Modified Cement Systems for Finishing Coatings

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Abstract. The processes of development of finishing coatings on the basis of cement colloidal systems are determined. The influence of processes of modification of colloidal cement systems on the properties of decorative coatings is studied. It is shown that the introduction of modifying additives in combination with mechanical activation allows using the optimal technological parameters of processing to give colloidal cement composites the necessary properties and increase the resistance of protective decorative coatings. The joint activation of the components of colloidal cement adhesive with a modifying additive leads to an increase in the strength of the samples at all times of hardening. Studies have shown that modifying additives and fillers have a positive effect on the thixotropic properties of the system and contributes to the formation of the hydrate with colloidale particles, which leads to hardening of the reinforcement system of a composite. Found that the addition of metakaolin enhanced the activity of fine cement systems. Studies have shown that fillers have a positive effect on the thixotropic properties of the system and contributes to the formation of the hydrate with colloidale particles, through which are formed the spatial packing, which leads to hardening of the reinforcement system of a composite.

1. Introduction

State the objectives of the work and provide an adequate background, avoiding a detailed literature survey or a summary of the results, [1]. Progress in building materials science, development of industrial methods of construction, as well as achievements in the field of construction chemistry and physics allowed to radically change the attitude to decorative coatings based on colloidal cement binder [1-3]. Increased and requirements for decorative coatings, they must have additional properties, which include permeability, water-holding capacity, hydrophobicity, adhesion to the base, increased strength for exterior and interior work-increased resistance to abrasion, etc. All of the above is due to the structure of the cement stone. To ensure operational reliability, the methods of processing of raw materials of mechanochemical activation and modification, allowing to obtain highly concentrated dispersed colloidal systems with low effective viscosity and high performance properties, were chosen. Usual mortar mixes intended for decorative finishing of front wall panels, ceased to satisfy growing to requirements. This is due to the low crack resistance, low Flexural and tensile strength and a number of other properties that do not provide the required durability. To ensure the necessary mobility of mortar mixtures based on colloidal cement systems and water-holding capacity, high rates of strength gain, low shrinkage or expansion deformation, good frost resistance, multi-component compositions were most often used, including in addition to cement, fillers and small aggregates, a complex of additives-modifiers of different nature [4-6]. Modern decorative coatings are a complex
system that includes chemical and mineral additives that allow you to adjust the properties in a wide range, and above all manufacturability, density, strength and durability. One of the most important conditions for improving the quality of colloidal cement binder is physico-chemical modified surfaces in heterogeneous systems with organic or active mineral additives and the maximum possible homogenization, which will be the key to the successful use of fine cement systems for coatings [4-6]. Modification of various complexes of chemical and mineral additives can significantly improve the physical and mechanical properties of colloidal cement adhesive and a solution based on it, including the necessary properties: mobility, plasticity, stickiness, high adhesion properties, water resistance and frost resistance [7-9]. The mechanism of action of additives of different chemical nature in cement systems (superplasticizers, polymeric, active mineral additives, etc.) is well studied [5-6, 10-13].

However, the use of powder modifiers has a number of features that are due to the process of their transition from solid to liquid at low water consumption. To obtain solutions based on colloidal cement binder that meets regulatory requirements, modifiers of multifunctional purpose are widely used on modern production lines, which, when introduced into the mixture during the grinding of the initial components or mixing, contribute to a significant change in properties and structure with virtually unchanged number of basic components. Therefore, to obtain decorative coatings based on colloidal cement systems, it is necessary to investigate the influence of chemical and technological factors modifying colloidal cement systems.

2. Methods

During the research, materials that meet regulatory requirements were used, which determines the possibility of obtaining colloidal cement material of specified technical characteristics. To obtain colloidal mixtures Portland cement of Bukhtarma cement company, natural sand of the Nikolaev Deposit, various fillers and additives were used. As a filler instead of natural sand used screenings crushing concrete scrap. For modifying cement colloidal materials used various additives. Additives were selected with a shade that will not affect the color of the colloidal cement binder. The effectiveness of the additives used was evaluated according to the criteria of GOST 24211 according to GOST 30459. The most widely used in the technology of cement colloidal binder are plasticizing, stabilizing and structuring action modifiers, hardening regulators, additives that give the cement colloidal glue special properties, as well as complex modifiers of multifunctional action [9, 14].

