Physico-chemical efficiency of mineral additives of various compositions in cement systems

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Abstract. Management of the pore volume and the mineral-morphological state of the hardening system through the use of chemical and mineral additives introduced both separately and in complexes is considered to be one of the defining directions of cement system structure formation. Currently, the nomenclature of mineral modifiers includes a wide list of materials of natural, artificial, and technogenic origin. The purpose of this study was to establish the influence regularities of mineral additives of various compositions (siliceous (microsilica, diatomite, opoka), aluminosilicate (metakaolin, fly ash), sulfoaluminate (expanding sulfoaluminate modifier), carbonate (microcalcite)) on the physical-mechanical properties of cement systems, with the identification of the most effective modifiers. According to the results of experimental studies, the influence of modifiers on the activity of the mixed cement binder, water demand, water-holding capacity and mobility of the cement paste was revealed. Condensed non-compacted microsilica, metakaolin and expanding sulfoaluminate modifier were selected as the most promising mineral additives.

1. Introduction

An important component of modern modified cement concretes is active mineral additives enabling the control of processes of structure formation and properties of cement systems. For the formulation of high strength composites, finely dispersed pozzolanic additives have the highest efficiency, which contain amorphous silica, alumina and have an increased reactivity [1–9]: condensed microsilica, metakaolin, finely dispersed fly ashes of thermal power plants, blast-furnace granulated slags, etc. Using these modifiers allows for a number of positive structural effects, which include two primary ones [10]: chemical effect, which consists in an opportunity to change the quality of the solid phase forming the frame of cement stone structure; physical effect related to the opportunity to change the porous space geometry by reducing the scope of capillary and process pores by filling the space between coarse cement particles with finely dispersed additive particles.

It is worth noting that one of the main factors of the chemical effectiveness of microsilica and metakaolin in the formulation of cement systems is the ability of amorphous silica (SiO\textsubscript{2}) and aluminosilicate (Al\textsubscript{2}O\textsubscript{3}·2SiO\textsubscript{2}) to interact with the calcium hydroxide of the hardening cement stone to form low-base hydroxilicates and calcium hydroalumosilicates, which, in turn, contributes to the strength of composites. The formation of these compounds is accompanied by an acceleration of hydration, a decrease in the content of Ca(OH)\textsubscript{2}, an increase in the amount of chemically bound water, and the specific surface area of the formed cement stone [7, 11].
Apart from siliceous and aluminosilicate modifiers, sulfoaluminate and carbonate mineral additives have increased efficiency in the formulation of cement systems. Using expanding modifiers of sulfoaluminate type allows for controlling linear and volumetric changes when hardening cement composites by forming increased volume crystals of hydrate phases (ettringite, etc.). [12, 13]. The action of carbonate rocks (limestones, dolomites) in cement systems is based on the ability of the rock-forming mineral calcite to act as a center of crystallization for new hydrate phases [14–16].

Due to the multi-component formulation of modified cement systems and the variety of additives used, many problems remain unsolved in this area. The purpose of this study is to establish the influence regularities of mineral additives (MA) of various compositions (siliceous, aluminosilicate, sulfoaluminate), carbonate on the physical-mechanical properties of cement systems, with the identification of the most effective modifiers.

To achieve this aim, the following tasks were solved:

- the effect of mineral additives of various compositions on water demand, water-holding capacity and mobility of the cement paste was researched;
- the influence of mineral additives on the activity of the mixed cement binder was studied;
- the most effective mineral additives have been established that allow to directed manage the technological and physical-mechanical properties of cement systems.

