Investigation into effect of metakaolin-based additives incorporation on formation of cement stone structure

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Abstract. The paper presents studies on the evaluation of the effect of complex additives, including metakaolin, microsilica and superplasticizer on the formation of the phase composition of cement stone. The change in the structure of the modified cement stone was studied and the dependencies were established. A comparative analysis of two complex additives to evaluate the effect of metakaolin on the change in the phase composition of cement stone was carried out. The possibility of obtaining high-performance concrete with low porosity, high early and vintage strength, durability, using additive accelerators and structure modifiers has been investigated. It is established that the use of metakaolin leads to the formation of a cement stone structure, mainly consisting of metastable calcium hydroalumates. It is necessary to use metakaolin together with microsilica and superplasticizer to create a dense structure of cement stone with low capillary porosity from stable low-basic weakly crystallized hydrate phases that are stable when the medium pH is changed.

1. Introduction

Today Russian and European standards divide active mineral additives (AMS) for natural and technogenic, with pozzolanic or hydraulic properties. In the production of concrete, complex additives are widely used including AMS of predominantly technogenic origin such as metallurgical slags, microsilica, etc. However, the characteristics of such additives as by-products of the industry are not stable because it depend directly on the technology of the main production. To stabilize the properties and expand the field of application of additives in the building technology materials more often use specially prepared AMS such as metakaolin [1].

Metakaolin in accordance with the requirements of EN and ASTM is a pozzolanic additive formed as a result of the dehydration reaction of kaolin clays [2,3]. Due to the amorphous structure and the weak bond between the ions, metakaolin interacting with water can both dissociate into aluminate and silicate parts, and reconstitute the lattice with attachment of various elements.

According to the research, the main products of the pozzolanic reaction of clinker cement minerals in the presence of metakaolin may be hydroaluminates and calcium hydrosilicates of various basicity and variable composition, such as $\text{C}_2\text{AH}_8$, $\text{C}_3\text{AH}_6$, $\text{C}_4\text{AH}_n$, and also hydroaluminosilicates of the hydrogelenite type $\text{C}_2\text{ASH}_8$ [4-6].
The hydration and formation of phase composition of the cement stone modified with metakaolin will be determined to a greater extent by the reaction conditions, concentration of calcium ions in the liquid phase and by the quality of feedstock and technology preparation metakaolin [7,8].

Metakaolin is an aluminosilicate so together with nSiO$_2$ we introduce nAl$_2$O$_3$ in cement, amount of which is strictly limited for concrete with high durability. Therefore, the dosage of metakaolin must be limited and administered together with microsilica to acidify the medium and to artificially create a calcium ion deficiency. In addition, metakaolin is a finely dispersed additive which has an increased water demand so it must be used in conjunction with water-reducing additives [8-10].

Thus, the purpose of this study is to analyze the change in the phase formation and structure of cement stone modified by complex additives, as well as to identify patterns of formation of hydrate phases in the presence of metakaolin, to assess the possibility of using additives in the production of high-performance concretes.

2. Materials and methods of study

The work used portland cement CEM I 42,5N manufactured by Dyckerhoff, which meets the requirements of GOST 31108-2003, metakaolin (MTK) produced by CJSC "Plast-Ripheus", TU 5729-095-51460677-2009 (2.5% and 5% by weight of cement); granulated microsilica (Novokuznetsk, Kemerovo region) (MS), TU 5743-048-02495332-96 (dosage 5%). The superplasticizer SP-1 of Novomoskovsk was used as a plasticizing additive, at a dosage of ~0.6% of the weight of the binder.

The studies were carried out using standard research methods and using the required number of samples of the same series to ensure a confidence probability of at least 0.95, on the certified equipment in a certified laboratory. The kinetics of the strength of cement stone was evaluated in accordance with GOST 10180 - 2012 "Methods for determining the strength of control samples," on cement stone (2x2x2cm). The samples were hardened at a temperature of 20 ± 50 °C and a humidity of 95-100% (normal conditions). Differential-thermal analysis (DTA) was used to study the phase composition of the cement stone using the Netsch LuxxSTA 409 derivatograph, X-ray phase analysis (XRF) on a DRON-3 diffractometer, upgraded with a PDWin attachment and a scanning electron microscope from Jeol Interactive Corporation, Japan JSM-700 1F.

3. Results and discussion

The results of the effect of additives on the kinetics of the strength of cement stone are presented in Figure 1. Samples of modified cement stone showed an increase in strength for 2 days in comparison with the control ones, and amounted to about 80% of the brand-name non-additive composition (Figure 1).

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On the 28th day of hardening, the strength of cement stone with the introduction of complex additives is 30% higher than the brand strength of the additive composition (Figure 1).

According to the DTA data, the introduction of MTK together with SP-1 on the 28th day of hardening contributes to the formation of the cement stone structure with the content of total chemically bound water increased to 18.5% (Figure 2). This, first of all, is associated with the formation of high-basic, high-water calcium hydroalumates. The additional introduction of microsilica into the complex leads to a decrease in the total chemically bound water to 14%, which is probably due to the formation of low-water hydrate compounds and is confirmed by earlier studies [7, 11, 12].

