Influence of the composition of cement systems on the activity of modifying additives

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Abstract. Modifiers of cement systems with different compositions of functional groups of polymers were studied: carboxymethylcellulose, methylcellulose, polyvinyl alcohol, polyacrylamide. The results of studies of the influence of active ions on the viscosity of aqueous solutions of water-soluble polymers using viscometry methods are presented. The influence of the type and composition of functional groups of polymer additives on the resistance to calcium, sodium and potassium ions is analyzed. It is shown that in the presence of calcium, sodium or potassium ions in the liquid phase of cement solutions, it is possible to reduce the effectiveness of polymers as stabilizers of binding systems. The most resistant to electrolytes are polymers with dominated hydroxyl groups. The composition of functional groups of water-soluble polymers and the possibility of their interaction with various ions contained in cement, aggregate, filler, in the closing water, in the composition of soils have a decisive influence on the compatibility of the polymer and the binder, the properties of cement-polymer compositions. The principles of regulating the rheological and technological properties of cement-polymer compositions, deformations of dispersed systems by selecting the rational composition of the dispersed mixture, mineral and chemical additives are given. The regularities of compatibility of components of cement systems, mineral and chemical additives in order to increase the adhesion and strength characteristics of materials based on them in the development of compositions of masonry solutions, injection and other compositions for chemical fixing of soils, individual housing construction, in order to carry out repair and restoration work to strengthen soil bases and stone structures are presented.

1. Introduction
Conducting high-tech research to establish patterns of compatibility of components of cement systems in order to regulate their rheological and technological parameters in the direction of improving the adhesion and strength characteristics of materials based on them is an urgent task in various sectors of construction production [1-10].

Compositions based on cement systems are widely used in construction works to fix chemically the soils. To improve the technological characteristics of mortar mixtures, physical and mechanical properties of solutions and structures based on them, various additives are added to cement dispersions: water-soluble polymers, electrolytes, which increase the level and quality of construction work, reduce shrinkage deformations and stresses, and increase the load-bearing capacity of soils in the conditions of existing building [3, 4, 11-13]. The search for effective chemical additives and rational composi-
tions of dispersed systems and products based on them is constantly conducted by national and foreign researchers and scientists [14-16].

Polymer modifying additives are added to binding systems that are used in thin-layer technologies of masonry and finishing works, in modern finishing compositions, recipes for chemical fixing of soils, dry building mixes, compositions for construction printing, self-leveling floors, etc. [3-6, 8, 13, 17, 18]. In this regard, research is needed to ensure compatibility and synergy of components of such building mixes to ensure their high technological and construction-technical characteristics. The issue is relevant both from the point of view of commercial interest, and in order to ensure the safety of structures under construction, including the exclusion of various cases of accidents and destruction of both natural and technogenic nature [3, 7]. To ensure the normal operation of objects, it is important to take into account all possible deformations of the ground bases, which can cause unacceptable deformations in the structures of buildings and structures [3, 7]. A number of works highlighted the special role of engineering and geological surveys on the construction site, including soil consolidation. Chemical methods of fixing soils by existing injection methods, has well-defined limits of application and in some cases are practically impractical. In this regard, further research is being conducted on ways to fix the soil, for example, the drilling method, with the creation of cement.

Issues of preserving the activity of modifying additives in the composition of multicomponent dispersions play an important role in such processes and phenomena as adhesion, shrinkage, dilatancy [3-6, 9, 12]. In [3] it is shown that calcium ions are the most active components of the cement system. However, in addition to Ca$^{2+}$, the composition of cement systems may contain other reactive cations or anions, currently the effect of which on the properties of cement-polymer compositions is insufficiently studied.

The aim of this work is to study the resistance of modifying additives of water-soluble polymers to the activity of certain chemical elements contained in cement systems. This will allow developing ways to control the properties of dispersed systems by selecting a rational composition of the binder, mineral components, polymer additives and other modifiers of cement systems. The obtained regularities will allow making scientific and technical choice of components of cement-polymer systems in order to strengthen the soil bases, strength of stone structures and their adhesive properties, regulate the rheological and technological properties of compositions, deformations of dispersed systems by selecting a rational composition of the dispersed mixture, mineral and chemical additives.

2. Materials and methods

2.1. Materials

For the research, modifying additives were selected - water-soluble polymers of national production: methylcellulose (MC), carboxymethylcellulose (CMC), polyacrylamide (PAA), polyvinyl alcohol (PVA). Drinking water was used, which meets the requirements of GOST 23732-2011 “Water for concrete and mortar. Technical conditions”. Cement CEM I 42.5 N according to GOST 31108-2003 of JSC “Belgorod cement”.

