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EFFECT OF COMPLEX MODIFIERS ON PROPERTIES OF CEMENT SYSTEMS

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Abstract: *The management of the rheological properties of the cement systems and the kinetics of solidification by the use of specially designed complex modifiers has been proved. Modification of cement systems was made possible by the use of a complex modifier (CM) obtained as a result of the interaction of the hyperplasticizer GLENIUM 313 with liquid glass. The peculiarity of this method lies in the gel removal of the mineral component contained in the modifier. This complex modifier is used in conjunction with water when cement systems are solidified. It has been established that the application of CM in 1.0% of cement mass allows to reduce the amount of cement dough by 1.5 times, extends the retention period, and increases the strength of the solid on the first day by 2 times compared to the unchanged systems.*

Keywords: *complex modifier, cement systems, polycarboxylate, gel, liquid glass, hyperplasticizer, viscosity, strength.*
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Introduction

Construction of complex structures is impossible without the use of new generation polyfunctional concrete with high construction and technical properties. Modifying cement systems for optimization of the concrete mixing process and remoteness during the construction of buildings on hot days of the year is one of the most important issues. At low or negative temperatures, it is necessary to shorten the hardening time so that concrete can quickly build up the strength of the brand. Therefore, the control over high-strength concrete retention and reinforcing modes is a pressing problem. In order to obtain a new generation of high-strength concrete, their structure must be modified by micro- and nanoparticles [1-4].

Modifiers play a special role in the structure of cement systems, including mineral, organic and organic-mineral [5, 6]. The application of micro and nanostructures close to the cement clinker minerals due to their crystallochemical structure allows obtaining high-density cement matrix. These particles regulate the hydration process of clinker minerals and provide the formation of stable, high-strength dense cement stone, consisting of low-base calcium hydrocyclates in cement systems [7, 8]. It is well known that the most widely used effective mineral-active additive (MAA) is SiO_2-based amorphous microsilica (d = 50 ÷ 150 nm) and nanostructures (d = 5 ÷ 10 nm) [9,10]. However, when they were incorporated into the cement composition, water content increased. This problem is solved by the addition of hyperplasticizers that reduce the water demand by 30-40% while preserving the rheological properties of cement dough [11,12]. According to modern concepts, the effect of hyperplasticizers on cement hydration and solidification involved complex physical and chemical processes. It revealed that the use of polycarboxylates is due to the electrostatic-steric mechanism induced by adsorption of organic matter molecules onto cement particles [6,12]. Polycarboxylate molecules formed a complex metastable complex with Ca^{2+} ions to provide low calcium-hydroxylate phases. During the interaction of polycarboxylate molecules with C_3A, a new structure of hydrate compounds was formed by the formation of stable member-mineral phases.The most effective complex modifier for cement stone modification is SiO_2 nanoparticles and organic-mineral additives derived from hyperplasticizer. The widespread use of silicon-containing nanoparticles in concrete production is due to the complexity of the SiO_2based nanopowders synthesis and their additon to cement systems. It matters from technological point of view that SiO_2 is a gel in the complex modifier and its mixing with water strengthens cement systems. Hyperplasticizer, which is involved in the process of obtaining a complex modifier, has two functions: it stabilizes the growth of colloidal aggregates in the silicon and regulates the technological problem of uniform distribution of complex additives and regulates the rheological properties of cement system development. It found that the incorporation of nanomodifying additives into the water-cement system increases the hydration of the cement several times [13,14]. It should be noted that the hydration rate in the cement systems with the modifier was added up to 75% of the daily room temperature at room temperature. However, the study into conditions of efficient nanomodification by identifying different functional carriers for transferring nanowires to cement systems is rather relevant. Also, the main focus of the current research is to identify the method of obtaining appropriate complex modifying additives for efficient transfer of SiO_2 particles to cement systems and explore their effect on rheological properties, retention time and formation of cement stone in the initial phase of solidification.

