BUILDING MATERIALS AND PRODUCTS

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ORGANO-MINERAL MODIFIER OF CLAY SOILS STRENGTHENED BY CEMENT

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Statement of the problem. The problem of deacceleration of cement stone setting in reinforced clay soils by means of a suggested complex organomineral modifier is presented.
Results. An organo-mineral additive for cement stone modification is synthesized. The dynamics of the structure formation of the additive particles in the process of synthesis is determined. The influence of the modifier on the strength of cement stone and soil cement is studied. The rational composition of the modified soil cement the strength of which exceeds the strength of the traditional soil cement by 1.5 times is specified.
Conclusion. The effectiveness of the use of **a** cement stone synthesized modifier as a soil stabilizer and deaccelerator of the cement laying rate of setting in the process of clay soils strengthening is proved. The prospects of the use of the designed modifier are presented, the most rational areas of its use, namely for soil bases structure and highway rural road pavement, are determined.

Keywords: organo-mineral modifier, clay soils, reinforcement of soils.

Introduction. Strengthening of clayous soils using modern modifiers has been very important following stipulated by the Address of the President of the Russian Federation to the Federal Assembly on December 12, 2012 on the double rate in the funds on construction and reconstruction of highways in 2013—2022 compared to the last decade. Soil modifiers are widely used in construction and reconstruction of highways and runways of different types: logistic sites and shopping centers, port and customs terminals, parking lots and forst/park pathways, hydroinsulation of (toxic) waste dump sites [3, 5, 7, 13, 17, 19].

The use of organic and organic and mineral stabilizers in soil strengthening is impossible without analyzing structural and functional features of modifiers and cement soils [11, 20]. Reactive functional oligomers certainly have a leading position in structure formation of strengthened soils [11] as well as processing of secondary raw materials [4, 12, 15]. It is essential that compatibility of a binder and filler at the contact area is evaluated in terms of thermal dynamics [9—12]. It is known that biopolymers is used to strengthen soils [9, 11, 21—22].

The most common soils that need stabilizing are clay and loam. In order to stabilize them, in Russia various compounds are used, e.g., organic (Permazime, USA), Dorzon (Ukraine), ECOROAD (USA), lime (*Roadbond* (South Africa), *SuperMix* (Russia), acid (*RoadPaker Plus* (Canada), *RPP*-235 (Germany), *CBR*+ (South Africa), polymer emulsions (*LBS* (USA), *M*10+50 (USA), *LDC*+12 (USA), Nanostab (Germany), Dorstab (Russia), ECOLUX (Russia) [13, 16]. The objective of strengthening clay soils and alkalis is to improve their operational characteristics, i.e. to enhance their resistance to cracks and water, wear and tear [6, 8, 14]. A supplement be competitive compared to other ones already in use in road industry.

Considering all of the above, we have synthesized an organic and mineral modifier based on water polyvinylacetate dispersion containing both mineral and organic binders.

1. An organic and mineral modifier of cement soil was synthesized using the following components:

— polyvinylacetate dispersion (PVA) D7D 51/15 v, homopolymeric rough disperse according to the GOST (ГОСТ) 18992-80 with the mass concentration of a solid residual of 50—55 %;

— a liquid natrium glass according to the GOST (ГОСТ) 13078-81 with the mass concentration of silicon oxide of 27—30 %;

— carboxymethylcellulose.

The chemical properties of PVA are determined by complex ether groups and graft chains joined with the main chain with complex ether bonds. PVA is soaped with water solutions of acids and alkalis and undergo alcoholysis under the effect of catalytic amounts of acids and alcohols of alkali metals in waterless media with the formation of polyvinyl alcohol. The equation of the reaction is given in Fig. 1 [18].

Along with the main reactions there are side reactions of saponification of small amounts of nonpolymerized vinyl acetate and acetic-acid ether as shown in Fig. 2 [18].

