

Condition of the Mechanoactivated Calcium Chloride Solution and its Influence on Structural and Mechanical Characteristics of Cement Stone

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Abstract

Using the method of dynamic light scattering we investigated the influence of the rotor and pulse impact on a dimensional change of particles in calcium chloride hydrosol used as texturing additives in concrete mixing. The mechanism of the strengthening action of the additive is shown by the results of an assessment of the parameters of the pore structure of the cement stone which is carried out by the method of the low-temperature adsorption and desorption of nitrogen vapors. With the use of the method of the low-temperature adsorption desorption of nitrogen for the analysis of porosity of the experimental exemplars of the cement stone received with the use of the mechanically activated CaCl₂ solution, decrease in the area of a specific surface area in 1.7 ... 2.1 times and the volume of pore spaces by 1.6 times that is caused by preferred decrease of the maintenance with the diameter over 6 nanometers and decrease in an upper bound of pore size from 160 to 90 nanometers is shown.

1. Introduction

The modern approaches to increasing the physical and mechanical properties of concrete are based on the formation of the optimum structure of the cement stone that can be achieved, in particular, by means of the chemical modifiers affecting physical and chemical processes of concrete hardening [1]. In building calcium chloride is more often used for softening and accelerating of hardening [2].

Due to the development of nanotechnology in recent years much attention is paid to the perspective direction of solid-phase construction of structural materials by using additives in a nanodispersible state and creation of the systems including nanodimensional elements as part of the structure [3]. At the same time an independent way of the development of nanotechnology can be considered the explanation of well known processes on a nanolevel [4]. Among similar processes an important place is taken by cement hydration, the incipient state of which is the mixing of cement paste. Because of the structural change of water by means of additives, it has a great influence on the process of hydration and morphology of new crystal growths [5].

Along side with chemical modification, the area of interest are the methods of mixing water activation providing its transfer to a metastable state and having a positive impact on the processes of hydration and structure formation in the received materials that is shown in the improvement of their production characteristics. Influence of electro-processing [6], electromagnetic [7] and ultrasonic [8] activations of water mixing on properties of cement composites is widely presented in literature. At the same time data on the condition of texturing agents in the mechanically activated solutions, on the extent of transformation of the structure of the formed materials to interrelations with changes of their strength characteristics are extremely limited [9], complicating the development of scientifically based approaches to the achievement of target effects of improvement of the physical and mechanical properties of concrete designs.

The purpose of the work consisted in carrying out by high-precision methods of the quantitative assessment of the influence of mechanoacoustic processing calcium chloride hydrosol widely applicable as the modifier of cement mortars on a dimensional change of particles of a disperse phase,

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parameters of porosity of the formed cement stone and its strength characteristics.

2. Experimental

In researches we used calcium chloride anhydrous (GOST 450-77) purity class «Clean» (technical specifications 6-09-4711-81), portland cement M500 D0 (GOST 10178-85).

Determination of the particle size in calcium chloride hydrosol is carried out by the method of dynamic light scattering [10] on the Zetasizer Nano ZS analyzer (Malvern Instruments Ltd England). For the elimination of methodical mistakes and achievement of the necessary degree of purity of the calcium chloride solutions, taking into account recommendations [11], were prepared with the use of the bidistilled water subjected to padding cleaning on the columns filled with KU-2 ion-exchange resin. Selection of solutions for research on the Zetasizer Nano ZS analyzer was carried out by using disposable syringes, and measurements were carried out in disposable basins of Rotilabo-disposable cuvettes (Carl Roth GmbH+Co.KG, Germany). Control of the measuring system of the device is carried out by taking into account a spherical form of particles and the recommended [12] Refractive Index values for a disperse phase (RI = 1.52) and a dispersion medium (RI water = 1.33).

Mechanoacoustic processing of calcium chloride solutions was carried out on the laboratory rotor and pulse A-1.00.00 PS installation providing complex impact on the processed system of shift loadings, cavitation and ultrasound [13, 14]. Results of effectiveness of carrying out mechanical activation in the mode: speed of rotation of a rotor of installation 4200 rpm and processing time 150 sec are presented in the present article.

When receiving the compared exemplars of the cement stone, preparation of the cement mass (a cement mixing) was carried out with the use of distilled water and the mechanically activated calcium chloride solution in the above mode with the concentration from 0.032 ... up to 0.965 mol/l that corresponds to the maintenance of an additive 0.1 ... 3% of the cement mass at water-cement ratio 0.28. Duration from the moment of mechanical activation of CaCl₂ solution before its application did not exceed 1.5 h.

For carrying out researches of mixing liquid mechanical activation influence on properties of the cement stone from the cement mass of normal thickness exemplars sized 40×40×16 mm were formed.