2. Materials and methods

2.1. Materials
In the studied compositions, the main component of the binder was Portland cement 500-D0-N (PC) produced by Mordovcement PJSC. The following mineral additives were used: MS-85 condensed non-compacted microsilica produced by Kuznetsk Ferroalloys SC (MS); HAMK-45 highly active metakaolin produced by Synergo LLC (HAMK); MKZhL-2 metakaolin produced by Plast-Rifey LLC (MKZhL); fly ash from Aleksin Ceramic Plant (FA); expanding sulfoaluminate modifier manufactured by Parad-Rus LLC (ESAM); microcalcite (MCC) produced by Polipark LLC, diatomite from the Atemar deposit of the Republic of Mordovia (grinding 15 min (DTMT1), 1 hour (DTMT2) and 3 hours (DTMT3)); opoka of the Alekseevsky deposit in the Republic of Mordovia (grinding for 15 min (OPK1) and 1 hour (OPK2)). The studied compositions were cement systems with the total dosage of mineral additives 10% of the weight of the binder (PC + MA). The composition without mineral additives was taken as a control. The investigated compositions of cement systems are shown in Table 1.

| Composition number | Type of mineral additives |
|--------------------|--------------------------|
| 1                  | -                        |
| 2                  | MS                       |
| 3                  | HAMK                     |
| 4                  | MKZhL                    |
| 5                  | FA                       |
| 6                  | ESAM                     |
| 7                  | MCC                      |
| 8                  | DTMT1                    |
| 9                  | DTMT2                    |
| 10                 | DTMT3                    |
| 11                 | OPK1                     |
| 12                 | OPK2                     |
2.2. Methods

Physico-chemical efficiency of the used mineral additives was evaluated by their influence on the following cement system indicators: water demand, water-holding capacity of cement paste, as well as the activity of mixed cement binder.

The water demand of cement systems was estimated in the mixed binder system (90% of Portland cement and 10% of mineral additive) by water/solid (water/binder) ratio \((W/(C+MA))\) of cement paste, corresponding to its normal density, determined on the Vicat apparatus in accordance with the method of the Russian State Standard GOST 310.3.

Water-holding capacity of cement systems was determined by the water separation of cement paste consisting of a mixed binder (90% PC+10% MA) and water (water-binder ratio \(W/(C+MA) =1\)), when settling the particles of the solid phase in a graduated cylinder in accordance with the Russian State Standard GOST 310.6. The volume of settled cement paste and water accumulated on its surface was recorded every 30 minutes after the first counting for 2 hours. The ratio of the volume of water accumulated on the surface of the paste to the initial volume of the suspension, expressed as a percentage (water separation coefficient by volume) was taken as the value of water separation.

Effectiveness evaluation of mineral additives was carried out according to the results of the study of their effect on the activity of cement binder with the definition of the activity index of the modifier. The activity index of the used mineral additives was determined in accordance with the procedure of the Russian State Standard GOST R 56178-2014 by comparing the results of tests on the compressive strength after steaming of modified cement-sand samples-beams of size 40×40×160 mm, made using 90% Portland cement and 10% mineral additive (by the weight of binder \((PC+MA)\)), and standard unmodified samples at a ratio of cement binder and standard monofractional Wolsky sand equal to 1/3. Water-binder ratio was taken the same for all compositions, equated to the value chosen for the most water-demanding composition when reaching the Hagermann cone spread diameter (form-cone from the shaking table according to the Russian State Standard GOST 310.4) of fine-grained concrete mixture equal to 106–108 mm. The procedure for making and testing samples-beams are taken in accordance with the requirements of the Russian State Standard GOST 310.4, the regime of heat and vapor processing is chosen according to the Russian State Standard GOST R 56178-2014 – \((3+3+6+2)\) h at a temperature of isothermal exposure of 80°C.

In addition to the analyzed indicators of cement systems, at the initial stage of the study, the specific surface area of the used mineral additives and Portland cement was determined. Determination of the specific surface of powders was carried out on the device of dispersion analysis PSKh-12 by the method of Kozeny- Carman, based on the establishment of air permeability and porosity of the compacted layer of the powder. Gas permeability of the powder layer was measured according to the duration of filtering through the device of a given volume of air at a fixed vacuum in the working volume of the device.

3. Results and discussions

According to the results of the study, there were established correlation dependences between indicators of water demand (Fig. 1), water-holding capacity (Fig. 2), mobility (Fig. 3) of cement systems and specific surface of mineral additives used. Moreover, in view of significantly higher dispersibility of microsilica relative to other kinds of MA (\(S_{\text{o}}=20\) vs. 0.25–2.85 \(m^2/g\)), results of research of cement systems of No. 2 composition were not taken into account at approximation of experimental data.

