STUDYING THE INFLUENCE OF BINARY MICROPRODUCER ON STRUCTURE FORMATION PROCESSES OF CEMENT BINDER

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Annotation In this article, the influence of a binary microwave on the structure formation processes of a cement Binder is studied with the widespread use of methods of differential-thermal analysis, X-ray and electron microscopy.

Key words: cement binder, binary microwave, hydration, ash spark, differential-thermal analysis, X-ray phase analysis, morphological studies

Introduction. In the studies conducted by the leading scientists of the world [1-4], the positive effect of various fog additives on the process of formation of the structure of cement stone was emphasized. The effect of blast furnace slag, fuel-energy slag, microsilica, steel industry slag, barcan sand, basalt, metakaolin and other similar microfillers of various origins on the hydration process of cement binder has been widely studied. On the other hand, the effect of binary microfiller based on fly ash (FA) and limestone (LS) on the structure formation process of cement stone has not been sufficiently studied..

In this paper, X-ray phase (XRP), differential thermal (DT) and morphological analyzes were used to determine the effect of binary microfiller on the hydration process..

Purpose and methods of research. In the research, TsEMI 32.5 N Portlandcement from the “Ohangarontsement” plant was used for the preparation of heavy concrete, new Angren TPP fly ash and limestone from the Muruntov mine were used as carbonate rock to obtain a complex microfiller (chemical composition is given in table 1).

Table 1

New Angren TPP chemical composition of ash spark

Type of microfiller	The composition of oxides, mas.%											
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	SO_3	TiO_2	P_2O_5	n.n
New Angren IES ash spark	49,7	19,1	10,5	11,5	3,6	-	0,9	1,4	1,4	0,2	-	1,2

The mineral composition of the carbonate rock is presented in Table 2.

Table 2

Mineral composition of carbonate rock

Mineralogical composition (%)	Limestone (Muruntov)
Calcite	98
Quartz	2
Muscovite	-
Montmorillonite	-
Dolomite	-

X-ray phase (RFT), differential thermal (DTT) and morphological analyzes were used in the research to determine the effect of binary microfiller on the hydration process..

A derivatographic analysis (DTT) was performed in the temperature range from 20 to 1000 °C to evaluate the possible changes in the cement system. Figures 3, 4 and 5 show the derivatograms of the studied samples[12].

In the derivatogram of the control sample (figure 3), the first peak of the endoeffect was observed at 109 °C, and the mass reduction due to the loss of free bound water was found to be 8.63 % with a peak area of 366 J/g.