The use of the 2.5% MTK + 0.6% SP-1 complex reduces the calcium hydroxide content in the cement stone structure by up to 50% compared to the non-additive composition (Figure 2) [11, 13]. An additional decrease in the content of calcium hydroxide using the complexes "2.5% MTK + 5% MS + 0.6% SP-1" to 70% is due to the high pozzolanic activity of the additives.

On the derivatograms of cement stone with and without additives, endo-effects at 110-140°C and 670-770°C were recorded for the 28 days of hardening, corresponding to the dehydration of highly basic calcium hydrosilicates (CSH), which is confirmed by the presence of peaks corresponding to the CSH (II) phase on XRF (d / n = 9.8, 3.07, 2.8, 2.0, 1.83Å).

The endo-effect at 140-160 °C corresponds to the loss of water of low-basic HSC, and the exo-effect 800-905°C indicates their crystallization into wollastonite, C-S-H (I) (d / n = 3.07, 2.81, 1.83Å) [14-16]. In addition, all derivatograms had an endo-effect at 480-510 °C, which refers to the decomposition of calcium hydroxide Ca(OH)₂ (d / n = 4.9, 2.63, 1.93, 1.79, 1.69; 1.49Å), (Figure 2) [16, 17]. With the use of the additive "2.5% MTK + 0.6% SP-1", high-basic CSHs and stable, crystallized hydroaluminates of the cubic syngony type C₃AH₆ prevail in the cement stone, losses at
340 °C, endo-effect at 490 °C d / n = 5.01, 4.4, 3.37, 2.82, 2.23, 2.07, 1.68 Å, with inclusions of low-basic CSHs of the type C-S-H (I) and C₃S₆H₆, endo-effect at 735, 840 °C (Figure 2b).

Introduction to the complex "2.5% MTK + 0.6% SP-1" 5% MS leads to a change in the phase composition of the cement stone, with the formation of a structure mainly from low-basic CSH (exo-effects at 800-900 °C), formation of calcium hydroaluminates type C₃AH₆ (endo-effect at 490 °C) and CAH₁₀ (endo-effect at 490 °C, d/n = 7.16, 3.72, 3.56, 3.27, 2.88, 2.69, 2.55, 1.94, 1.64 Å), hydrogarnates of the type C₃ASH₄ and C₃AS₂H₂ (endo-effect at 490 °C, d/n = 2.8, 2.72 Å), which subsequently, with a change in the alkalinity of the medium, do not undergo recrystallization processes and contribute to increase the strength of the stone (Figure 2 c) [18, 19]. The elongation and increase of the background in the region of small angles and the decrease in the intensity of the crystalline phase peaks indicate amorphization of the cement stone structure, which is confirmed on X-ray diffraction patterns by an elevated background in the region of small angles and a decrease in the intensity of the crystalline phase peaks (Figure 2 c) [18-20].

The study of the open porosity and structure of the formed cement stone, the degree and nature of its crystallization was conducted by means of electronic raster microscopy. The dependences of the effect of additives on the change in open porosity of cement stone at the age of 28 days are shown in Figure 3.

![Figure 3. Effect of additives on the open porosity of cement stone, %](image)

**Figure 3.** Effect of additives on the open porosity of cement stone, %

(Fₜₐₚ = 1.29 <Fᵣₑₜ = 3.0).

The micrograph of a cement stone chip at the age of 28 days: a) without additives, an increase of 5000; b) "2.5%MTK+0.6% SP-1"

**Figure 4.** Micrograph of a cement stone chip at the age of 28 days: a) without additives, an increase of 5000; b) "2.5%MTK+0.6% SP-1"
The introduction of complex additives reduces the open porosity by 75-78% compared to the control samples of the additive cement stone. This indicates that the structure is more compact, and the hydration processes are more complete.

The study by the method of electronic raster microscopy and local chemical analysis confirmed the results obtained earlier with the help of DTA and XRF. Samples of cement stone without additives have a non-uniform structure, also on the surface of the cleavage there are: calcium hydroxide, weakly crystallized high-basic CSH with CaO / SiO₂ = 2 ... 2,90 and amorphous phase (Figure 4, 5).

The introduction of "2,5% MTK + 0,6% SP-1" results in the formation of a more uniform, dense and fractured structure of cement stone which preferably includes CSH and hydroaluminates of different basicity and degree of crystallization (Figure 4,5).

The use of a complex including metakaolin leads to the formation of a dense homogeneous structure of cement stone, mainly consisting of calcium hydrosilicates of reduced basicity CaO / SiO₂ = 1,2 ... 1,5. Since the fine crystalline portlandite is found only in closed pores, it means that its crystallization occurs after the formation of the basic structure of the cement stone (Figure 5) [20].

4. Conclusions
1. It is necessary to direct the formation of a dense, self-protecting structure of cement stone with low capillary porosity from stable low-basic weakly crystallized hydrated phases and a local concentration of calcium hydroxide in the closed pore space necessary to maintain a stable pH environment for obtaining highly functional durable cement materials. To achieve such an effect is possible only through the combined use of metakaolin with microsilica and superplasticizer.
2. The use of complex additives, including metakaolin and superplasticizer is possible only to increase the rate of hardening of cement stone. Metastable aluminates prone to recrystallization processes will be formed without artificial acidification of the medium.

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