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X-ray diffraction of concrete composites of high structural strength and density

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The processes of microstructure development and hydration of concrete composites of high structural strength and density, which were modified by a complex of modifiers based on microsilica and metakaolin, have been studied. It was found that the addition of 10% microsilica in combination with 5% metakaolin and 5% polycarboxylate ether by weight of cement, create conditions for the conversion of unstable and soluble calcium hydroxide into a strong crystalline hydrate of calcium silicate. It has been shown that the presence of compounds that include Al and Fe in the late stages of hydration is a sign of the formation of secondary phases of hydroaluminates and calcium hydroferrites. The 36% increase in strength is due to the optimal use of free calcium hydroxide and amorphous silicon dioxide.

Keywords: High resolution X-ray diffractometry, ultrafine modifiers, microsilica, metakaolin.

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Introduction

The introduction of a set of X-ray, correlation-optical, electron-raster methods for diagnosing the state of polycrystalline materials, as well as establishing the features of phase transformations at the microstructural level, is an urgent task today. New approaches to the chemical modification of the cement matrix pose the task of substantiating the cause-and-effect relationships of the processes of structure formation and quality control of the source material, which is a necessary condition for obtaining high-strength composites. The experience of research in [1-4] indicates that their structure is formed mainly from low-basic calcium hydrosilicates (CSH-I). However, there are a number of factors that can affect the physical and mechanical properties of such structures. First of all, these are microcracks caused by autogenous shrinkage [5], which significantly reduces their resistance to aggressive media and contributes to the formation of defects in the interphase transition zone between the cement matrix and large aggregate aggregates [6]. The development of ways to reduce structural defects and limit the deformable properties of high-strength composites is becoming an important task for both research and engineering practice. This is relevant for high-strength concrete composites, for which an important characteristic is the packing density of grains at the micro- and nanostructured level. Currently, active experimental studies are being conducted to determine the physical and mechanical characteristics of high-strength concrete. However, the problem of field testing and research of their application in the construction industry is relevant [7-11]. This requires a detailed analysis and creation of models of physicochemical processes of microstructure development depending on changes in the phase composition of the cement composite.

I. Objects of research

To study the processes of structure formation in concrete composites and their influence on strength indicators, a formulation of high-strength composite was developed - modified with a complex of fine additives based on microsilica and metakaolin (with compressive strength over 120 MPa), respectively. According to this recipe, a series of samples was formed to analyze the

processes of structure formation during 365 days of hydration.

II. Research methods

For the analysis of physicochemical processes and models of structure of a cement matrix, high-resolution methods of X-ray diffractometry (PANalytical Philips X'Pert PRO diffractometer), energy-dispersive X-beam spectroscopy (Hitachi SU70 scanning electron microscope), scanning electron microscope, Zeiss EVO 50 XVP). Experimental X-ray diffraction patterns were processed and analyzed by the Rietveld method using Match3 software. Determination of mechanical properties was carried out using a hydraulic press TMC-3224.

III. Results

X-ray analysis of the phase composition of cement

In order to control the quality of input materials, the qualitative and quantitative composition of clinker cement minerals was determined, the X-ray diffraction pattern of cement is shown in Fig.1. The diffraction pattern shows the main crystalline phases, which significantly affect the formation of the strength characteristics of concrete composites. In particular, for cement characteristics, typical for cement phases were chosen, which correspond to the following intensity maxima on the X-ray diffraction pattern (Fig. 1); for phase C_3A 2θ = 33.18 deg (bed period d = 2.70Å); for phase C_4AF 2θ = 33.94 deg (d = 2.64 Å); the C_3S phase is characterized by the recurrence of intensity maxima (d = 3.04 Å). For the C_2S phase, most intensity maxima are superimposed on the corresponding maxima of other clinker minerals, in particular the C_3S phase (at 2θ = 29.38 deg). Therefore, a maximum was chosen for this mineral at 2θ = 30.94 deg (d = 2.89 Å).