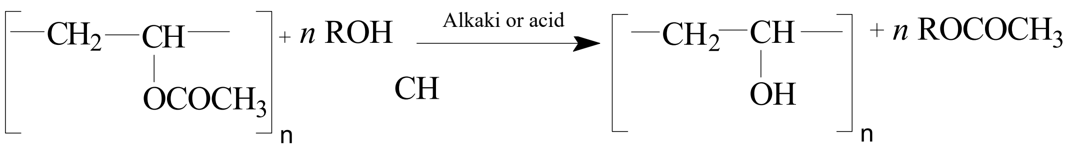

Fig. 1. Alcoholysis reaction of PVA

$$CH_2{=}CHOCOCH_3{+}ROH \xrightarrow{\text{Alkaki or acid}} CH_3CHO + ROCOCH_3$$

Fig. 2. Saponification of vinyl acetate

The carboxymethylcellulose is a poly-1.3-glycol. This structure is predominant, but there is always some small amount of additives by means of α-carbon atomб which results in up to 2 % of hydroxyl groups in the carboxymethylcellulose being located in the same way as in 1.2-glycol. The formula of the carboxymethylcellulose is given in Fig. 3 [18].

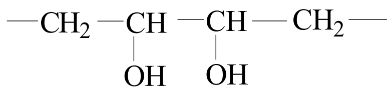

Fig. 3. Formula of the carboxymethylcellulose

The liauid natrium glass (alkaline solution of sodium silicates Na_2O (SiO_2) n) during hydrolysis forms a silicic acid gel that is a construction glue, i.e. a binding component.
The silicic acid gel is formed according to the scheme shown in Fig. 4 [2, 13].

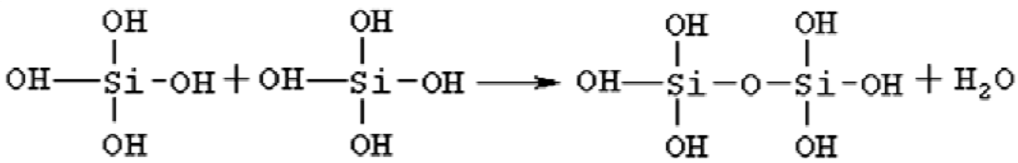

Fig. 4. Formation of the silicic acid gel

All the components of Portland cement clinker of the compound and phase interact with water and show hydration activity. As a result, there are hydrated cations-coagulants Ca^{2+}, Mg^{2+}, Al^{3+} , Fe^{3+}, etc. in the solution. They are absorbed by the surface of silica colloidal particles between the particles transforming them into aggregates. An approximate scheme of aggregation is shown in Fig. 5 [1, 2].

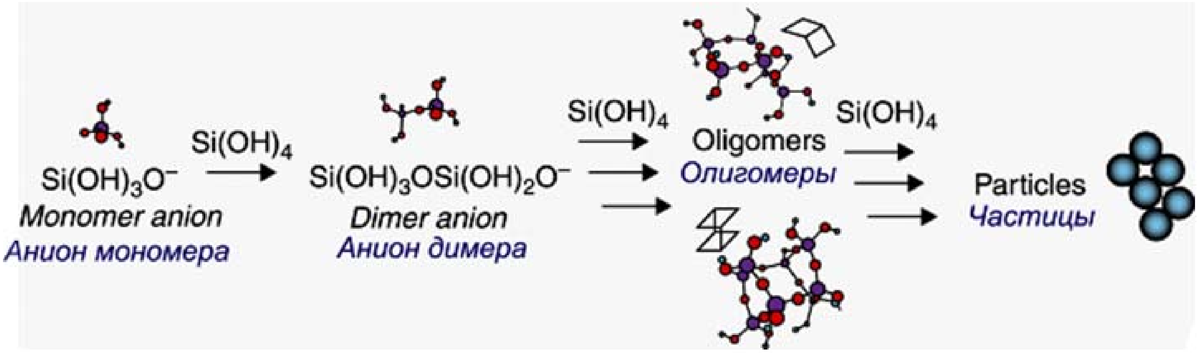

Fig. 5. Aggregation of silica colloidal particles

In the liquid glass there are hydrated ions-silicates and hydrosilicates that form a solidification system $CaSiO_3$ with free hydrated ions of Ca^{2+} of the cement water solution. A reduced ionic equation of the system is shown in Fig. 6 [15].