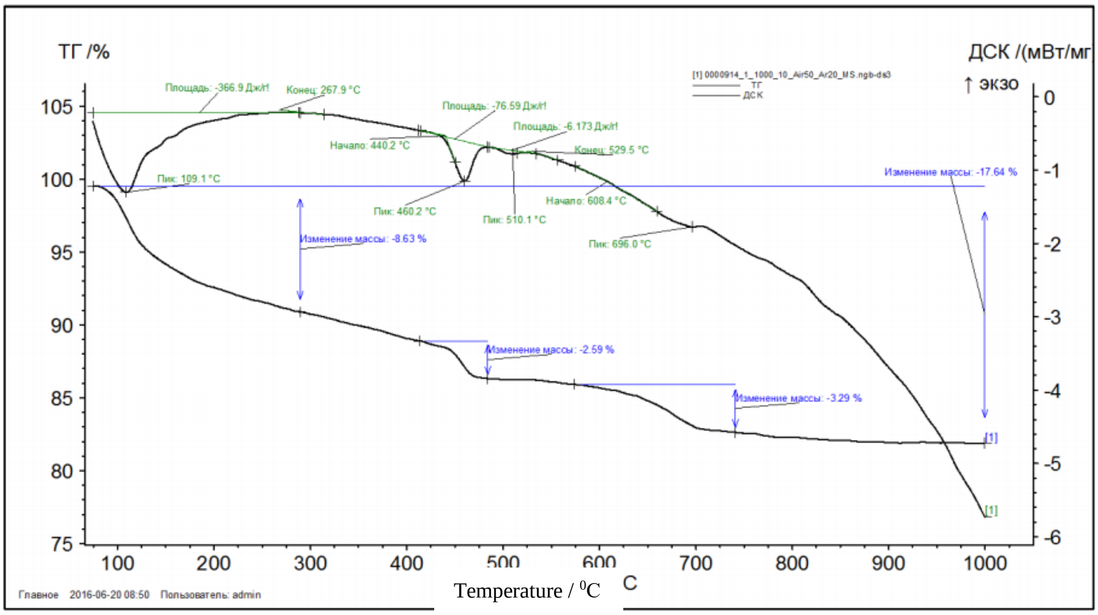

Figure 1. Derivatogram of standard composition

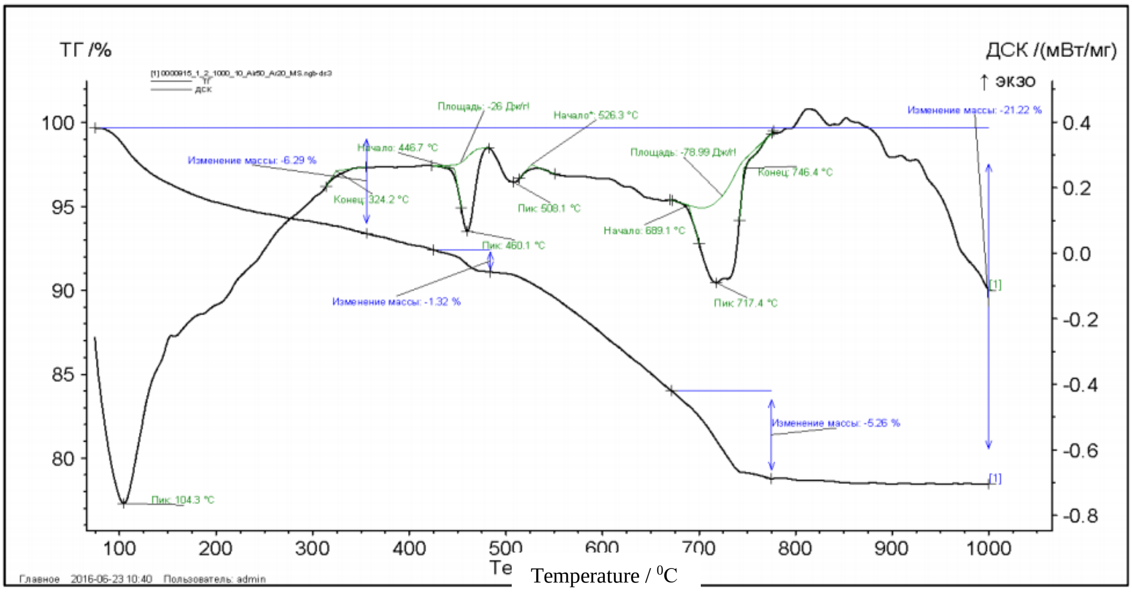

Figure 2. Derivatogram of the investigated composition 2 (PTs 75 %+FA 25 %)

The endoeffect peak at a temperature of 100-120 °C corresponds to the dehydration of C_2SH_2 and $C_2S_3H_2$; And the endoeffect at 2.59 % mass loss at 460 °C refers to the dehydration of $Ca(OH)_2$ and $C_2SH(B)$, C_2SH_2. A mass loss of 3.29 % at 696 °C is due to dehydration of highly basic calcium hydrosilicates (tobermorite phases, decarbonization of $C_2SH(C)$, C_2SH_2 and $CaCO_3$)

In the 28-day-old cement stone modified with 25 % FA in composition 2 (fig. 1), endoeffects were detected in the range of 97-104 °C. A 6.29 % mass loss was observed due to the loss of weakly bound water. Further endoeffects appeared when heated to 460 °C and 689 °C, where the mass loss was 1.32 % and 5.69 %, respectively. This refers to the decomposition of hydrosilicate calcium C_2SH_2 $C_2S_3H_2$ according to the endoeffect [5,6]

Using the DTT method, it was found that in cement stone modified on the basis of binary microfiller (fig. 2), hydration products increased, and the amount of ettiringite and thaumasite minerals decreased several times compared to the remaining contents.

