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On Relationship of Surface and Structural Properties of Nano-Modified Cement Composites

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***Abstract* – Surface and structural properties of the cement stone were studied using a complex nanostructured modifier. The surface properties of mixing water with surface-active substances in combination with nanoparticles of bentonite deposits of the Chechen Republic were investigated. The surface tension isotherms were presented. Compositions of complex nano-modifiers reduce surface tension of mixing water. The study on physicomechanical properties of the cement stone with complex nanomodifiers showed an increase in mechanical strength and density. Optimal concentrations of complex nano-modifiers affecting cement composites and their rheological properties were identified. The relationship between surface tension and density of the structure of cement stone was established. Based on the X-ray diffraction patterns obtained using the Selyakov-Scherer model, the sizes of crystallites were calculated.**

Keywords – superplasticizer; surface tension; X-ray studies; nanosuspension; bentonite; dispatching; strength.

I. Introduction

The study of the effect of various complex additives on density and homogeneity of the structure of concrete is an important task in the production of building materials based on cement composites. One of the most effective complex additives is natural and activated bentonites in combination with superplasticizers which are widely used for the production of building concrete.

To achieve a homogeneous structure and optimum density, various plasticizing agents are used. They reduce tension of water and cement which causes its dispersion [1, 2]. However, from economic and ecological points of view, it is necessary to study cheap local natural materials, in particular bentonite as nanostructured concrete additives [3,4].

Since nanostructured additives are systems with a highly developed surface, the leading role of interphase phenomena in forming their properties and interacting with the cement matrix is obvious. It is known that dispersion in aqueous suspensions of bentonites which is a hydrophilic system is spontaneous.

Spontaneous dispersion is uniform distribution of the dispersed phase (distribution of the solute in true solutions). Nano-sized particles can be produced during spontaneous dispersion. These particles can have sizes from 10 nm to 100 hundred nm in width and length, and from 1 to 1.5 nm in thickness [5,6]. They can participate in thermal motion, accumulate at the interface, affect surface tension. The combined use of sparingly soluble surfactants in liquid media should reduce surface tension according to the Antonov rule [9]. The presence of nanoscale particles determines the nature of interaction between suspension and cement in the concrete mixture, being weak stress concentrators causing compaction and hardening of the material. [7]. In [8, 9, 17, 18] emphasize that a decrease in the surface tension increases activity of the dispersion system, causes smoothing of the surface and condensation of the structure of the disperse system.

The purpose of this work is to study the role of surface tension of bentonite suspensions separately and in combination with the Frem Giper S-TB hyperplasticizer in forming the dense structure of the cement stone. In addition, the dependence of surface properties of the dispersed system on concentration is was studied since the concentration factor is one of the important factors determining properties of disperse systems.

II. Methods and materials

The following materials were used: Hyper plasticizer Frem Giper S-TB (Belarus); natural bentonite (the Chechen Republic); Portland cement M500 brand Chiri-Yurt cement plant (the Chechen Republic); tap water.

To measure the surface tension, the samples were produced: water and bentonite powder were measured using the electronic scales. The Frem Giper S-TB hyperplasticizer was added with a DV 100 micropipette, and mixed thoroughly using a PE-6110 magnetic stirrer for 1 minute. Bentonite suspensions were prepared. The study of the size of bentonite particles and their quantitative distribution was carried out on using a Horiba LB 550 laser particle analyzer.

Suspensions were prepared as follows: 120 grams of water were weighed. The amount of bentonite was determined by calculating the concentration of the component, and thoroughly mixed using a magnetic stirrer PE-6110 for 1 min. The suspension was subjected to ultrasound treatment with an IL 100-6 / 2 ultrasound unit for 10 seconds.

Measurements of the surface tension were carried out using a DSA100 tensiometer [10, 11, 13]. The error of measurement was less than 1%. Using the water obtained, cement paste of normal thickness was prepared in six batches for each series of samples. The content of bentonite increased with a step of 0.2% of the mass of cement. The compositions of cement paste and water were selected for each component and for their complex use. The normal density of cement paste was determined according to GOST 310.3-76 "Cements. Methods for determining normal density and setting time. The density of the cement stone was determined by hydrostatic weighing according to GOST 12730.1-2002 Concretes. Methods for determining density. X-ray phase studies of cement stone samples were carried out using a Shimadzu XRD-6000 diffractometer.