$$Ca^{2+} + SiO_3^{2-} \rightarrow CaSiO_3\downarrow$$

Fig. 6. Formation of water insoluble calcium silicate

We believe that polymerization of carboxymethylcellulose can also be accompanied with the formation of bridges through the calcium ions resulting in the structures exemplified in Fig. 7. According to the above theoretical concepts, a preliminary analysis of the original data was performed and the experiment was planned.

The synthesis was carried out with 1 litre of an organic and mineral additive. In a beaker per 1 litre 200 g of 46 % dispersion of PVA with pH = 7 was weighed. As it was heated up to 60—70 °C and constantly stirred, 500 ml of water was added followed by 25 ml of liquid natrium glass. pH was measured as 12. Mixing as the temperature was maintained took place over 7 days till complete homogenization. pH was found to drop to 9. Then 50 % solution of $CaCl_2$ (40 ml) was gradually introduced with pH being controlled.

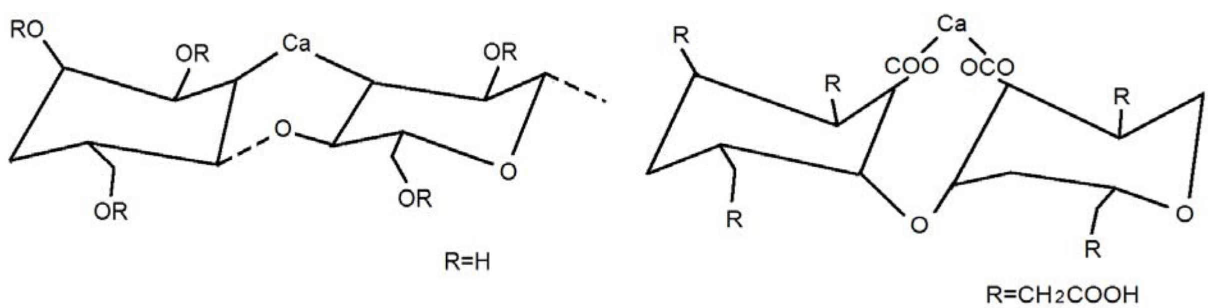

Fig. 7. Polymerization of carboxymethylcellulose

As pH dropped to 7, 100 g of 14 % of carboxymethylcellulose as a dispersion stabilizer was added. As a result we obtained 450 ml of organic and mineral modifier (24 % solution).

2. **Study of the influence of synthesized organic and mineral modifier on the properties of cement soils.** In order to make samples of non-modified and modified cement soils, Portland cement (PC) by the Stariy Oskol Cement Plant (CEM I according to the GOST (ГОСТ) 31108-2003), clayous soil and synthesized complex additive (CA) were used.

The samples were of a cylindrical form sized 3 × 3 cm according to the recipes presented in Table 1 and 2.

Table 1

Composition of cement samples

System	Mass concentration, %	Loading during formation, MPa	Mass of cement, g	Mass of CA, g	Mass of water, g
PC + water 10 %	0	10	37	—	3.7
PC + CA + water 10 %	0.05		37	0.075	3.6
	0.10		37	0.15	3.58
	0.50		37	0.77	3.1
	1.00		37	1.54	2.53
	2.00		37	3	1.44
PC + water 10 %	0	20	40	—	4
PC + CA + water 10 %	0.05		40	0.08	3.94
	0.10		40	0.16	3.88
	0.50		40	0.83	3.37
	1.00		40	1.66	2.74
	2.00		40	3.33	1.47

The analysis of the kinetics of an increase in the strength of the samples made under the load of 10 MPa found that the use of a complex additive in different concentrations reduces the strength of a modified cement rock compared to that in the samples by 1.5—2 times.