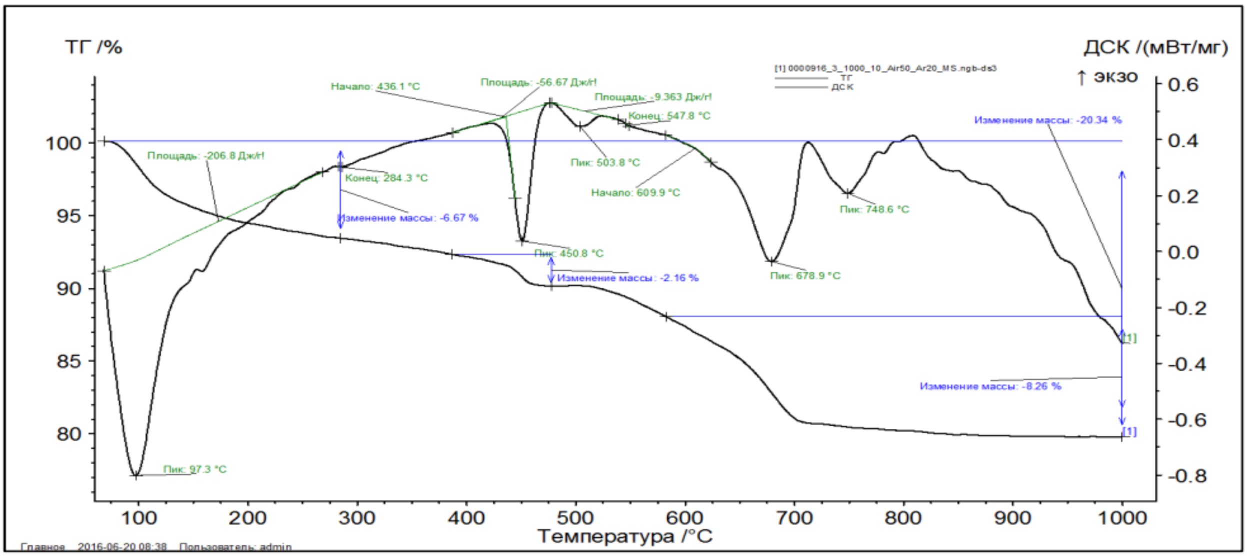

Figure 3. Derivatogram of the studied composition 3 (PTs 75 %+FA 10 %+LP 15 %)

All obtained derivatograms have endoeffects in the range of 466-495 °C. But weight loss in all samples has a different indicator (1st composition 2.59 %; 2nd composition 1.32 %; 3rd composition 1.95 %). The different values of mass loss in the samples may be due to the decomposition of low-base calcium hydrosilicates due to different temperature stability and the increased hydration level in the modified samples compared to the standard.

The results of the X-ray phase analysis are presented in Figures 4 and 5.

As a result of the introduction of FA, the intensity of the diffraction lines of portlandite is significantly reduced due to the high pozzolanic activity of amorphous silicon, as shown in Fig. 4 (C_2S_2H - d/n=2,09; 1,82; 1,76*10^{-10} m; CSH(B) - d/n=3,02; 2,8; 1,83*10^{-10} m; $C_3S_2H_3$ - d/n=1,92; 1,87; 1,69*10^{-10} m; $C_3S_3H_3$ - d/n=2,74; 2,35; 1,92*10^{-10} m).

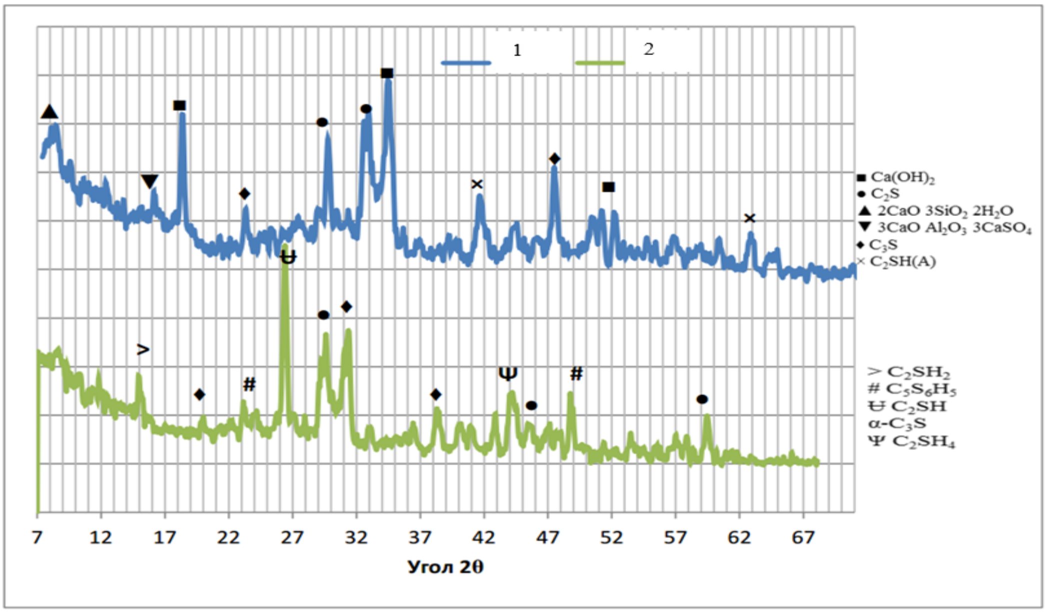

Figure 4. X-ray of the samples under study
(1-control composition; 2-PTs 75 %+FA 25 %)

An increase in additional peaks of affilitic $C_3S_2H_3$ (d/n=1,924*10^{-10} м) low base hydrosilicates was observed in the X-ray image of cement stone modified with binary microfiller.