In 24 h exemplars were out of the form and hardened under standard conditions. Values of ultimate strength of exemplars during compression and bending were defined after endurance within 28 days.

The assessment of porosity and the specific surface area of the cement stone exemplars are carried out by the method of low-temperature (77 K) adsorptions and desorption of vapors of nitrogen on the NOVA Series 1200e gas analyzer. The area of the specific surface area was calculated according to the BET equation [15]. The total pore volume in the analyzed materials and pore distribution by the sizes was determined with the application of the BJH model.

Tests of exemplars for durability were carried out by a reference technique according to the requirements of GOST 310.4-81 on the hydraulic presses PG-100 and IPS-200.

3. Results and Discussion

Chloride of calcium belongs to a number of restrictedly dissociating connections, in this regard it is logical to expect existence of a disperse phase in its solutions. At the same time in the studied range of concentration 0.032 ... 0.965 mol/l solutions possess an optical transparence both at a direct vision and at an assessment by the method of laser diffractoscopy on the Analysette 22 Compact analyzer of particle size which is widely used in studying conditions of dispersions with the particle size in the micrometer range. Lately for the analysis of particle sizes the wide prevalence finds the method of dynamic light scattering DLS (Dynamic Light Scattering) [16, 17] in sols. Its physical basis consists in measurement of fluctuations intensity of scattered light when passing a laser beam through environment in which, because of a Brownian motion of dispersible particles or macromolecules fluctuations of the local concentration of particles take place. Local inhomogeneities of refraction index according to fluctuation of intensity of the scattered light take place as a result.

As shown in Fig. 1, the DLS method allows recording reliably the existence of the disperse phase in CaCl₂ solution on an upper bound of the nanometer range. With salt strengthening the provision of an intensity response of light scattering is displaced towards the micrometer range, showing polyfractional composition of the system and the presence of forms with a different extent of agglomeration.

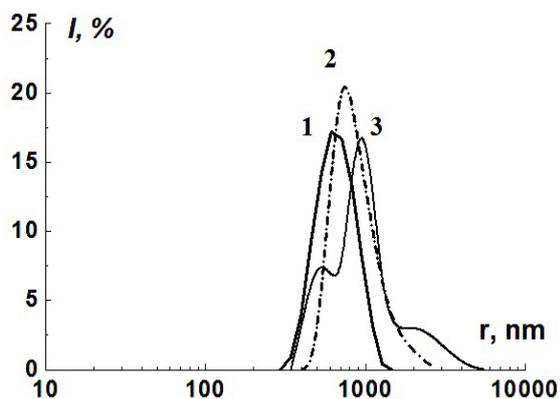


Fig. 1. Particles size distribution (r , nanometer) of the light scattering relative intensity indicator (I , %) in CaCl_2 solutions (mol/l): 1 – 0.032; 2 – 0.48; 3 – 0.965.

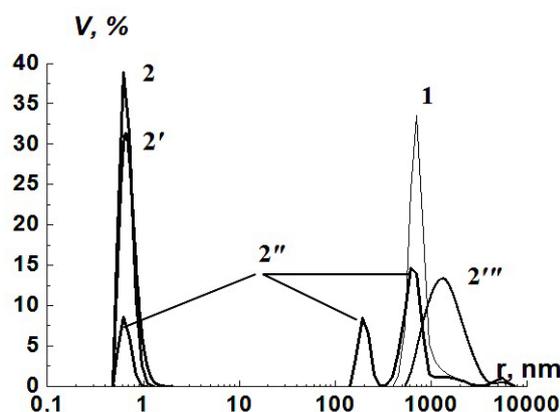


Fig. 2. Size distribution of the indicator of the particles relative volume (V , %) in initial (1) CaCl_2 solution (0.032 mol/l), after mechanoactivation (2) and additional endurance within 1, 3 and 7 days (corresponding 2', 2'' and 2''').

The computer program of the device allows along with data of change of the relative intensity level of light scattering presented in Fig. 1 (I , %) to receive information in the form of the fractional distribution on particle size (r , nanometer) indexes of the relative volume of a disperse phase (V , %) and a relative number of particles (N , %). For the solution containing 0.032 mol/l of salt as a result of mechanical activation the same nature change of these indexes of a condition of hydrosol which is shown in Fig. 2 as an example of transformation of the schedule of distribution of $V = f(r)$ right after carrying out processing and at the subsequent endurance within 1–7 days is recorded.