Materials and research methods

During the studies, the samples were made from fixed water/Sem cement dough with 0.28. Portland cement CEM I 52,5N was used for preparation of cement stone samples in accordance with of AZS EN 197-1 requirements from the NORM cement plant. Experiments were carried out with the addition of cement stone and CM modified components. As a complex modifier, CM was synthesized on a 40% liquid glass with GLENIUM 313 (ρ = 1050 kg / m3, pH = 5.5) branded with BLAF based on polycarboxylate esters. During the preparation of fine-grained concrete, Bahramtapa tea sand (Mir = 2.1) and Guba crushed sand (Mir = 3.4) were used as fillers.The following characteristics of cement systems were revealed in the experiments:

- Rheological characteristics of the cement dough are determined by its RV-8M rotation viscosity.
- Kinetics of solidification of cement dough was determined through measuring the plastic strength when measuring cone-shaped plasticity of the Moscow State University MV Lomonosov [15].
- Impact of CM on the strength of cement stone was evaluated based on the results obtained during the determination of the strength of compression after 1, 3, 28 days of 2x2x2 cm solid samples under normal conditions. Determination of durability was made on the AUTO 105/250 CEMENT COMPRESSION and FLEXURAL MACHINE.
- Effect of CM on properties of small concrete was made in 10x10x10cm samples of solid state under normal conditions.

Results and their discussion

CM was obtained by shaking the polycarboxylate solution with a diluted 1: 3 water bottles. Vibration was carried out until the ambient pH = 7.5. When the hyperplasticizer solution was neutralized with a liquid glass solution by continuous stirring at 30^0C, colloidal aggregates of SiO_2 form and stabilized by carboxylate molecules.

Application of CM in the same Water/Sem ratio in all variants allowed to reduce the content of cement paste by 1.6-2 times as compared to the unchanged benchmark system and at the same time increase the strength of cement stone (Table 1). The largest reduction of cement dough was observed when the modifier was used in 1.2%

of cement mass. This was due to the large amount of superplasticizer in the system. The content of SiO_2 gel in the 2nd, 3rd and 4th constituents is 0.073%, 0.082% and 0.10% cement by mass.

Table 1. Rheological and strength characteristics of cement systems

№	Additive quantitiy	Viscosity of cement paste, SPZ	Cement stone strength, MPa		
			1 day	3 days	28 days
1	Non-additive	8.25	7.2	21.8	49.6
2	0.8% CM	5.12	28.8	35.3	70.2
3	1.0% CM	4.84	29.2	41.3	82.6
4	1.2% CM	4.12	28.5	38.7	76.4

Changing the amount of bride does not have a sharp impact on the cement paste itself. A sharp decrease in the cement paste content was due to the effect of the hyperplasticizer. Based on the results obtained, it can be concluded that the use of this supplement allows regulating the rheological characteristics of cement paste and contributes to their application in obtaining high-flow concrete mixes. It revealed that the Pm kinetic curve of plastic strength of cement systems changed in the course of the CM use (Fig.1). In this case, the regularity of capture kinetics was determined by the amount of CM. In the CM systems with 0.8% and 1.0% mass of cement mass, the effect of increasing the plastic strength after 5 and 8 hours after mixing with water was revealed.

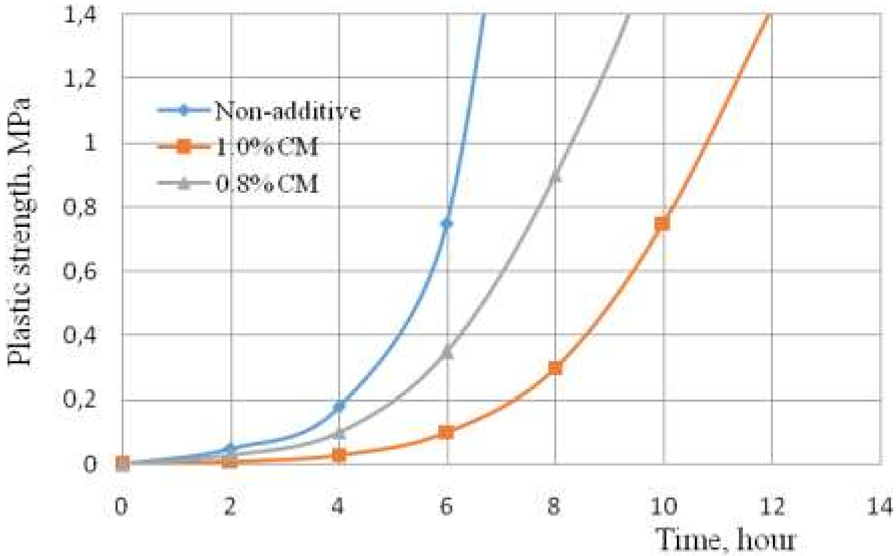
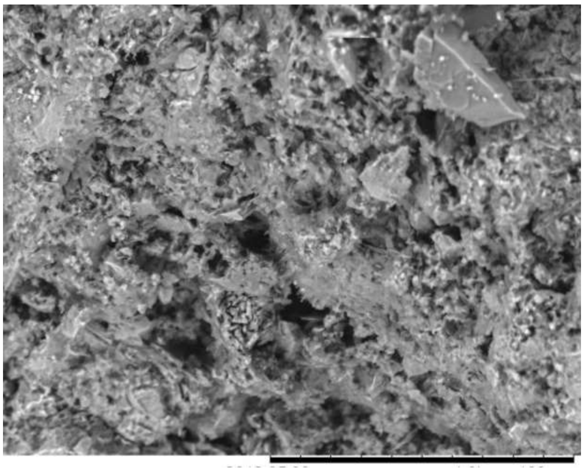