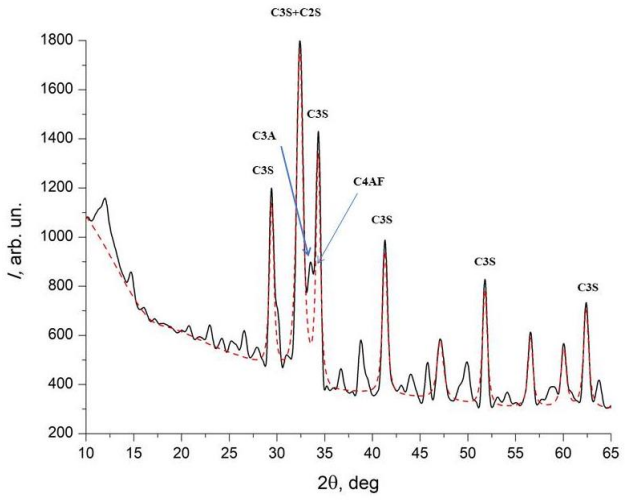

Fig. 1. X-ray diffractogram of cement powder.

The ratio of the main phases of clinker minerals in cement is given in table 1. In general, it should be noted that this ratio of clinker minerals is within normal limits. The use of cement with low C_3S content significantly complicates the production of high-strength concretes, in particular with the use of microsilica and metakaolin, as the effectiveness of these additives implies the presence of excess Portlandite $Ca(OH)_2$ in the hardening system, while systems with low C_3S content are characterized by low content $Ca(OH)_2$.

Table 1.

The proportion (in%) between the main phases of cement in Fig.1

№	Clinker minerals	Chemical formula	Content, %
1	C3S	Ca_3O_5Si	60.4
2	C2S	Ca_2O_4Si	22
3	C4AF	$Al_2Ca_4Fe_2O_{10}$	11.6
4	C3A	$Al_2Ca_3O_6$	6

It is important that the use of cement with a low content of C_3S (less than 50%) significantly complicates the production of high-strength concrete, in particular, when using silica and metakaolin. This is due to the fact that the effectiveness of such additives implies the presence of excess portlandite in the cementing system, while the system with a low content of C_3S is characterized by a reduced content of calcium hydroxide $Ca(OH)_2$ [12].

X-ray analysis of the development of the phase composition of high-strength concrete composites

The data of X-ray and spectral analysis show that in a series of samples of strength of 120 MPa (formulation №2) in the process of hydration of clinker minerals during the hardening of concrete a number of chemically active substances is formed. These are, first of all, calcium oxide hydrate, calcium silicate hydrate (CSH) and such structural models of gel as genite and tobermorite [2-3]. The results of the identification of the formed phases are given in table.2. In Fig. 2 for samples of high-strength composite indexed maxima of intensity correspond to the characteristic products of hydration, in particular: ettringite compounds (1 - $Al_2Ca_6H_{66}O_{49.68}S_3$ - d / n = 0.974; 0.563; 0.388; 0.278 nm); calcium hydrosilicate (4 - $Ca_3H_2O_{7.5}Si_{1.5}$ - d / n = 0.278; 0.335; 0.181 nm); genite (5 - $Ca_9H_{22}O_{32}Si_6$ - d / n = 1.049; 0.262; 0.278 nm); tobermorite (6 - $Ca_2H_3O_{11}Si_3$ - layer thickness 1.1 nm, d / n = 0.308; 0.297; 0.351 nm) [2-3]. Importantly, these maxima are in the same angular positions as the intensity maxima for clinker minerals, in particular for alite (C_3S) and belite (C_2S). This indicates their decisive role in the formation of the cement matrix. Tricalcium aluminate (C_3A), interacting with water and gypsum ($CaSO_4$), forms insoluble calcium hydrosulfoaluminate ($3CaO\text{-}A1_2O_3$ - $3CaSO_4\text{-}31H_2O$), which over time is transformed into calcium hydroaluminates of various basicities. This is observed on the diffraction patterns (Fig. 2). The products of the pozzolanic reaction in the presence of metakaolin can be calcium hydroaluminates of different basicity and variable composition: C_2AH_8, C_3AH_6, C_4AHn. Analysis of the calculated diffractogram (by Rietveld method) for the main hydration compounds (calcite, portlandite,