Therefore, to study the basic properties of fine cement systems with fillers of different Genesis was investigated additive polymer powder (RPP). To improve the hydrophobic properties of colloidal cement systems, powder hydrophobizators of various chemical bases were used [11, 15]. Hydrophobic powder of triple copolymer ethylene, vinyl acetate and vinyl chloride Vinnapas 8034 H was used as a hydrophobic additive. Superplasticizers were used as surfactants to obtain the greatest plasticizing effect at a lower concentration. In the technology of colloidal cement materials used active mineral admixtures (metakaolin) [16-17]. Fine-dispersed metakaolin lamellar particles provide the modified cement binder and mortar mixtures based on its high plasticity and resistance to delamination, as well as the absence of stickiness. The high content of amorphous alumina in the composition of metakaolin allows to use it as one of the components of complex non-shrink or expanding additives. The use of dispersed modifying additives in the production of colloidal cement binder allows to significantly realize the potential of cement binders, which leads to an increase in the most important properties of the modified colloidal glue. The effect of modifying additives is due to the fact that they are able to affect the process of hydration hardening of cement systems, micro-reinforce the formed artificial stone and contribute to the redistribution of mechanical stresses between the particles of modifying additives and cement stone [5, 18]. It should be noted that in order to ensure high efficiency of the modifying additives are important not only its properties, but also the method of administration and the input amount.
3. Results and discussions

Production of colloidal cement binder is impossible without the use of modifying additives. Polymer dispersion additive in combination with colloidal cement binder (CCB) allows to create ready-made modified dry mixtures of stable quality [19]. To determine the optimal content of this additive in the solution colloidal cement mixture intended for decorative coatings, a range of quantities of 0.1-0.8% by weight of cement was used (Figure 1-2). The optimal content of active and modifying additives was determined by changing the ultimate strength in bending and compression of beam samples 4x4x16 cm in size at different times of hardening. Tests have shown that the investigated property is improved with increasing the input of this additive to the optimal content. As can be seen from the figures, the best is the introduction of a mixture of 0.6% of the polymer powder from the mass of the cement. Further increase in the amount of additives (more than 0.6 %) has little effect on the properties of colloidal cement materials and is not economically feasible. An important property for decorative coatings based on colloidal cement mortar mixtures is their ability to retain water, as mortar mixtures are usually applied to a porous base, which intensely absorbs water. As a result, the solution is dehydrated, water becomes insufficient for hardening and normal strength. The limit of water-holding capacity is considered to be such a value of it, when not less than 15% compressive strength of standard samples made in forms without a bottom, placed on a brick, increases, compared with the strength of samples prepared in forms with a metal bottom. Limit water-holding capacity was determined by the mobility of colloid-cement mortar mixture from 3 to 6 cm water holding capacity is characterized by the property of a solution does not decompose and retain adequate humidity in a thin layer on a concrete base.

![Figure 1. Dependence of tensile strength in bending on the content of the additive](image1.png)

![Figure 2. The influence of polymer additives on the water retention capacity](image2.png)
The effect of surfactants on the properties of dispersed cement systems was studied on laboratory samples with dimensions of 4×4×16 cm after 28 days of normal hardening. Mobility of the closed cement-sand mixtures was determined at the identical water-cement ratio. The results are shown in table.

Table 1. Properties of cement systems depending on the surfactant content

| The amount of surfactant additives, % (by weight of cement) | Normal density, % | Mobility (for Attardo), cm | Tensile strength at, MPa compression | bend |
|-----------------------------------------------------------|------------------|---------------------------|-----------------------------------|------|
| 0                                                         | 27.4             | 15                        | 46.1                              | 10.4 |
| 0.1                                                       | 22.1             | 23                        | 51.6                              | 12.1 |
| 0.3                                                       | 21.6             | 25                        | 53.2                              | 12.2 |
| 0.4                                                       | 20.7             | 28                        | 61.7                              | 14.2 |
| 0.5                                                       | 20.8             | 29                        | 60.9                              | 13.6 |

There is a decrease in water demand and increased mobility in samples with surfactant additives (superplasticizer) in comparison with samples without additives. The obtained data show that the content of superplasticizer 0.4% by weight of cement provides optimal properties of dispersed cement systems. Studies have shown that surfactants have an impact on surface phenomena in dispersed cement systems. With an increase in the content of surfactant additives, a decrease in the viscosity of the system is observed. It is determined that the surface tension at the solid - solution boundary decreases with increasing surfactant concentration. With an increase in the content of the additive in the dispersed system, the shear stress limit practically vanishes, and the viscosity takes a low constant value. The mechanism of the plasticizing action of surfactants, apparently, is that the molecules of the additive are adsorbed on the surface of the particles, forming a monomolecular layer, formed hydrate layers around the particles due to the presence of hydrophilic groups in the molecules of the additive, there is a transition to the complete aggregate stability of the system, peptization of aggregates to primary particles, the rheological nature of the flow of the suspension with a yield point greater than zero at the yield point equal to zero. Reducing the viscosity of dispersed cement systems leads to a decrease in water demand and improve the mobility of the closed mixture, which will improve the manufacturability of solutions (pumpability), which is especially important in the factory method of obtaining materials. Surfactants contribute to the reduction of surface tension, which helps to reduce the size of crystallization nuclei and the formation of a large number of fine crystalline hydrates and, as a consequence, reduce the overall permeability of cement stone.