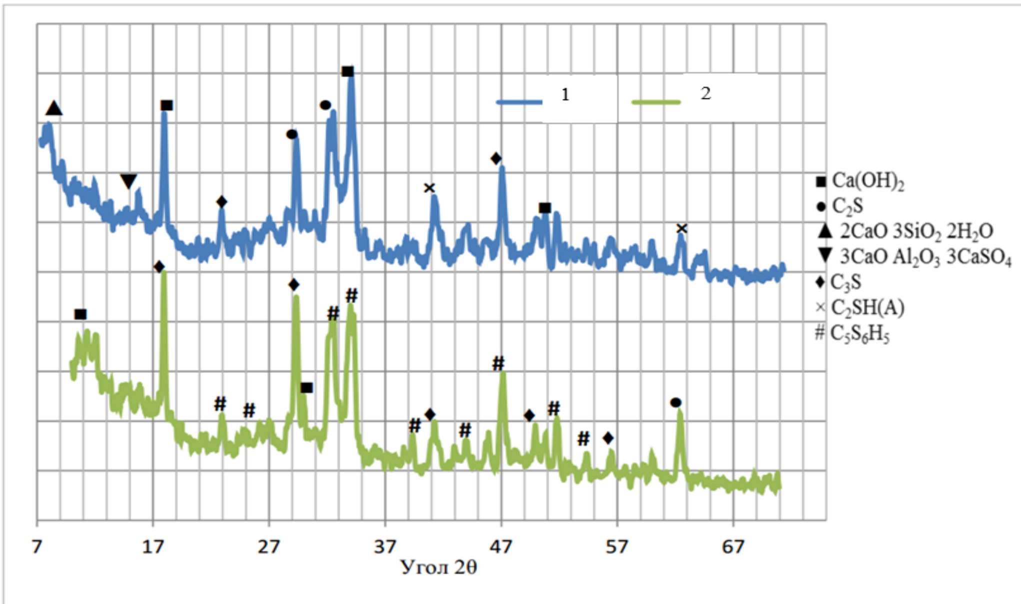

Figure 5. X-ray of the samples under study

(1st control composition; 2nd PTs 75 %+FA 10 %+LP 15 %)

In addition, in composition 3, the intensity of tobermorite compounds $C_5S_6H_5$ (d/n=3,02; 3,34; 2,61*10^{-10} m), as well as truscottite $C_6S_{10}H_3$ (d/n=1,762*10^{-10} m) also increased. A significant decrease in the content of free calcium hydroxide, ettyringite and thaumasite was observed in the cement stone modified with binary microfiller, which leads to a further increase in the corrosion resistance of concrete[14-15]. Photomicrographs of the studied samples are presented in fig. 5