Samples for cement stone were produced in standard metal forms, cubes with a fin size of 20 mm. Manufactured samples were removed from the forms after 20 hours, and prior to the strength test they were stored in water at a temperature of 293 K for 28 days. The compressive strength of cement stone was determined by a mechanical destructive method by testing samples using an FS150AT testing machine.

III. RESULTS

It is known that natural bentonites consist of solid particles with sizes of 100-1000 nm. For nanostructured additives, particles of 10 - 100 nm are required. Therefore, in order to disperse, the samples of aqueous suspensions of bentonite were subjected to ultrasonic treatment for 10-15 seconds (frequency - 19.5 kHz, amplitude of alternating sound pressure - 6 atm, amplitude of particle oscillations - 2.42 μm, amplitude of the component influencing the processes in the interfacial layer (3.6x104 m/s^2).

The studies have shown that ultrasound exposure increases stability of the suspension of bentonite and stability factors of coagulation structures by 1.2–1.5, i.e. suspension peptization occurs indicating the effect of ultrasound on the structural and mechanical properties of bentonite.

The surface tension of samples of the bentonite suspension was measured at a temperature of 293K. The results are presented in Fig. 1.

The extremum was observed on isotherms of surface tension at a concentration of 3% by mass (isotherm 2). The monotonic reduction of surface tension to 3% of the mass of the solid phase suggests the maximum accumulation of bentonite particles of colloidal size in the interfacial layer - the left part of isotherm 2. Isotherm 3 shows that the complex use of Frem Giper S-TB and bentonite powder decreases the surface tension and increases concentrations of hyperplasticizer and bentonite (isotherm 1). It reaches its minimum at a concentration of 2% of bentonite mass and surfactant in water.

At an initial concentration of up to 2% of the solid phase in a suspension of bentonite, a decrease in the surface tension to 12 mN/m was observed. It speaks for efficiency of highly dispersed bentonite.

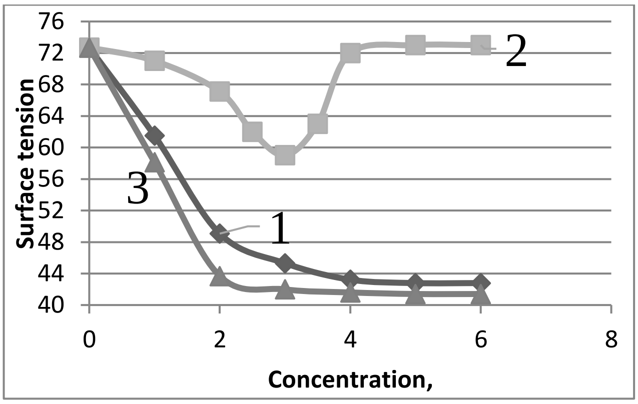

Fig. 1. Tb in water; 2-bentonite suspension in water; 3-bentonite suspension complex FrostGiperS-TB in water.

In order to study the effect of nanoscale additives of bentonite and bentonite combined with surfactants on physicomechanical properties and surface structure of the cement matrix, strength properties of the cement stone were studied.

Using the produced solutions, isoplastic cement mixtures were prepared. Using these mixtures, cement stone samples were produced with dimensions of 20x20x20 mm which were hardening in water for 28 days.

TABLE I. PROPERTIES OF CEMENT STONE PRODUCED USING NANOSTRUCTURED COMPONENTS AND HYPERPLASTER

Cement consumption, g	FremGiper S-TB, % wt. of cement	Bentonite concentration powder,% wt. of cement	Surface tension mN / m	Normal density (ND),%	Density of the cement stone, g / cm ^{3}	Strength, MPa
500			72.7	23.25	2.18	112.5
500		0.2	71.0	23.25	2.204	117.4
500		0.4	67.1	23.25	2.2	121.9
500		0.6	62	24.2	2.16	120.5
500		0.8	60.1	25.3	2.16	114.3
500		1.0	72	26.8	2.11	114.8
500	0.2		63.1	21.2	2.28	122.4
500	0.4		49.1	19.6	2.32	127.6
500	0.6		45.3	18.4	2.32	132.9
500	0.8		42.79	18.25	2.32	131.3
500	1.0		42.75	18.25	2.32	130.2
500	0.2	0.2	56.7	18.5	2.35	133.6
500	0.4	0.4	43.1	17.6	2.35	137.2
500	0.6	0.6	41.6	17.75	2.35	136.8
500	0.8	0.8	41.4	17.8	2.35	132.1
500	1.0	1.0	41.4	17.8	2.34	128.2

Table I shows the indicators of normal density of cement paste according to GOST 310.3-76, density according to GOST 12730.1-2002 “Methods for determining density, surface tension of water with additives and physico-mechanical characteristics of the sample cubes of cement stone 20 * 20 * 20 mm”.