Hence after day 1 the strength of the samples was 31 MPa and that of the CA samples was 19, 20, 17, 15 and 14 MPa with 0.05, 0.1, 0.5, 1 and 2 % of the additive respectively.

After day 3 the strength of a cement rock went up two-fold except the samples with 0.1 % of CA. From day 3 to day 7 the solidification showed a significant slowdown in the samples with the compositions 2 and 6. By day 14 the strength of the samples with 0.05 and 0.1 % of CA dropped to 23 and 21 MPa respectively. By day 28 the strength of the samples was 63 MPa, while in those with the additive only by 30—39 MPa. The strongest out of the modified samples were the samples with 1 % of the additive and the least strong ones with 0.1 %.

Table 2

Composition of cement soil samples

System	Mass concentration of CA, %	Loading durinf formation, MPa	Mass of soil, g	Mass of cement, g	Mass of CA, g	Mass of water, g
Soil + CA (10 %) + + water (17 % of the mass of CS)	0	10	33.5	3.35	—	6.26
Soil + PC (10 %) + + CA + water (17 % of the mass of CS)	0.05		33.5	3.35	0.08	6.10
	0.10		33.5	3.35	0.15	6.00
	0.50		33.5	3.35	0.75	5.60
	1.00		33.5	3.35	1.50	5.00
	2.00		33.5	3.35	3.00	4.00
Soil + PC (10 %) + + water (17 % of the mass of CS)	0	20	36.0	3.60	—	6.70
Soil + PC (10 %) + + CA + water (17 % of the mass of CS)	0.05		36.0	3.60	0.08	6.60
	0.10		36.0	3.60	0.16	6.58
	0.50		36.0	3.60	0.83	6.00
	1.00		36.0	3.60	1.66	5.40
	2.00		36.0	3.60	3.33	4.20

The formation was perfomed using a universal testing machine UMM-20 with an extra load of 10 and 20 MPa. The formed samples were stored in a desiccator at room temperature for 28 days. The compressive strength limit was determined after 1, 3, 7, 14 and 28 days according to the Russian standards and international practices [7, 25]. The kinetics of an increase in the strength of the samples from non-modified and modified soils is presented in Fig. 8—11.

The analysis of the kinetics of an increase in the strength of the samples made under a load of 20 MPa found that after 3 days the strength of the samples with the additive is 10 MPa as much as for the samples (35 МПа). By day 7 there was a drop in the strength of the samples containing 0.1 and 0.5 % of a complex additive. From day 7 to day 14 there was a sharp decrease in the strength from 48 to 21 MPa in the samples containing 0.1 % of CA. Then the strength was also on a sharp rise and after 28 days it was 45 MPa. The strength of the remaining samples was increasing with no changes in the speed. The strength of the samples on day 28 was 107 MPa.