From the analysis of obtained data (Fig. 1), it was found that there is close enough correlation dependence \((R^2=0.885)\) between water demand of cement binders according to normal density and specific surface of investigated types of mineral additives (except MS), introduced in an amount of 10% by weight of the binder. An increase of specific surface of mineral additives leads to an increase of water demand of cement systems.

The water separation coefficient by volume, on the contrary, decrease with an increase in the specific surface of mineral modifiers (Fig. 2). The linear dependence between the specified index of
cement systems and the specific surface of the MA types under study, except for microsilica, which has the highest dispersibility, is characterized by a sufficiently high coefficient of determination equal to 0.863.

**Figure 1.** Correlation dependence between water demand of cement systems by normal density and specific surface area of mineral additives.

**Figure 2.** Correlation dependence between the water separation coefficient of cement paste by volume and specific surface area of mineral additives.

**Figure 3.** Correlation relationship between the mobility of cement systems, estimated by Hagemann cone spread diameter, and the specific surface area of mineral additives.
The mobility of cement systems, estimated by Hagermann cone spread diameter at constant water content of cement systems, also decreases with increasing specific surface MA (Fig. 3), but the correlation is much lower ($R^2=0.600$). In this case, given the high water demand of the compositions No. 8 and 10 (see Table 1), which is 39.75–41.00% by the weight of solid phase (PC+MA), these mixed binders were not used in assessing the mobility and determining the activity index of MA. The mineral powders used in the above compositions were obtained after grinding of diatomite for 15 minutes (No. 8) and 3 hours (No. 10).

To evaluate the effectiveness of various mineral additives used in the work, we determined the coefficients of polynomial equations describing the contribution of the type and proportion of MA in the total index:

$$y = b_{PC} \cdot x_{PC} + b_{MS} \cdot x_{MS} + b_{HAMK} \cdot x_{HAMK} + b_{MKZhL} \cdot x_{MKZhL} + b_{FA} \cdot x_{FA} + b_{ESAM} \cdot x_{ESAM} + b_{MCC} \cdot x_{MC} + b_{DTMT1} \cdot x_{DTMT1} + b_{DTMT2} \cdot x_{DTMT2} + b_{DTMT3} \cdot x_{DTMT3} + b_{OPK1} \cdot x_{OPK1} + b_{OPK2} \cdot x_{OPK2},$$

where $b_i$ – are coefficients of polynomial equation; $x_i$ – are varied components of cement systems, taking values from 0 to 1 (sum of all components of mixtures of each composition equals 1); $i$ – is the notation of mineral additive (see Section 2.1).

The coefficient numerical values of the polynomial equation (1) for the four studied indicators (water demand by normal density, water separation coefficient by volume, mobility, estimated by Hagermann cone spread diameter, and activity index of MA) are presented in Table 2.

| Variable prescription components of cement systems (section 2.1) | Coefficient numerical values of the polynomial equation (1) for the investigated properties of cement systems |
|---------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Water demand by normal density, % | Water separation coefficient by volume, % | Mobility, estimated by Hagermann cone spread diameter, mm | Activity index of mineral additive, rel. units |
| PC | 26.5 | 20.4 | 124 | 1.0 |
| MS | 74.0 | -59.6 | -66 | 3.0 |
| HAMK | 74.0 | -33.6 | 64 | -0.2 |
| MKZhL | 86.5 | -43.6 | 64 | 1.1 |
| FA | 56.5 | 31.4 | 214 | 0.6 |
| ESAM | 34.0 | -5.6 | 84 | 1.4 |
| MCC | 24.0 | -7.6 | 244 | -0.4 |
| DTMT1 | 159.0 | -112.6 | - | - |
| DTMT2 | 161.5 | -116.6 | -116 | 2.3 |
| DTMT3 | 171.5 | -131.6 | - | - |
| OPK1 | 64.0 | -49.6 | -36 | 1.3 |
| OPK2 | 66.5 | -52.6 | -66 | 1.5 |