Addition of powdered natural bentonite (Table I) increases the compressive strength of the samples. he maximum value of density and strength is achieved in the range of bentonite concentration from 2.28 to 3.38% in the mixing water.

Data on the strength of concrete depending on the concentration of bentonite (table I) and the surface tension of bentonite suspensions are presented in Fig. 2. The minimum is observed in the concentration of about 3% bentonite weight on the isotherm of the dependence of the surface tension (isotherm 2). Isotherm 1 presents experimental data on the dependence of the strength of concrete samples on the concentration of the solid phase of bentonite in an aqueous suspension used as a combined concrete additive. In the concentration range of 3-4% bentonite weight of the solid phase in the composition of the combined additive, the strength is maximum.

Comparison of the surface tension isotherms of bentonite suspension and isotherms of concrete with bentonite additions at which the minimum is observed in the suspension (Fig. 2) shows that there is a correlation between minimum and maximum parameters. The data indicate the existence of a relationship between the surface tension of water with a complex additive (bentonite-Frem Giper S-TB) and the strength of a cement stone produced using this additive.

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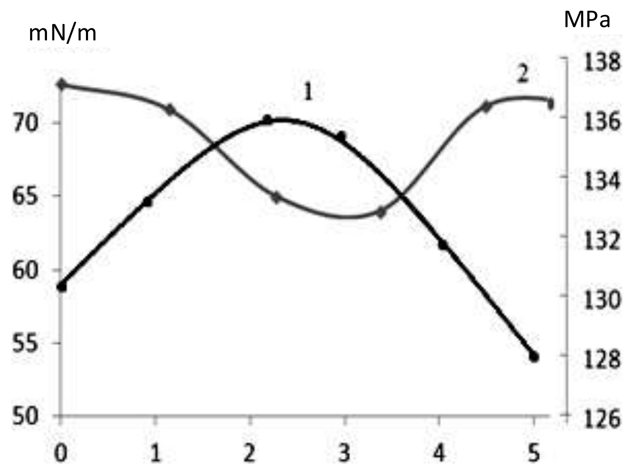

Fig. 2. The dependence of the surface tension and strength of concrete on concentration of the solid phase of bentonite, used as a combined additive to concrete. 1 - dependence of concrete strength on concentration of bentonite in the composition of the complex additive; 2 - dependence of the surface tension on concentration of bentonite in suspension.

The normal density of the cement paste varies slightly. When using Frem Giper S-TB, this value differs from the control one by 24%. The strength of samples produced using bentonite powder as an additive exceeds the control value by 8.4%. This distinctive feature is due to the fact that under complex application of a hyperplasticizer and a bentonite clay, the value of surface tension decreases more significantly than when using each of these additives separately. This contributes to fulfillment of stability conditions for the boundary films of the liquid phase according to [8, 9].

$$\frac{\partial \Pi}{\partial h} < -\frac{m\sigma}{(r+h)^2}$$

where m=2 for convex spherical particles; r – particle radius; h – liquid film thickness; $\partial\Pi$ - propping pressure.

When using Frem Giper S-TB and nanoparticles of a bentonite powder, reduction of the surface tension from 72.7 mN/m to 42 mN/m reduces the film thickness on the convex surfaces of the particles while maintaining stability of this film, which allows for fixing the dispersed particles phase in the dispersion medium at short distances (h). A further increase in the concentration of both components adversely affects strength characteristics of the cement stone, which results from excessive dispersion of cement when mixing with water with a low surface tension value.

To substantiate the reliability of the results and establish their relationship with the microstructure of the cement stone using a X-ray diffractometer Shimadzu XRD-6000, the X-ray structural analysis of the cement stone was conducted.