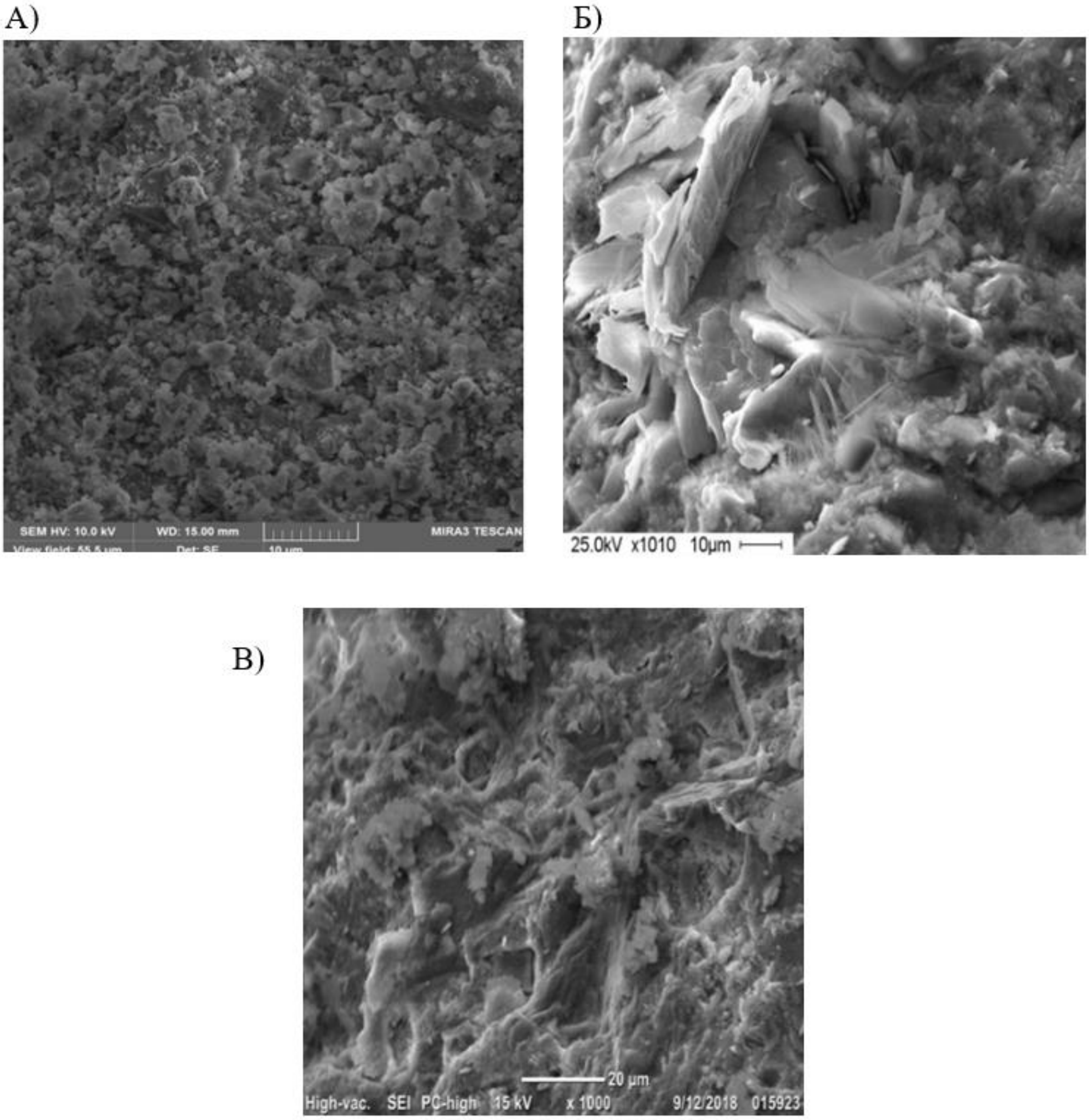

Figure 6. Photomicrographs of the studied samples
(A-reference content; B-PTs 75 %+FA 25 %; V-PTs 75 %+FA 10 %+LP 15 %)

The microstructure analysis showed that FA and LP particles are surrounded by gel derivatives. Individual particles were plastered together and formed uniform clusters with a specific order. Such cement stone is characterized by the presence of needle-shaped hydrosilicate minerals, their length is 3 microns, and the diameter is about 0.3 microns (Fig. 6, c).

Adding the amount of gypsum stone to the cement stone in a fixed amount according to [7] (not to exceed ≤3 %) made it possible to control the number and size of ettringite and thaumasite crystals, which helps to increase the corrosion resistance of cement and concrete based on it. On the other hand, carbonate-containing rocks form dense bonds with cement stone, which is explained by the formation of epitaxial bonds between cement hydration products and OK.

Thus, the addition of finely dispersed OC is a chemical factor in increasing the activity of the binder and filler and the interaction of FA, while having a catalytic effect on the reactivity of the surface of the components. The fact that the introduction of mineral additives into the composition of the binder activates the hydration process was confirmed in the study of micrographs.

The hydrate structure of a composite binder based on a binary modifier is represented by two categories: primary and secondary. Primary structure occurs through the mechanism of structure formation within the cement matrix, and the resulting minerals fill the interpore spaces with amorphous products. In the secondary category, it strengthens the adhesion and cohesion bonds in the "binder+filler" system due to the elimination of defects in the contact zone.

Studies have shown a clear synergistic effect of the components of the binder composition on the mineral composition of the hydration products and the rate of interaction of clinker minerals with water, as well as on the morphology of the hydration products and the microporosity of the rock.

An important feature of cement systems based on such binders is that during the first 4-5 hours of reaction with water, the processes of structure formation are significantly slowed down, followed by intensive crystallization and hardening.

Conclusion. Thus, the structural analysis showed that the use of binary microfiller based on FA and OK in the cement system leads to the intensification of the hydration process, in particular, the increase of minerals belonging to the tobermorite group, and at the same time, it causes a significant reduction of ettiringite and thaumasite phases in the structure. This ensures that the cement stone is resistant to sulfate corrosion. It should also be noted that the use of binary admixture leads to the formation of a dense structure, reduction of cement stone defects and microcracks. This creates an opportunity to obtain high-quality, long-lasting concrete.

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