It was found (Fig. 1) that the systems with the addition of milled diatomite (compositions No. 8, 9 and 10) have the highest water demand, 1.5 times higher than the same indicator for Portland cement. Also, a higher thickening capacity than that of Portland cement was found in several MA under study, decreasing in the series: MKZhL → HAMK or MS → OPK2 → OPK1 → FA → ESAM (Fig. 1 and Table 2). The use of microcalcite in the formulation, on the contrary, contributes to the reduction of water demand of modified cement systems. The reduced thickening ability of MCC is confirmed by the lower value of the corresponding coefficient of polynomial equation (1) in comparison with Portland cement (24 vs. 26.5 (Table 2)).

Analyzing the results of experimental studies, it was found that Portland cement and fly ash have the lowest water-holding capacity from the investigated components of cement systems, as evidenced by the increased values of the water separation coefficient by volume of compositions 1 and 5 (20.4
and 21.5% respectively (Fig. 2)) and positive coefficient values of the polynomial equation (1) (20.4 and 31.4 respectively (Table 2)). The lowest water separation is observed for the compositions modified by MA on the basis of diatomite and opoka, as well as microsilica. For cement systems with diatomite additives, the water separation coefficient by volume does not exceed 5.2–7.1%. Of the two types of investigated metakaolin HAMK has a slightly higher coefficient of water separation (15%, composition No. 3) than MKZHL (14%, composition No. 4) (Fig. 2).

Cement systems containing 10% microcalcite (composition No. 7) or fly ash (composition No. 5) are characterized by high mobility, exceeding by 7.3–9.7% the indicator of unmodified composition (Fig. 3). The increased rheological efficiency of MCC and FA in the formulation of cement systems is also confirmed by the highest values of the corresponding coefficients of polynomial equation (1) – 244 and 214, respectively (Table 2), which is 97 and 73% higher than that of Portland cement. For a number of compositions with additives MS, DTMT2, OPK1 and OPK2 (Nos. 2, 9, 11 and 12) negative coefficient values of polynomial equation (1) were obtained, indicating their high thickening ability. Mobility of these cement systems, estimated by Hagermann cone spread diameter, at a constant water content does not exceed 100–108 mm, which is 13–19% lower than the indicator of composition without MA (124 mm).

Analysis of the activity indexes of mineral additives determined in accordance with the Russian State Standard GOST R 56178-2014 at the same water-binder ratio indicates (Table 2) that the greatest efficiency of replacing 10% of Portland cement with MA is achieved when using MS and DTMT2. The activity indexes in these cases reach 1.20 and 1.13 relative units, and the coefficient values of the polynomial equation (1) for the characteristic in question are 3.0 and 2.3, respectively (Table 2). Also, compared with Portland cement higher values of activity index (1.01–1.05 vs. 1.00) and the coefficients of polynomial equation (1) (1.1–1.5 vs. 1.0) have mineral additives based on ESAM, metakaolin MKZhl-2 and opoka (OPK1 and OPK2). Comparative analysis of two investigated types of metakaolin showed undoubted promising use of MKZhl-2 brand modifier supplied by Plast-Rifey LLC.

4. Summary

The following results were obtained from experimental studies:

- the effect of mineral additives of various compositions (siliceous (microsilica, diatomite, opoka), aluminosilicate (metakaolin, fly ash), sulfoaluminate (expanding sulfoaluminate modifier), carbonate (microcalcite)) on water demand, water-holding capacity and mobility of the cement paste was established;
- the influence of mineral additives on the activity of the mixed cement binder was revealed;
- the most effective mineral additives have been established that allow to directed manage the technological and physical-mechanical properties of cement systems.

The following types of mineral additives were selected as the most promising for further work based on the aggregate of the studies: MS-85 condensed non-compacted microsilica (Kuznetsk Ferroalloys SC), MKZhl-2 metakaolin (Plast-Rifey LLC) and expanding sulfoaluminate modifier (Parad-Rus LLC).

5. References

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**Acknowledgments**

The reported study was funded by RFBR according to the research project № 18-29-12036.