Figure 3 presents the results of X-ray analysis of cement stone using modifying additives which showed that with increasing strength of cement stone, the intensity of peaks belonging to Portlandite (CH) gradually decreases. In addition, compared with the no-add sample and cement stone based on the addition of bentonite and hyperplasticizer, the intensity of peaks of Alita in the composition with the complex additive is reduced which also implies an increase in the strength of these samples.

The intensity value of the peaks belonging to low-base calcium hydrosilicates CSH (B) in samples with modifiers increased compared with the additive-free composition, and decreased in the peaks of highly basic calcium hydrosilicates CSH (A). This circumstance indicates improved structural characteristics of the cement stone and increased strength of the modified specimens.

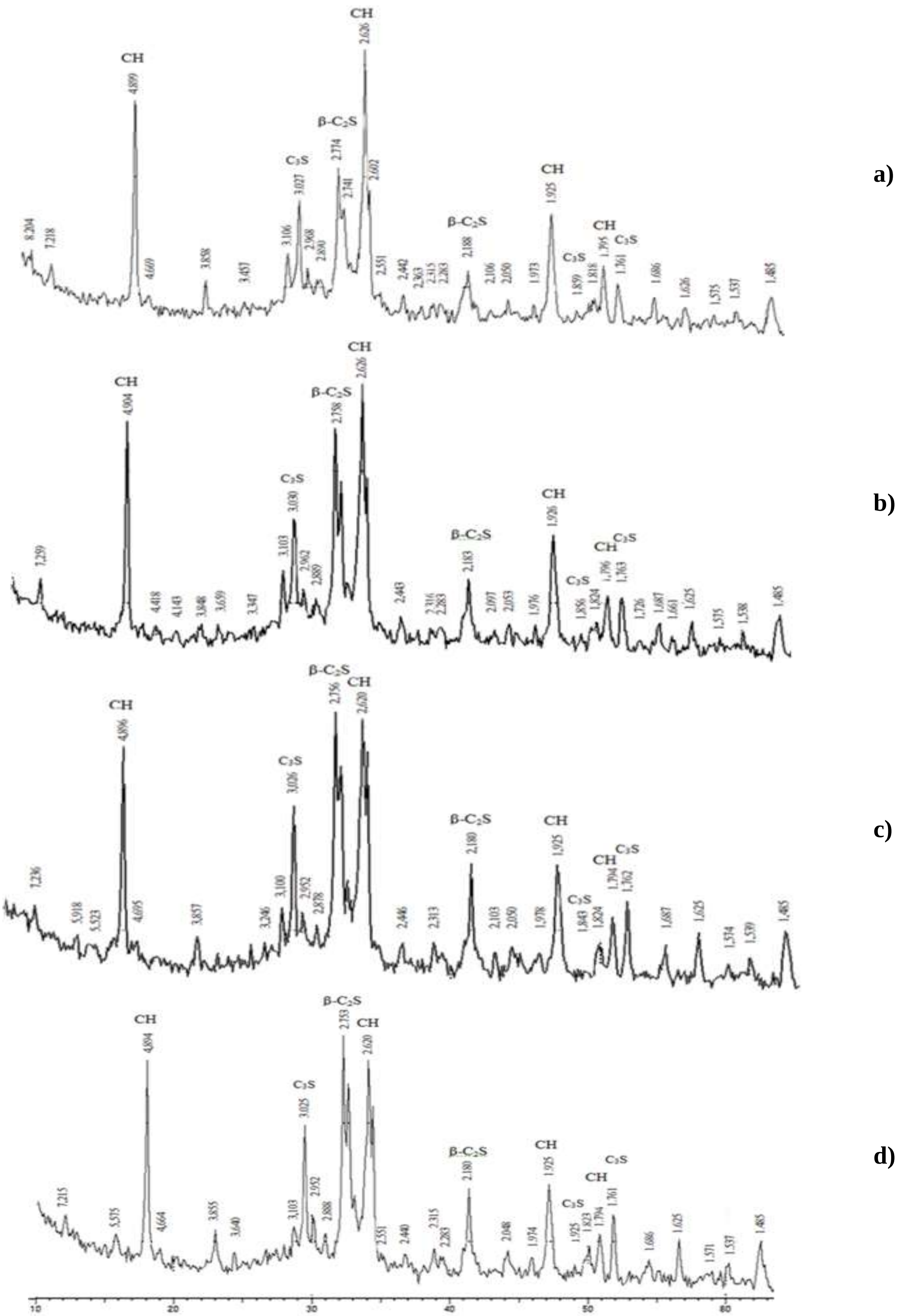

Fig. 3. X-ray phase analysis of cement stone: a) without additives (control); b) with bentonite powder; c) with Frem Giper S-TB; d) with bentonite powder and Frem Giper S-TB.