calcium hydroaluminate and calcium hydrosilicates of different basicity) confirms the presence of these compounds in the phase composition of hydration products, because the geometry of diffraction maxima (fig.2a). At the same time, on the 365th day of hydration on the experimental diffractograms for composites there are differences in the angular positions of the maxima of the compounds of hydroaluminates and highly basic calcium hydrosilicates (Fig. 2b). Such differences are probably related to the generation of a large number of different types of hydrosilicates and calcium hydroaluminates in the phase composition and are a consequence of structural relaxation.

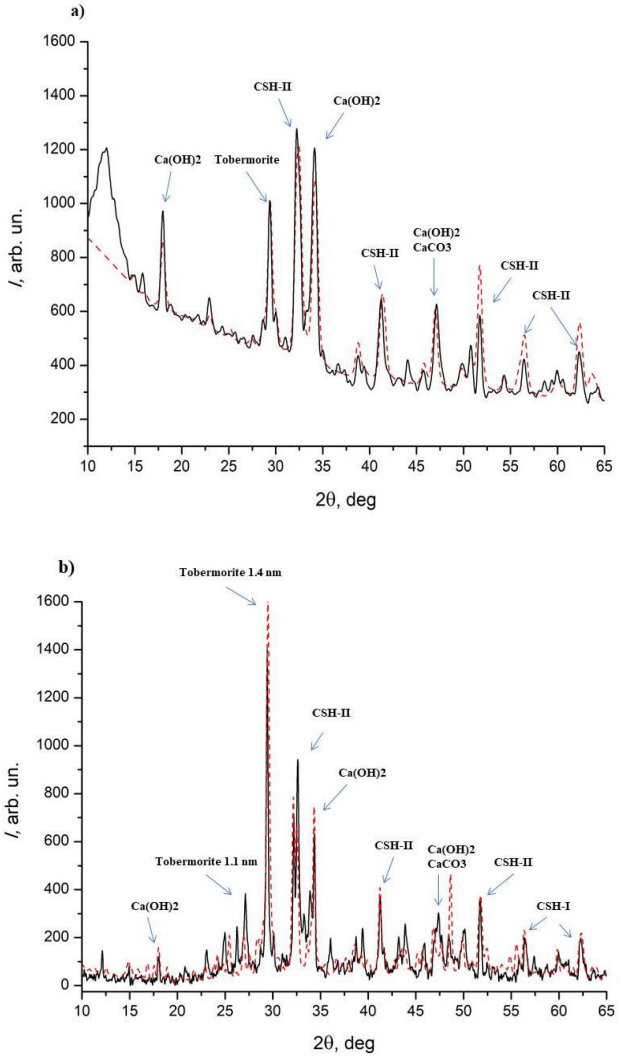

Fig. 2. Calculated (by the Rietveld method, red curve) and experimental (black curve) diffraction patterns of hydration compounds, a) 28 days of hydration; b) 365 day of hydration.

As a rule, the experimental distributions of intensity I (θ) in the region of angles 10-30º (Fig. 2) show strong high-frequency noise and inhomogeneous background, which gradually decreases with increasing angle (. Wavelet filtering techniques were used to eliminate it. This made it possible to more accurately determine the angular positions of the main hydration compounds of the modified composite on X-ray diffraction patterns (Fig. 2).

In general, during the year of hydration (under normal conditions) with the introduction of silica and aluminosilicate modifiers there is a significant weakening of the intensity of $Ca(OH)_2$ peaks (d/n, nm: 0.491; 0.262; 0.192) and highly basic calcium hydrosilicates CSH-II (d/ n, nm: 0.278; 0.335; 0.181). At the same time, the increase in the intensity of the peaks of genite (d / n, nm: 0.262; 0.278) and tobermorite (d/n, nm: 0.308; 0.297; 0.351), which were transformed from low-basic calcium hydrosilicates and are probably intermediate phases before the formation of complex structures. Figure 3 (from Figure 2) shows a separate diffraction pattern of compounds of Ca (OH)2, which is characterized by a weakening of the maxima and integral intensity of the peaks of this compound after a year of hydration is a sign of conversion of soluble calcium hydroxide to strong crystalline CSH-II.