The studied polymer additives had different composition of functional groups: methylcellulose (MC) - methoxyl group (-OCH$_3$); carboxymethylcellulose (CMC) - carboxylate (-COO$^-$); polyacrylamide (PAA) - amide group (-CONH$_2$); polyvinyl alcohol (PVA) - hydroxyl group (-OH).

Chlorides were used to assess the resistance of water-soluble polymers to various active chemical elements. Water solutions of CaCl$_2$, NaCl, and KCl were used as a source of calcium, sodium, and potassium ions. The dosage of chlorides was 10, 20 and 30% of the weight of the polymer additive in terms of dry matter. As protective reagents for carboxylate additives, soda ash (Na$_2$CO$_3$) of the ChDA brand was used.
2.2. Methods
The viscosity of aqueous solutions of polymers of various concentrations was measured using capillary viscometers VPJ-2 (GOST 10028-81) according to the instructions specified in the passport of the device. The capillary diameters of viscometers were 1.31 and 0.56 mm.

The resistance of aqueous polymer solutions to the action of Ca\(^{2+}\), Na\(^{+}\) and K\(^{+}\) ions was estimated by the relative viscosity (\(\eta_{\text{rel}} = \eta_1/\eta_2\)). This value is equal to the ratio of the viscosity of the polymer solution when adding an electrolyte (\(\eta_1\), MPa\(\cdot\)s), to the viscosity of an aqueous polymer solution of the same concentration (\(\eta_2\), MPa\(\cdot\)s).

It is proposed to predict the behavior of polymer additives with different composition of functional groups in the liquid phase of binders by the relative viscosity of the aqueous polymer solution.

3. Results
Some water-soluble salts, including sodium, potassium, calcium, and magnesium chlorides, are aggressive to building materials. Mg\(^{2+}\), Ca\(^{2+}\), Na\(^{+}\), K\(^{+}\) cations are small in size and can be contained as part of the cement system, and enter it from the external environment. For example, K\(^{+}\) and Na\(^{+}\) cations are present in cement as sulfates in the silicate and aluminate phases. Active elements can enter cement systems from mineral and chemical additives or aggregates [18-22]. The technical closing water may also contain the above-mentioned ions in various dosages.

The results of studies of the influence of calcium, sodium and potassium cations on the viscosity of water solutions of water-soluble polymers are presented below (table 1).

The composition of their functional groups plays an important role in the resistance of water-soluble polymers to the components of cement or other matrix. In this regard, it is necessary to pay special attention to the study of the properties of additives-modifiers, taking into account the chemical nature of the polymer.

| Table 1. Dependence of relative viscosity of water solutions of polymers on the content of potassium, sodium, calcium and sodium carbonate chlorides. |
|---------------------------------------------------------------|
| Relative viscosity (\(\eta_{\text{rel}}\)) of aqueous polymer solutions | Electrolyte content, \% by weight of the polymer additive | 0 | 10 | 20 | 30 |
|---------------------------------------------------------------|
| CaCl\(_2\) | Carboxymethylcellulose (CMC) | 1.000 | 0.888 | 0.769 | 0.715 |
| | Methylcellulose (MC) | 1.000 | 0.989 | 0.989 | 0.989 |
| | Polyvinyl alcohol (PVA) | 1.000 | 1.080 | 1.080 | 1.000 |
| | Polyacrylamide (PAA) | 1.000 | 0.502 | 0.443 | 0.438 |
| NaCl | Carboxymethylcellulose (CMC) | 1.000 | 1.000 | 0.962 | 0.938 |
| | Methylcellulose (MC) | 1.000 | 1.018 | 0.978 | 0.945 |
| | Polyvinyl alcohol (PVA) | 1.000 | 1.026 | 1.022 | 1.011 |
| | Polyacrylamide (PAA) | 1.000 | 0.538 | 0.453 | 0.369 |
| KCl | Carboxymethylcellulose (CMC) | 1.000 | 1.050 | 0.969 | 0.945 |
| | Methylcellulose (MC) | 1.000 | 0.957 | 0.929 | 0.961 |
| | Polyvinyl alcohol (PVA) | 1.000 | 1.000 | 1.000 | 1.000 |
| | Polyacrylamide (PAA) | 1.000 | 0.473 | 0.394 | 0.385 |
| Na\(_2\)CO\(_3\) + 20%CaCl\(_2\) | Carboxymethylcellulose (CMC) | 1.000 | 1.389 | 1.146 | 0.911 |
Table 1 shows that the least resistant to the action of calcium ions are water-soluble polymers carboxymethylcellulose (CMC) and polyacrylamide (PAA). Methylcellulose (MC) and polyvinyl alcohol (PVA) practically do not lose their activity in this medium. The viscosity of almost all non-ionic cellulose esters under study increases with growing KCl concentration. The viscosity of aqueous solutions of carboxymethylcellulose (CMC), which is a non-ionic polymer, decreases when interacting with potassium ions largely than with sodium ions. Aqueous solutions of polyacrylamide (PAA) sharply lose their viscosity under the action of sodium and potassium cations. The most resistant to electrolytes are polyvinyl alcohol (PVA), which is dominated by hydroxyl groups.

