical for the dehydration of ettringite and low-basic hydrated calcium silicate. The total weight loss in the temperature range 0–250 ºC is 4.78 %. The mass loss in the temperature range 250.0–421.0 ºC is equal to 2.34 %.

The endothermic effect with the temperature maximum of 456.8 ºC and a weight loss of 1.78 % in the temperature range 421–505 ºC is characterized mainly by the decompounding of portlandite. The magnitude of the thermal effect was 22.09 J/g, which is 49.95 % less compared to the control composition No 1 and 22.44 % less compared to sample No 2.

In the temperature range of 505.0–763.0 ºC, the endothermic effect characterizing the decompounding of calcium carbonate is observed. The total weight loss in the temperature range 505–763 ºC is 3.73 %.

Буланов П.Е., Ермилова Е.Ю., Мавлиев Л.Ф. Структура и минеральный состав цементогрунта с комплексной добавкой // Инженерно-строительный журнал. 2018. № 7(83). С. 38–48.

In the range 763.0–1000.0 ºC, in which the total mass loss is 0.93 %, an exothermic effect at 901 ºC is observed, associated with the formation of spinel from the clay minerals present in the polymineral clay. In general, when the sample is heated up to 1000 °C, the total weight loss is 13.57 %.
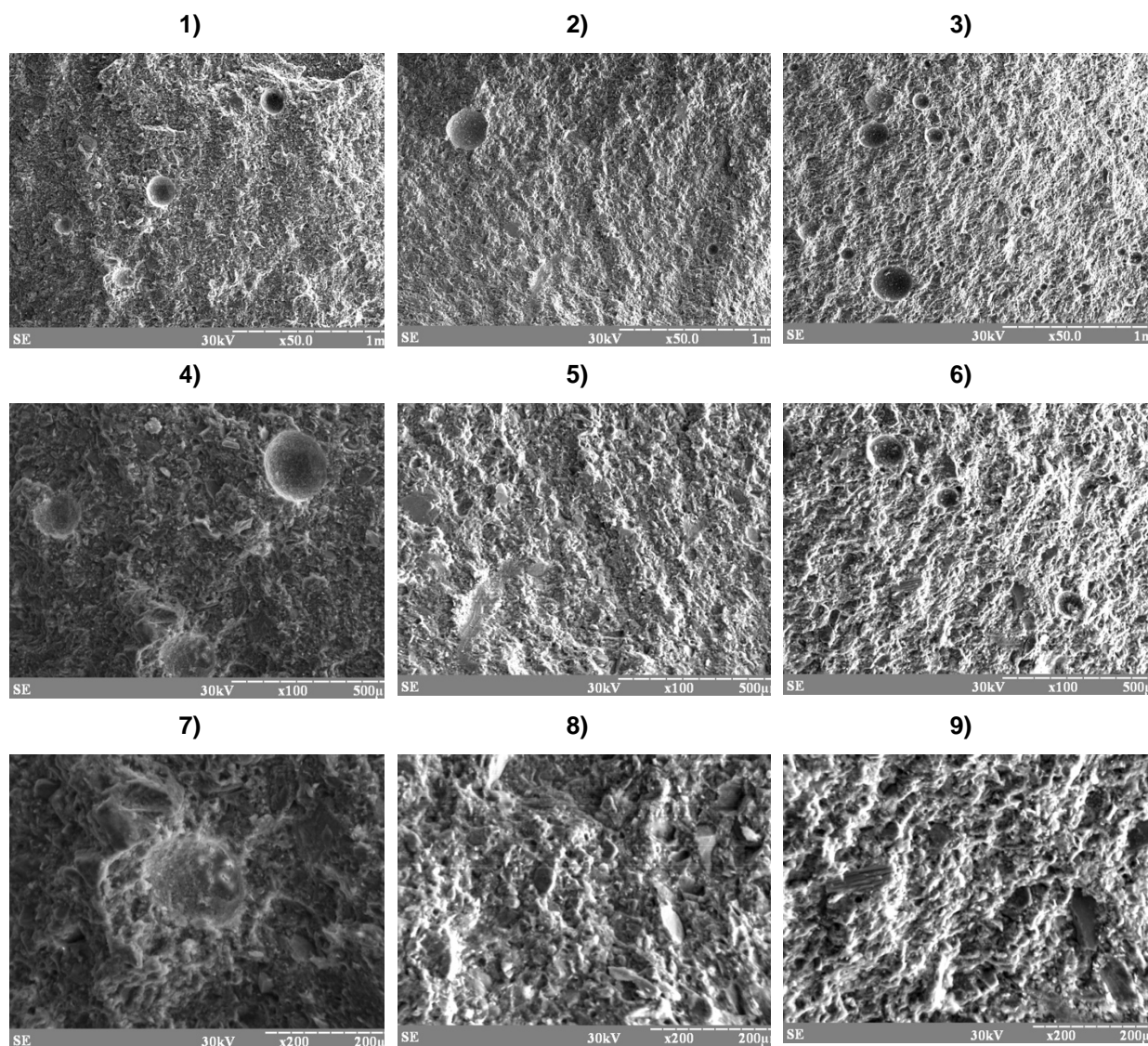
1) 2) 3)