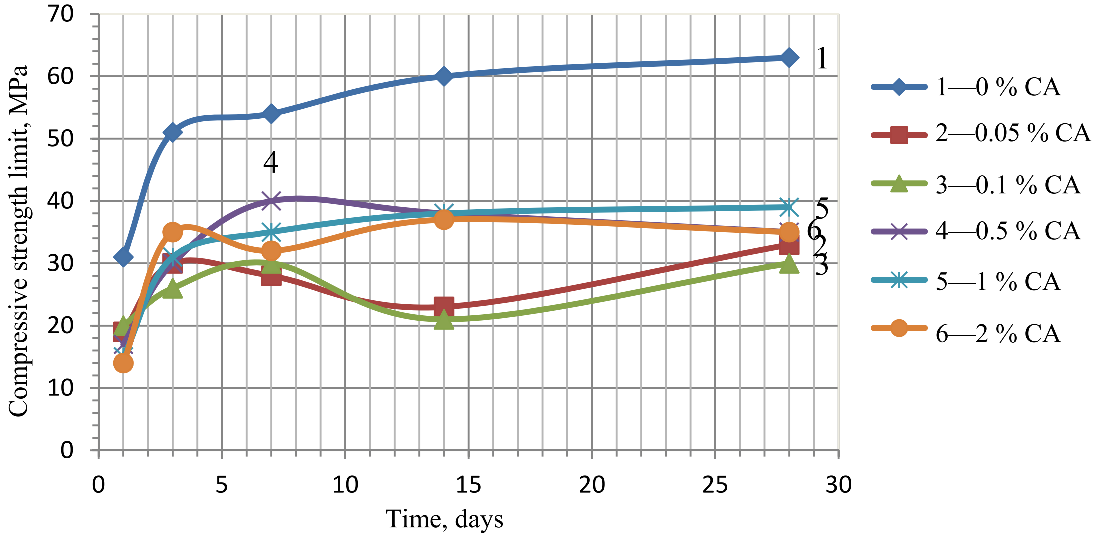

Fig. 8. Kinetics of an increase in the strength of the samples of a cement rock with the water content of 10 % formed under a load of 10 MPa

It was noted that the strength of the samples made at the pressure 20 MPa for both the samples as well as those containing 1.5 times as much CA as those made at 10 MPa.

The tests of the cement soil samples formed under the press pressure of 10 MPa found that an addition of CA has no effect on their daily strength while on day 3 the strength went up from 4.6 to 5 MPa in the samples with 0.05 and 0.1 % of CA.

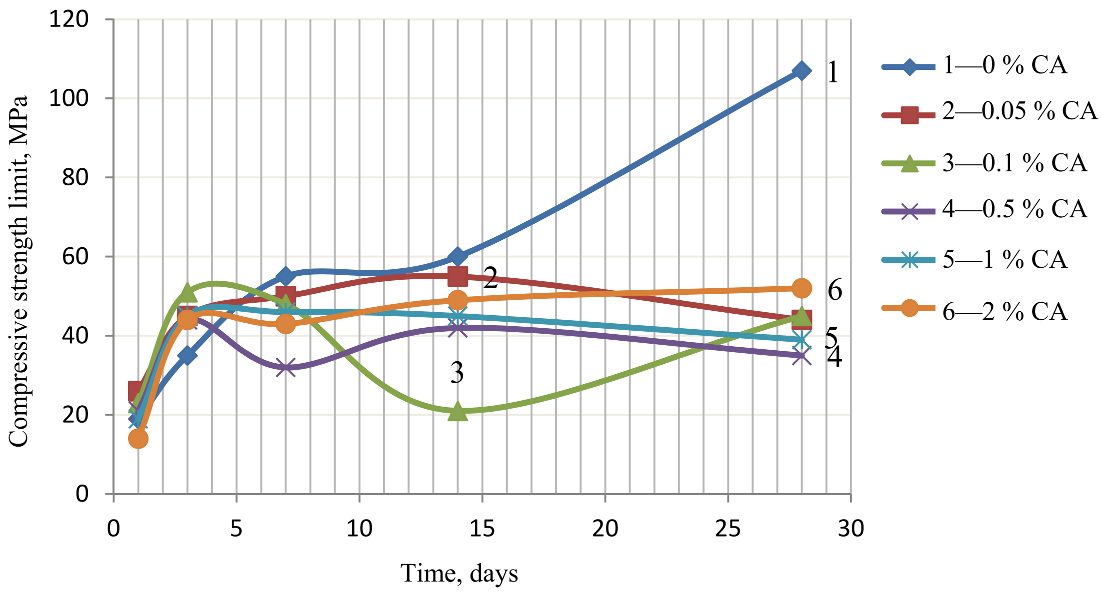

Fig. 9. Kinetics of an increase in the strength of the cement rock samples with the water content of 10 % formed under the load of 20 MPa