The pore space of colloidal cement systems is one of the main characteristics of their microstructure, a slight change in the pore space in terms of voids leads to a change in the basic properties. Porosity depends on the initial water-cement ratio, the composition of tumors of their specific volume and degree of hydration. Therefore, the influence of modification of colloidal cement systems by surfactant additives on the basic physical and technical properties of hardened cement materials, in particular on the porosity of cement stone, was studied. Among the many factors affecting the technical properties of colloidal cement systems (mineral and chemical composition of components, water-cement ratio, specific surface area), the main role is played by the characteristics of the emerging pore structure of cement stone (total number, radius, curvature, isolation), which, in turn, depends on the size and stability of the existence of hydrated cement dough formed during the hardening of hydrated phases. In order to reduce the porosity and therefore the water demand of the raw material mixture, a significant number of particles of the smallest size are required to fill the voids of the system. A specific feature of the effect of surfactant on the microstructure of cement stone is the fact that in its presence in the cement stone formed crystalline tumors much less dispersion than without it. In the study of the structural characteristics of solidified stone from colloidal cement-sand mixtures at different hardening time, it was found that the total and open porosity of hardened cement
stone based on the compositions with the addition of surfactants is lower than the porosity of samples without additives (table 2).

Table 2. Porosity of a cement stone with addition of surfactants

| Hardening time, days | The composition without the additives | The composition with the additive surfactant |
|---------------------|---------------------------------------|-----------------------------------------------|
|                     | general open                          | general open                                  |
| 1                   | 13.62 10.18                           | 12.67 9.78                                   |
| 3                   | 13.41 11.54                           | 12.31 9.08                                   |
| 7                   | 15.23 12.36                           | 9.75 6.27                                    |
| 28                  | 14.89 12.19                           | 8.48 5.24                                    |

A surfactant, changing the surface phenomena in disperse systems, colloid cement, and is influenced by the nature of crystallization of tumors on the morphology of crystals. It should be expected that the addition of surfactants to the aqueous solution that reduce the amount of surface tension, as well as the use of more soluble initial compounds, will lead to a decrease in the critical size of the crystallization nuclei, contribute to the formation of a large number of fine crystalline hydrates and reduce the permeability of cement stone. The smaller the critical size of the crystallization embryo, the higher the number and smaller the size of the crystallohydrates formed. The study of the microstructure of samples from colloidal cement systems with and without surfactant (fig. 3) showed that the introduction of surfactants reduces the size of hydrated grain crystals. These phenomena are undoubtedly associated with the adsorption of SP molecules on the surface of growing crystals. Adsorption increases in time and reaches a maximum of 3-5 minutes after the closure of the dispersion. Superplasticizer molecules, adsorbed on positively charged particles of growing crystals, complicate their growth and contribute to the emergence of many new crystals. As a result, the structure of the cement stone becomes fine-grained, less defective than that of the sample without additives.

Mineral particles, grains and their associations, forming the structural skeleton of a composition, in the samples with the addition of a surfactant adjacent denser than in the specimen without additives, thereby eliminating the possibility of the appearance of the pore space. Individual fragments it is evident that the composition of the modified surfactants, the observed neoplasms. Formed during further hydration reactions "coagulated gel" of hydrosilicate composition fills the pores in the physical structure of the hardened stone, which increases the density of the stone.
Decorative coating based on colloidal cement systems can be attributed to the class of mineral waterproofing and is a rigid waterproof coating applied to the concrete surface. The porosity of such materials is their specific feature and mainly depends on the structure of the cement stone. Water resistance of porous materials is achieved by the introduction of sealing additives that provide clogging of the pores, or a combination of physical, chemical and mechanical (vibration) effects at the initial stages of coagulation and crystallization structure to reduce the size of the pores. Essential for facade coatings is the adhesion of the coating to the base.

The main requirements for coatings based on colloidal cement systems are water resistance, minimum water absorption, preservation of adhesion of the coating to the base and its continuity during the operation of the coating [20]. To reduce shrinkage in the coating composition of the colloidal cement materials injected coarse aggregate – sand, combined with comprehensive modifying additive (surfactant – superplasticizer, a metakaolin, wollastonite, and polymer additives).

The finished decorative coating consists of highly dispersed cement (Sr = 5300-5500 g/cm²) with additives, highly dispersed mineral filler and larger sand (filler) in combination with low water content and obtained by a combination of surfactant and vibration, which provides the required mobility and relatively low water content. Coating compositions were prepared on the basis of modified colloidal cement systems (binder) with different amounts of aggregate (sand or concrete scrap crushing screenings) from 30 to 70 wt. parts (a part 1 binder – 100 %; the composition of the binder 2 – 70 %; the composition of the binder is 3 to 50 %, binder 4 composition of -40 %; the composition of the binder 5 to 30 %).