Figure 1. Modifier cement dough plastic the effect on strength

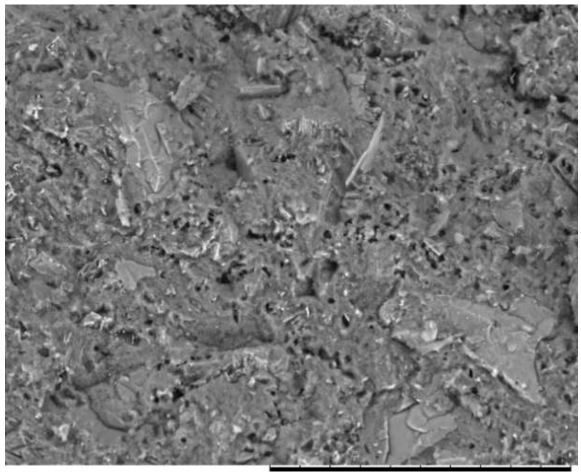
The value of Pm = 0.02 MPa which corresponded to the beginning of the retention period in non-additive cement samples, was obtained 160 minutes after water mixing with cement, that is, after the standard starting time of catching. When using CM in the mass of 0.8-1.0%, the plastic strength value of 0.02 MPa was achieved 4-5 hours after mixing the water with cement. Plastic strength value of 0.08 MPa corresponding to the end of the setting period was 6 hours in the supplementary samples and 8–10 hours with 0.8-1.0% CM added. Thus, the addition of CM increased the setting period of the cement test. As a result, rheological characteristics of the modified cement systems proved more stable than unmodified systems.

Rising strength of cement stone during the CM use was proved. First of all, the acceleration of strength of cement stone was determined (Table 1). Application of complex additives in all quantities provides that the three-day cement stone gains 50% of the 28-day strength. Note that the modified systems gained strength up to 28.8-32.2 MPa per day and up to 33.3-38.3 MPa in three-dayshardness. Value of strength in non-additive systems was 7.2 MPa per day and 21.8 MPa per 3 days. At the same time there was rise in the price of the strength limit to 70.2-82.6 MPa, as opposed to 49.6 MPa for non-additive systems. The highest strength is observed when the amount of additive is used in the amount of 1.0% of cement mass. This difference is explained by the modifying effect of the additive on the dispersive and morphological composition of new compounds of cement stone.This is where the modified structure has a higher resistance to collapse.

Electronic microscopy shows micro-pores between newly formed composite. In the newly formed compositions, large crystals of high-base hydrocyclates (size 10-15 μm) and large plates of ettringite were observed (Fig. 2a).



a)



b)

Figure 2. Microstructure of cement stone, 1000X magnification
a - cement stone non-additives; b - cement stone with 1.0% CM added

The structure of the cement stone attached to the CM mainly composed of low-grade hydrocyclates (sizes 10-15 μm) (Fig.2.b).

A 1: 3 cement filler (50% sand and 50% crushed sand) was prepared to study the effect of CM on properties of fine concrete. The amount of supplement was 0.8-1.0% of the cement mass in the solution. At the same time, the concentration of SiO_2 gel at the given ratio of the complex modifier was 0.073-0.1%. Results of the experiment are shown in Fig. 3.

It can be seen that CM raises the compression strength of fine-grained concrete from 49.25 MPa to 70.49 MPa. In the early stages of reinforcement, the strength of the modified samples rose by 50-55% as compared to non-additive samples, and by 43% in 28 days. As can be seen from the results, the nanomodifier provides a faster accumulation of strength in the initial stages of solidification. This was due to the interaction of SiO_2 gel with the Portlandite formed during the hydration of clinker. Samples with additives of complex modifiers gain up to 3 days of labeling strength without additional samples.