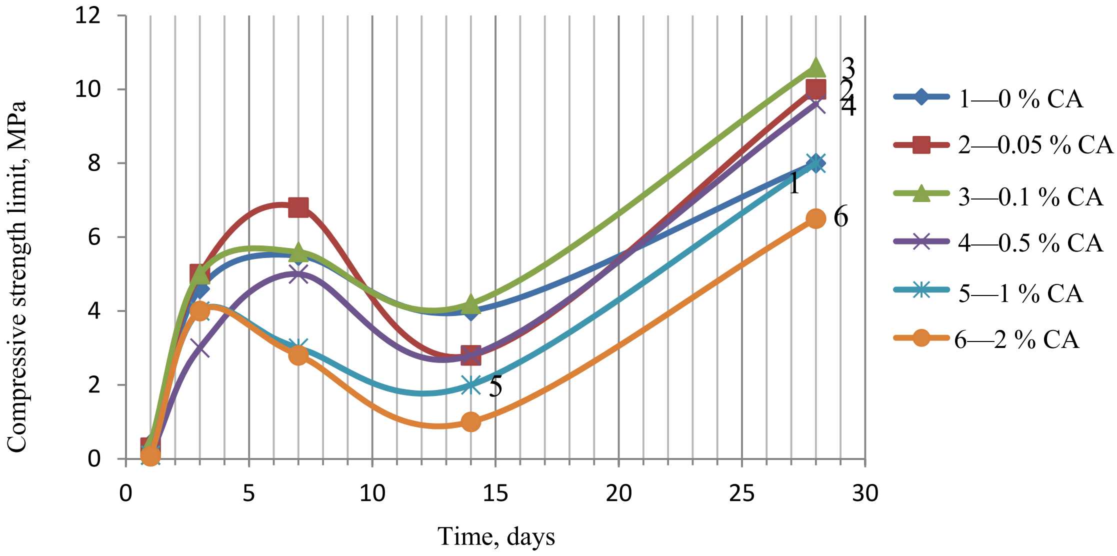

Fig. 10. Kinetics of an increase in the strength of the cement soil samples with the water content of 17 % and PC 10 % formed under the load of 10 MPa

From day 3 to day 7 solidification slowed down in the samples of the compositions 5 and 6, the strength of the remaining samples did not change. On day 14 there was a significant drop by 1.5—2 times in the strength of the smaples of all the compositions as well as a sharp rise on day 28. Hence the strength of the samples was 10, 10.6, 9.6, 8 and 6.5 MPa with 0.05, 0.1, 0.5, 1 and 2 % of CA with the strength of the samples being 8 MPa.

A similar thing holds true for the tests of the samples formed at 20 MPa where the introduction of CA has no effect on the daily strength.