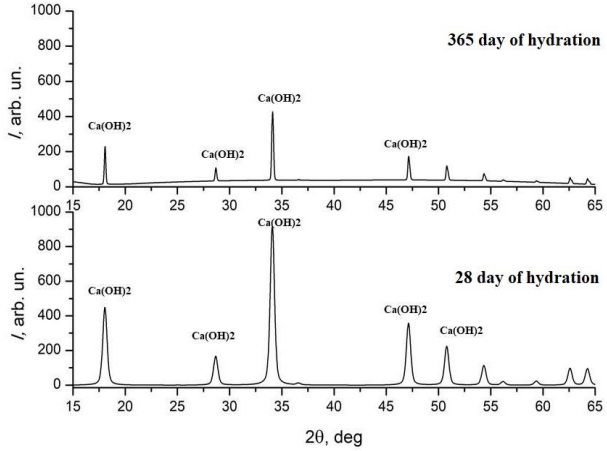

Fig. 3. Characteristic changes in the intensities of the peaks of the compound $Ca(OH)_2$ during the year.

Thus, from the analysis of characteristic changes in peak intensities from the main compounds on the diffraction patterns (Fig. 2) it follows that different types of nanostructures of calcium hydrosilicates with Ca / Si ratio 0.7-1.8 can be obtained from Portlandite Ca $(OH)_2$, SiO_2 and as a result of exchange reactions of compounds of highly basic calcium hydrosilicates with CSH gel.

Conclusion

1. Modification of the cement matrix with a complex of fine silica and aluminosilicate compounds at a certain ratio leads mainly to the formation of low-basic calcium hydrosilicates and such structural models of CSH as genite (d/n, nm: 1.049; 0.262; 0.278) and tobermorite. nm: 0.552; 0.310; 0.301; 0.308; 0.297; 0.351), which have a layered structure and are essentially nanomaterials. These phases were formed from the components of $Ca(OH)_2$ and active silica in the ratio of Ca/Si - 1.1-1.2

2. The introduction of metakaolin promotes the formation of stable hydroaluminates of calcium silicate with maxima on the X-ray diffraction pattern corresponding to d / n ≈ 0.305; 0.275; 0.268; 0.263; 0.262 (nm) and hydroaluminates d/n ≈ 0.276; 0.309 (nm).

3. It is established that on X-ray diffraction patterns

the main maxima of intensity of hydration products are in the same angular positions as the maxima are intense for clinker minerals, in particular, for alite (C_3S) and belite (C_2S). This indicates their decisive role in shaping the structure of the cement matrix.

4. During the year of hydration with the introduction of silica and aluminosilicate modifiers there is a significant decrease in the content of $Ca(OH)_2$ and highly basic calcium hydrosilicates CSH-II with a simultaneous increase in the content of genite and tobermorite, which probably transformed with CSH, which causes strength.

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Х-променева дифракція бетонних композитів високої структурної міцності та щільності

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Досліджено процеси розвитку мікроструктури та гідратації бетонних композитів високої структурної міцності і щільності, які були модифіковані комплексом модифікаторів на основі мікрокремнезему та метакаоліну. Виявлено, що додавання 10% мікрокремнезему в комплексі з 5% метакаоліну та 5% полікарбоксилатного ефіру від маси цементу, створюють умови для перетворення нестабільного і розчинного гідроксиду кальцію в міцний кристалічний гідрат силікату кальцію. Показано, що наявність сполук, які включають Al та Fe на пізніх етапах гідратації, є ознакою утворення вторинних фаз гідроалюмінатів та гідроферитів кальцію. Підвищення міцності на 36% пояснюється оптимальним використанням вільного гідроксиду кальцію та аморфного діоксиду кремнію.

Ключові слова: високороздільна Х-променева дифрактометрія, ультрадисперсні модифікатори, нанокремнезем, метакаолін.