Thus, it was experimentally proved that the use of polycarboxylate either and synthesized CM based on liquid glass can significantly reduce the cement paste viscosity. At the same time, the optimal use of CM provides the stability of rheological characteristics of the modified cement systems more than twice as compared to the unmodified systems. The use of complex modifying additives in the amount of 1.0% of cement mass contributed to the production of high-viscous concrete mixes (which maintains the flow for, at least, 3 hours).

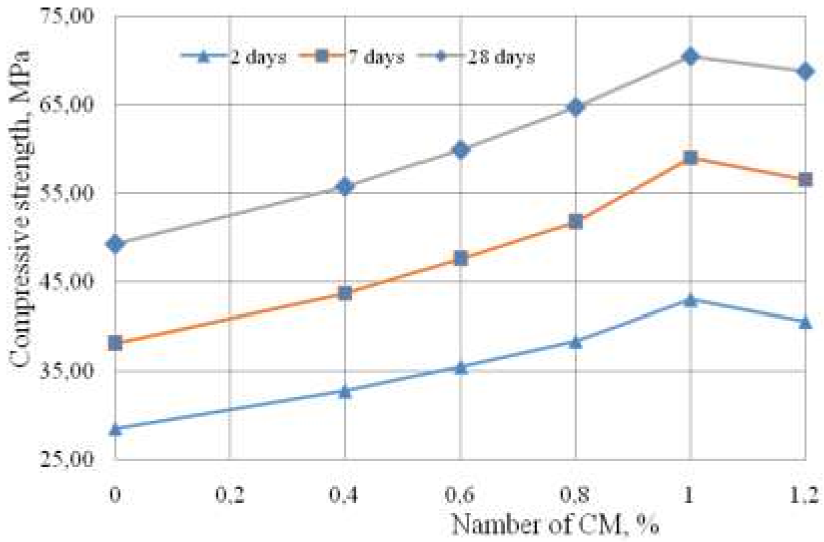


Figure 3. The influence of CM on the compressive strength of fine-grained concrete

It should be noted that due to the accelerated formation of concrete structure at early stages of reinforcement, the shortening of the reinforcing period makes it particularly efficient for monolithic structures. Thus, improvement of comfort placement of concrete mixes in monolithic structures, their transportation to long distances and reduction of labeling efficiency are important issues.

Reference

1. Guvalov A.A. Regulation of properties of cement systems using complex modifiers. Monoqraph. Azerbaijan Architecture and Construction University. Baku, 2019, 276 p. (In Azerbaijan).
2. Garsia-Taengua E., Sonebi M., Hossain K.M.A., Lachemi M. et.al. Effects of the addition of nanosilica on the rheology, hydration and development of the compressive strength of cement mortars. *Composites Part: Engineering*, 2015, vol. 81, pp. 120-129. https://doi.org/10.1016/ J.compositesb.2015.07.009
3. Singh L.P., Agarwal S.K., Bhattacharyya S.K. Preparation of silica nanoparticles and its beneficial role in cementitious materials. *Nanomaterials, nanotechnology*. 2011, vol. 1, no. 1, pp. 44–51.
4. Raki L., Beaudoin J., Alizadeh R., Makar J. & Sato T. Cement and Concrete Nanoscience and Nanotechnology. *Materials*. 2010, no. 3, pp. 918–942. Doi:10.3390/ma3020918
5. He Yongjia, Mao Ruitao, Lü Linnü, Hu Shguange. Hidration products of sement-silica fume-guarts powder mixture under different curing regimes. *J.Wuhan Univ. Technol. Mater. Sci. Ed.* 2017, vol. 32, no. 3, pp. 598-602.
6. Huang Haoliang, Qian Chunxiang, Zhao Fei, Qu Jun et al. Improvement on microstructure of concrete by policarboxylate superplastisizer (PCE) and its influence on durability of concrete. *Constr. And Build. Mater.* 2016, vol. 110, pp. 293-299. Doi10.1016/j.conbuildmat.2016.02.041
7. Guvalov A.A., Abbasova S.I., Kuznetsova T.V. The effectiveness of modifiers in regulating the properties of concrete mixtures. Scientific, technical and production journal. *Building Materials*, 2017, no. 7, pp. 49-51. (In Russian).
8. Koizumi K., Umemura Y., Tsuyuki N. Effects of chemical admixtures on the silicate structure of hydrated portland cement. Proceedings of the 12th International Congress on the Chemistry of Cement. - Montreal, 2007, pp. 64–71.