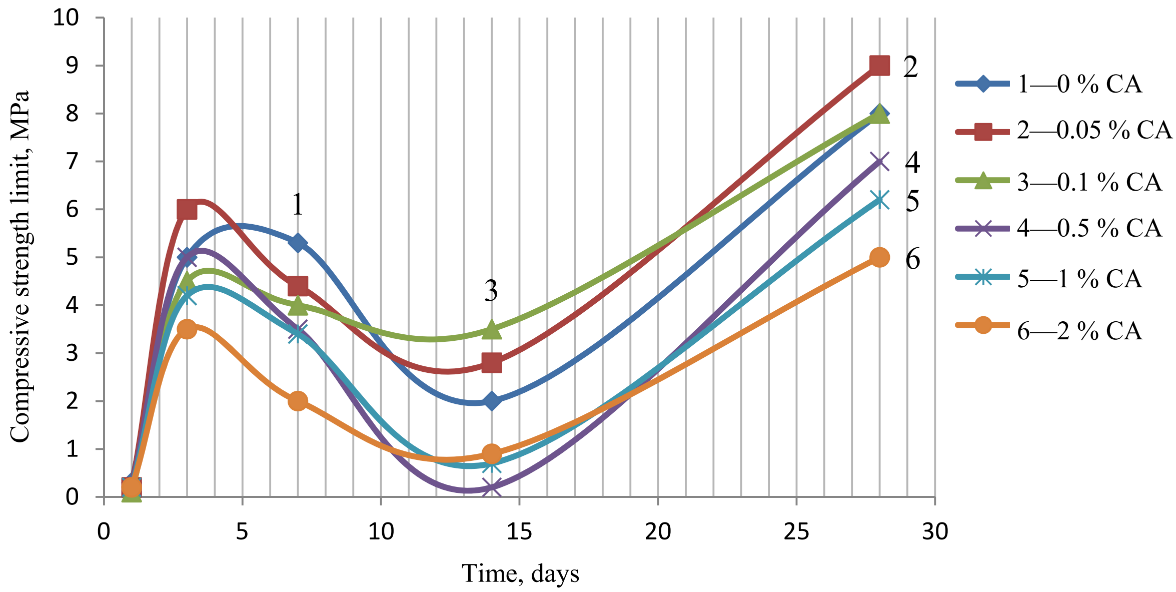

Fig. 11. Kinetics of an increase in the strength of the cement soil samples with the water content of 17 % and PC of 10 % formed under the laod of 20 MPa

However, on day 3 the strength of the samples with 0.05 % of the additive rose from 6 MPa at 5 MPa for the samples while the strength of the remaining samples was no more than 3 MPa. Then up to day 14 the strength of the samples of all the compositions saw a considerable decrease and was on a sharp rise by day 28. On day 28 the strength of the samples with 0.05, 0.5, 1 and 2 % of CA was 9, 7, 6.2 and 5 MPa respectively at the strength of the samples of no more than 8 MPa.

Summarizing the results of the experiment, note that high concentrations of an organic and mineral additive in the mixing water contributed to a slow down in the setting, solidification and reduced the strength of the cement rock whil in low concentrations, particularly 0.05—0.1 %, there is an increase in the strength of cement soil, which correlates with the data presented by the authors in [7].

Conclusions. The comparison of the kinetic curves of solidification of the cement rock samples formed under the press pressure of 10 MPa revelaed that during the formation of a crystallizing structure the strength drops due to an amorphous group of polymers and dominance of coagulation structures:

a) at the stage of the formation of fetuses of a new phase, agglomeration of colloidal particles;

b) at the stage of the formation of a spatial coagulation structure, coalescence of emerging crystals;

c) at the stage of the formation of an entire carcass of a crystallizing structure;

d) at the stage of the growth of the crystals and formation of the contacts of intersection and intergrowth;

e) at the stage of "aging" of hydrate new formations, i.e. crystallization and recrystallization of metastable crystals of hydro-sulphate-aluminates of calcium.

CA increases the sstrength of the cement rock formed at the pressure of 20 MPa, at the 2nd—3rd stage of the solidification due to a decrease in the thickness of a layer of the polymer component and an increase in the number of contact and condensation and crystal bonds [7].

The comparison of the kinetic curves of solidification of the cement soil samples formed at the pressure of 10 and 20 MPa revealed that the introduction of 0.05—0.1 % of CA provides growth in the strength of the solidification systems by almost 1.5 times due to structural and functional groups of a complex modifier with active centres of clayous soils.

The improvement of the physical and mechanical properties of the indices is indicated by the capacity of CA to fill a capilalr structure of clayous soils with subsequent structure formation due to Ca^{2+} ions and polar groups of clay micelles, a polymer part of CA according to the above schemes. A practical importance is determined by the capacity of a modifier to enhance the strength and operational functions of temporary entry ways and long areas of highways designed using challenging clayous soils.

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