Table II shows data on X-ray studies of cement stone under the influence of modifying nano-additives. Widths of the peaks in radians at half height were calculated. Table II presents the values of interplanar distances.

TABLE II. X-RAY PHASE STUDIES OF THE CEMENT STONE OF VARIOUS MODIFICATIONS

	Control cement stone (a)		**Cement stone with bentonite powder (b)**		**Cement stone with Frem Giper S-TB (c)**		**Cement stone with a complex additive of bentonite powder and Frem Giper S-TB (d)**	
No of the peak	***Peak width at half height, degrees, θ***	***Interplanar distance d, Å***	***Peak width at half height, degrees, θ***	***Interplanar distance d, Å***	***Peak width at half height, degrees, θ***	***Interplanar distance d, Å***	***Peak width at half height, degrees, θ***	***Interplanar distance d, Å***
1	0.5	4.899	0.56	4.904	0.26	4.986	0.5	4.894
2	0.24	3.858	0.135	3.859	0.22	3.857	0.48	3.855
3	0.31	3.106	0.225	3.103	0.11	3.100	0.28	3.103
4	0.44	3.027	0.465	3.03	0.21	3.026	0.41	3.025
5	0.36	2.741	0.563	2.758	0.28	2.756	0.75	2.753
6	0.55	2.626	0.725	2.626	0.31	2.620	0.47	2.620
7	0.54	2.188	0.5	2.183	0.33	2.180	0.38	2.180
8	0.6	1.925	0.55	1.926	0.51	1.925	0.57	1.925
9	0.32	1.795	0.59	1.796	0.31	1.794	0.41	1.794
10	0.31	1.761	0.375	1.763	0.38	1.762	0.34	1.761
11	0,35	1,626	0,276	1,625	0,28	1,625	0,31	1,625

The structural properties and phase composition of the layers before and after the application of nano-modifying complex additives were studied using the X-ray phase analysis in the region 2θ = 10-80 degrees on CuKα radiation (λ = 1.54056 Å) with a nickel filter.

Assuming that the crystal sizes of the samples have similar sizes in different directions, the Selyakov-Scherer model can be used to estimate crystallite sizes in the polycrystalline system of cement stone [15].

$$L = \frac{K\lambda}{\beta\ cos\theta}$$

On the basis of this model, the dimension of the crystals formed in the cement stone modified with bentonite powder and Frem Giper S-TB separately and in complex was estimated. The analysis of the data (Table II) identified changes in crystallite sizes which may be due to changes in the intermolecular forces of the mixing water expressed in the surface tension (Fig. 1). In addition, according to Table II, with an increasing strength of the cement stone, interplanar distances along the high peaks belonging to the main minerals of the cement stone decrease. The sizes of crystallites calculated by the Selyakov-Scherer model and interplanar distances of the cement stone produced with (compositions 2, 3, 4) and without (composition 1) modifying additives are correlated.

Taking into account the results of structural analysis of the cement ston, as well as the main role of the chemical composition of minerals binder, we can assume a deeper degree of hydration when using water with low surface tension [16]. There is the highest accumulation of hydrosilicates and their hardening which involves convergence of submicrocrystals, displacement and thinning of liquid interlayers, a decrease in interplanar distances and an increase in the strength and density of the cement stone.

IV. CONCLUSION

The research identified the impact of nanostructured mineral complex additives on structural and physicomechanical properties of cement stone. The reduction in surface tension as a result of the use of the Frem Giper S-TB hyperplasticizer and bentonite powder caused thinning of the water film on the convex surfaces of the cement particles while maintaining its stability, which allows cement particles to be located at the closest possible distances. This contributes to consolidation of the structure of cement stone, formation of stronger bonds between closely located particles of cement during its hydration. According to the data obtained by X-ray phase analysis of cement stone, a decrease in interplanar distances and crystallite sizes was identified.

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