9. Kopanitsa A.V., Sarkisov Yu.S., Demyanenko O.V. The use of nanosized silica in the production of building mixtures. *Vestnik Tomskogo gosudarstven nogo arkhitekturno-stroitel'nogo universiteta. Journal of Construction and Architecture*. 2016, no. 5, pp. 140-150. (In Russian).
10. Tyukavkina V.V., Kasikov A.G., Gurevich B.I. Structural formation of cement stone - modified by the addition of nanodispersed silicon dioxide. *Stroitel'nye Materialy - Construction Materials*. 2018, no. 11, pp. 31–35. (In Russian). DOI: https://doi.org/10.31659/0585-430X-2018-765-11-31-35
11. Guvalov A.A. The effect of polyaryl sulfon sulfonate superplasticizers on the properties of cement systems. *Journal of Advanced Concrete Technology*. 2019, no. 3-4, pp. 24-27. (In Russian).
12. Plank J., Bassioni G., Dai Z., Keller H., Sachsenhauser B., Zouaoui N. Neues zur wechselwirkung zwischen zementen und polycarboxylat-fliefimitteln // Proceedings der 16 Internationalen Baustofftagung. Weimar, 2006, Band 1, pp. 579-598.
13. Artamonova O.V., Sergutkina O.R., Ostankova I.V., Shvedova M.A. Synthesis of SiO2-based nanodispersed modifier for cement composites. *Condensed Matter and Interphase*. 2014, vol. 16, no. 1, pp. 152–162. (In Russian).
14. Chernyshev E.M., Artamonova O.V., Slavcheva G.S. Concepts and technology base nanomodification of structures of building composites. Part 3: effective nanomodification of systems and structures of cement hardening cement stone (criteria and conditions). *Stroitel'nye Materialy - Construction Materials*. 2015, no. 10, pp. 54–63. (In Russian).
15. Butt Yu.M. Timashev V.V. Workshop on chemical technology of binders. Moscow: Vysshaja shkola Publ. 1973, 530 p.

KOMPLEKS MODİFİKATORLARIN SEMENT SİSTEMLƏRİNİN XASSƏLƏRİNƏ TƏSİRİ

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Xüsusi hazırlanmış kompleks modifikatorların tətbiqi ilə sement sistemlərinin reoloji xüsusiyyətlərinin və bərkimə kinetikasının idarə olunması sübut edilmişdir. Sement sistemlərinin modifikasiyası GLENİUM 313 hiperplastikləşdiricisinin maye şüşə ilə qarşılıqlı təsiri nəticəsində alınmuş kompleks modifikatorun (KM) istifadəsi ilə aparılmışdır. Bu üsulun özünəməxsusluğu modifikatorun tərkibinə daxil olan mineral hissəciyin gel halında alınması ilə bağlıdır. Bu kompleks modifikator sement sistemlərinin bərkiməsi zamanı su ilə birlikdə istifadə olunur. Müəyyən edilmişdir ki, sementin kütləsinin 1.0 %-i miqdarında KM tətbiqi sement xəmirinin özlülüyünü 1.5 dəfə azaltmağa imkan verir, tutma müddətini uzadır, bərkimənin ilk günündə möhkəmliyi modifikasiya olunmamış sistemlərlə müqayisədə 2 dəfə artırır.

***Açar sözlər**: kompleks modifikator, sement sistemləri, polikarboksilat, gel, maye şüşə, hiperplastikləşdirici, özlülük, möhkəmlik.*

ВЛИЯНИЕ КОМПЛЕКСНЫХ МОДИФИКАТОРОВ НА СВОЙСТВА ЦЕМЕНТНЫХ СИСТЕМ

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Доказано управление реологическими свойствами цементных систем и кинетикой затвердевания с использованием специально разработанных сложных модификаторов. Модификация цементных систем стала возможной благодаря применению комплексного модификатора (КМ), полученного в результате взаимодействия гиперпластификатора GLENIUM 313 с жидким стеклом. Особенность этого метода заключается в том, что минеральный компонент, который содержится в модификаторе, получается в виде геля. Этот комплексный модификатор используется вместе с водой при затвердевании цементных систем. Установлено, что применение КМ в количестве 1.0% от массы цемента позволяет уменьшить вязкость цементного теста в 1.5 раза, увеличивает время схватывания и повышает прочность цементного камня в первый день в 2 раза по сравнению с немодифицированными системами.

Ключевые слова: *комплексный модификатор, цементные системы, поликарбоксилат, гель, жидкое стекло, гиперпластификатор, вязкость, прочность.*