4) 5) 6)

7) 8) 9)

Figure 6 – Microstructure of the chips of soil-cement samples modified with polycarboxylate ether and complex hydrophobic-plasticizing additive: 1, 4, 7) control composition; 2, 5, 8) modified polycarboxylate ether; 3, 6, 9) modified complex hydrophobic-plasticizing additive; 1, 2, 3) increase in x50; 4, 5, 6) increase in x100; 7, 8, 9) an increase in x200

As can be seen from table 4, for all samples, unreacted minerals of clinker alite and belite are observed. At the same time, the introduction of polycarboxylate ether or complex hydrophobic-plasticizing additive leads to a decrease in the intensity of the peaks corresponding to the non-hydrated phases of the alite and the belite, which indicates an increase in the degree of hydration of the clinker minerals.

The content of portlandite is reduced in all compositions in comparison with the no-additive composition. Especially noticeable decrease in the amount of calcium hydroxide up to 2 times in composition No 3, that is, with complex hydrophobic-plasticizing additive. According to studies [19–21], polycarboxylate ether molecules are able to form metastable complexes with Ca^{2+} ions, which leads to a decrease in the basicity of hydrated silicate. On the other hand, when interacting with C_3A, they are able to be incorporated into the structure of hydrates formed with the formation of stable organomineral phases [22]. On the basis of which it can be concluded that Ca^{2+} ions of portlandite and calcium carbonate participate in the reaction with polycarboxylate ether to form other compounds that are not identified by X-ray diffraction pattern and differential scanning calorimetry.

The changes that occurred during the modification of the soil-cement from polycarboxylate ether or complex hydrophobic-plasticizing additive were confirmed in the analysis of the microstructure. Studies of

the microstructure of clayey soils strengthened with cement were carried out on samples aged 28 days. Figure 6 shows the results of the fracturing of clay soil samples strengthened with cement.

Table 4. Semiquantitative X-ray diffraction pattern analysis of soil-cement samples modified with polycarboxylate ether and complex hydrophobic-plasticizing additive

Name of mineral/phase	Amount of mineral/phase in the control composition, %	Amount of mineral/phase in composition with polycarboxylate ether, %	Amount of mineral/phase in the composition with the complex hydrophobic-plasticizing additive, %
Ettringite	-	8.90	7.70
C-S-H (I)	-	8.00	4.64
Alite, belite	10.43	6.68	7.62
Minerals of polymineral clay	71.79	68.96	73.02
Portlandite	13.01	7.46	7.02
Gypsum	4.77	-	-
Amorphous phase	38.10	46.00	44.20

In the control sample of soil-cement, a number of pronounced chaotic defects are mainly observed: in the form of separate particles, shells, strata, which break the solidity of the material, which reduces strength and increases drainage capacity. With the introduction of polycarboxylate ether or complex hydrophobic-plasticizing additive, a change in the microsurface is observed: a decrease in the number and size of shells and caverns, a transition to a more ordered dense structure.

In general, it can be noted that the cement grout with polycarboxylate ether or complex hydrophobic-plasticizing additive formed a dense structure with a pronounced overgrowth of the pores formed by gel-like hydrated calcium silicate, which in large quantities are densely formed on the minerals of the strengthened soil.

Thus, by means of electron-raster microscopy it was established that during the hydration of soil-cement, modified polycarboxylate ether or complex hydrophobic-plasticizing additive, a uniform distribution of hydration products in the volume of the composite is observed, which provides enhanced physical and technical properties.

4. Conclusions

1. The regularities of the effect of the complex hydrophobic-plasticizing additive based on polycarboxylate ether and octyltriethoxysilane on the formation of cement hydration products in a strengthened clayey soil are established. Changes in structure and composition include the following: the formation of a strong skeleton of the crystallization phase due to the increase in the number of hydrated new formation in the form of low-basic hydrated calcium silicate and ettringite, decrease in portlandite content, as well as an increase in the amount of amorphous phase (up to 16 %) in the form of tobermorite gel filling intercrystalline spaces. In soil-cement hydrated silicate calcium are formed in an amount of more than 4 % and ettringite in an amount of more than 7 %, the amount of portlandite reduced by 46 %.

2. It is established that as a result of modification of the complex hydrophobic-plasticizing admixture of soil-cement, a denser and homogeneous structure with a pronounced "overgrowth" of the pores formed by gel-like hydrated calcium silicate is formed, which are deposited in a large amount on the minerals of the strengthened soil.

3. The established changes in the composition and structure of soil-cement based on polymineral clay when introducing the complex hydrophobic-plasticizing additive studied explain the increase in its physical and technical properties.

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