The water-astringent ratio is 0.35 for the technological processing of mixtures with an increase in the sand content. According to the changes in linear shrinkage determined that the most optimal is a composition containing 70 wt. % sand's. The introduction of sand as a filler in the coating compositions leads to a decrease in shrinkage deformation and, accordingly, to an improvement in crack resistance. Since the developed materials are waterproofing coatings, studies have been carried out on the effect of the amount of filler on the water resistance and water absorption of hardened coatings based on colloidal cement systems (table 3).
Table 3. The effect of filler content on the properties of the waterproofing coatings

| Mixture composition | Water resistance when you are working on, MPa | Water absorption, % |
|---------------------|---------------------------------------------|---------------------|
|                     | pressing | detachment |                     |
| Composition 1       | 1.9      | 0.9        | 10.9                |
| Composition 2       | 1.7      | 0.8        | 10.3                |
| Composition 3       | 1.4      | 0.7        | 7.6                 |
| Composition 4       | 1.1      | 0.7        | 4.7                 |
| Composition 5       | 0.8      | 0.3        | 9.1                 |

On waterproofing properties as the most appropriate mixtures include compositions with a filler content of 50 and 60 wt. %, but more optimal is the composition of 4. Studies have also shown that the main construction and technical properties and data on shrinkage properties for further research taken compositions 4 and 5.

To improve the waterproofing properties, hydrophobic additives were introduced into the developed compositions of the mixtures. The results of preliminary studies have shown that sodium stearate and oleate in comparison with other surfactants hydrophobic type to a lesser extent reduce the strength characteristics and increase hydrophysical characteristics. This makes them more suitable for the development of hydrophobized cement-filled systems. The selected water repellents were introduced in powder form in an amount of 0.25-1.00 % by weight of the binder. Studies were conducted at different filler binder based on natural fine Sands, and screenings from the concrete crushing. Evaluation of waterproofing properties was carried out on water resistance, water absorption, sorption moisture (table 4).

Table 4. The waterproofing properties of the samples

| Composition | Показатели затвердевших растворов | Water absorption, % | Watertightness, class | Sorption moisture, % |
|-------------|---------------------------------|---------------------|-----------------------|----------------------|
|             |                                 |                     |                       |                      |
| Composition 4 | 4.7/4.7                        | W16/W16             | 2.1/2.5               |                      |
| Composition 5 | 5.2/5.4                        | W12/W12             | 2.3/2.5               |                      |

Note – Before the slash is the filler of quartz sand after slash – screenings from the concrete crushing

The data obtained show that solidified solutions based on modified colloidal cement materials have good waterproofing properties.

4. Conclusions

The main conclusions of the study may be presented in a short Conclusions section, which may stand alone or form a subsection of a Discussion or Results and Discussion section. The introduction of modifying and active mineral additives can improve the physical and mechanical construction and technical properties and performance properties of finishing coatings based on colloidal cement systems. The influence of the modifying additive on the properties of colloidal cement systems is a consequence of the changes in the structure of cement stone. The introduction of a modifying additive in fine cement systems in the process of mechanical activation contributes to a more uniform distribution of components and uniform distribution of additives on the surface of cement particles and filler.

The use of metakaolin as active mineral additives improved the quality of neoplasm in colloidal system, provides a good plasticity of the mixtures and the lack of build-up, which is very important for the application in decorative coatings. The introduction of metakaolin in the amount of 7% by weight
in the composition of fine cement systems, improves the strength and deformation properties of cement stone.

It is determined that the introduction of polymer additives allows to adjust the plastic characteristics of fine cement systems and solutions based on them, affects the kinetics of hydration of cement clinker minerals, thereby determining the rate of formation of the structure of cement stone and its parameters. It is revealed that the introduction of modifying additives leads to an increase in the amount of low-basic calcium hydrosilicates in the cement stone, which have adhesive ability and contribute to an increase in the adhesive strength of the solution for decorative coatings. It is determined that the microstructure of samples of solidified solutions based on colloidal cement materials in the presence of a complex modifier is formed more dispersed and homogeneous, which will contribute to ensuring high physical, mechanical and operational properties of the resulting coatings. Good waterproofing properties of the obtained materials in the presence of hydrophobic additives suggests a wide range of applications of coatings based on colloidal cement systems.

Thus, the studies have shown that the use of modification, mechanochemical activation can be purposefully regulate the processes of structure formation, improvement of technological properties of decorative coatings based on highly dispersed colloidal cement systems.

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