Studies on the stabilization of polymers containing carboxyl group (COO\(^-\)) with additional protective additives are shown on the example of increasing the stability of carboxymethylcellulose CMC to calcium ions with the use of soda ash (Na\(_2\)CO\(_3\)) ChDA brand (table 1, 2). Data of viscometric studies (table 1) are consistent with the physical and mechanical properties of modified cement-sand mortar (table 2), confirming the stabilization effect of soda polymer additives.

Table 2. Physical and mechanical characteristics of solutions with additives of carboxymethylcellulose (CMC) and soda (Na\(_2\)CO\(_3\)).

| Content of CMC, % | Content of Na\(_2\)CO\(_3\), % | Water-cement ratio (W/C) | Coagulation of the polymer | Adhesion strength, MPa, at the age of 28 days |
|------------------|-------------------------------|-------------------------|---------------------------|---------------------------------------------|
| -                | -                             | 0.48                    | -                         | 0.09                                        |
| 1                | -                             | 0.64                    | yes                       | 0.12                                        |
| 1                | 1                             | 0.66                    | no                        | 0.26                                        |
| 1                | 2                             | 0.64                    | no                        | 0.33                                        |

Stabilization of solutions with the addition of 1% CMC with Na\(_2\)CO\(_3\) soda (table 2) significantly increases the adhesion strength of cement-sand solutions (the ratio of cement: sand 1:2.5 by weight) with silicate bricks in comparison with solutions without the addition of a protective reagent.

4. Discussion

Thus, in the presence of calcium, sodium and potassium ions in the liquid phase of cement solutions, it is possible to reduce the effectiveness of polymers as stabilizers of binding systems.

All water-soluble polymers, the main functional group of which is carboxylate (-COO\(-\)), are deactivated in the cement medium mainly due to Ca\(^{2+}\) ions, while they practically cease to function, while non-ionic water-soluble polymers remain active in the cement medium.

Polymers containing carboxylate groups are poorly compatible with Portland cement, and also require the introduction of additional protective additives.

Solutions of methylcellulose and polyacrylamide are highly sensitive to monovalent potassium and sodium ions. However, studies showed that potassium was more aggressive than sodium.

Polyacrylamide (PAA) is insoluble to calcium, potassium and sodium ions, so it is not recommended to use it in cement-polymer compositions.

There is a special sensitivity of methylcellulose to sodium and potassium ions.

It is shown that the most resistant to electrolytes are low-viscosity polymers - polyvinyl alcohol, where hydroxyl groups dominate. PVA reacts weakly to sodium and potassium cations and is the most stable among the studied polymers.

According to experimental studies, additives of methylcellulose and polyvinyl alcohol are the most resistant to the action of aggressive ions among other additives of water-soluble polymers studied in the work, which determines the prospects for their use in construction solutions.
5. Summary
It is established that the composition of functional groups of water-soluble polymers and the possibility of their interaction with various ions contained in the cement, aggregate, filler, in the closing water, in the composition of soils have a decisive influence on the compatibility of the polymer and the binder, the properties of cement-polymer compositions.

The conducted research allows giving some principles for selecting rational compositions of cement-polymer dispersed systems, taking into account the established regularities of the influence of the composition of functional groups, the dosage of water-soluble polymers and electrolytes on the properties of cement-polymer dispersions. Thus, water-soluble polymers containing carboxylate groups are incompatible with Portland cement and require the introduction of additional protective reagents. It follows from the research that the properties of cement-polymer compositions with the addition of carboxylate polymers and protective reagents made on various binders may differ significantly, which should be taken into account when developing formulas of cement-polymer dispersions. Additives of non-ionic polymers are the most resistant to the action of aggressive ions and, therefore, are the most promising for use in construction solutions for various purposes.

When selecting the rational composition of a dispersed mixture, mineral and chemical additives, taking into account the laws of compatibility of components, it is possible to regulate in the right direction the rheological, technological, adhesive, physical and mechanical properties of cement-polymer compositions, deformations of dispersed systems.

The research results are expected to be used in the development of masonry mortar compositions, injection and other compositions for chemical soil fixing, in individual housing construction, in order to carry out repair and restoration work to strengthen the soil bases and stone structures.

6. References
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