As presented in the monomodal type of the distribution curve of the relative volume of particles takes place both for the mechanically activated system, which shows completeness of the course

of processes of sampling. The analysis of curve 2 showed that over 97% of the volume of a disperse phase consists of fractions of particles with the size of 0.53 ... 0.83 nanometers. The condition of the system is metastable to which decrease in the peak of the dominating fraction of 0.62 nanometers by 5.6% a day after imposing of the rotor and pulse influence and increase in the relative volume of fractions with particle size more than 1 nanometer to 8.06% testifies. Three days later the bulk volume of fractions less than 1 nanometer makes only 20% and the distribution curve takes a polymodal form. It is apparent that the system not simply runs down in an initial state, and finds new structural formations to the existence of a brachium on a curve 2'' in the range of 1 ... 2.6 microns and also emergence fashion in the range of 5 microns testifies. After seven-day endurance the fractions in the near micrometer range with preservation of 1.5% – shares of the relative volume of particles in the zone of 5 microns are dominating.

At the same time it is possible to take for granted that for technologically acceptable time period making not less than 24 h as a result of mechanoacoustic processing sampling of a disperse phase to the sizes less than 1 nanometer is provided. The strengthening action of the mineral additives entered into structural compositions is connected, as a rule, with the emergence of multiple crystallization centers in the cement mortars promoting increase of speed and uniform of formation of the spatial structure of the baked material [18]. Considering the nature of proportionality growth of the particles number filling the unit volume at decrease of their size, it is logical to expect that the 2nd reduction of the dimensional parameter observed is followed by the particles number increase in the system 9 decimal orders.

The avalanche origin of nanoparticles of a solid phase after imposing of rotor and pulse influence is fair to connect with the course of the initiated hydrolysis sols with the formation of the oxyhydroxide:



Its water solubility at a temperature of 20 °C is 465.6 times lower than for the mother compound [19]. Replacement as a part of a molecule chloride ion, possessing high electrophilic properties, is the factor favoring the interaction the hydrosol particles with the low-polar forms of the calcium silicates – the bases of a cement clinker, as well as with the molecules of the knitting portland cement components.

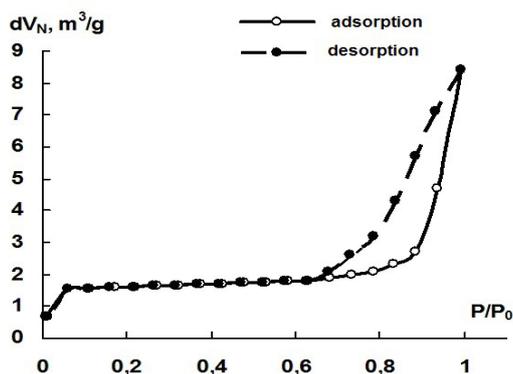


Fig. 3. Isotherms of low-temperature adsorption-desorption of nitrogen on a sample of a cement stone № 1: dV_N – the volume of the sorbing and desorbing nitrogen, m^3/g ; P/P_0 – change of nitrogen vapors pressure.

Validity of the made assumptions confirm the results characterizing change of the pore structure of the cement stone when used for distilled water for mixing cement (exemplar 1 control) and the mechanoactivated calcium chloride solution with concentration of 0.032 mol/l (test item 2, the experimental). In Fig. 3 the course of adsorption isotherms and a desorption of nitrogen at change of vapors pressure P/P_0 nitrogen for exemplar 1 is shown. Received for the studied objects the adsorption isotherms of nitrogen belong to the IVth type on classification of IUPAC. Such type of isotherms is characteristic for the solid bodies having a mesopore according to Dubinin's classification [15, 20]. The sharp raising

of a sorption curve which is therefore observed at P/P_0 values close to 1, indicates existence of large pores in exemplars.

The data of the analysis of the course of the increasing (adsorption) branch of the curve with application of the VET method and on the falling (stripping) branch presented in Table 1 by means of the BJH model show consistent result of the use of the mechanically activated calcium chloride solution. It is expressed in the reduction of indexes of the area of the specific surface area by 1.7 ... 2.1 times and the volume of pore spaces by 1.6 times.

Data shown in Table 1 are supplemented with characteristics of distribution of indexes of S_{sa} and V_p presented in Fig. 4 by the size of the pores (D , nanometer). Results of the analysis confirm that the studied objects are mesocellular bodies with a small contribution of micropores. In the control specimen the range of the diameter makes from 3 to 160 nanometers. In the experimental exemplar the lower bound of the pore size did not change and the top bound decreased to 90 nanometers. Thus distinctions of indexes of porosity are shown more significantly in the process of increase of the pore size.

The contribution of different diameter porosity indexes can be reflected by means of the differential characteristics provided on Fig. 5. The given type of dependence reflects the relative size of the increment of the index of porosity in the process of the padding accounting of pore fractions with higher values of the diameter.

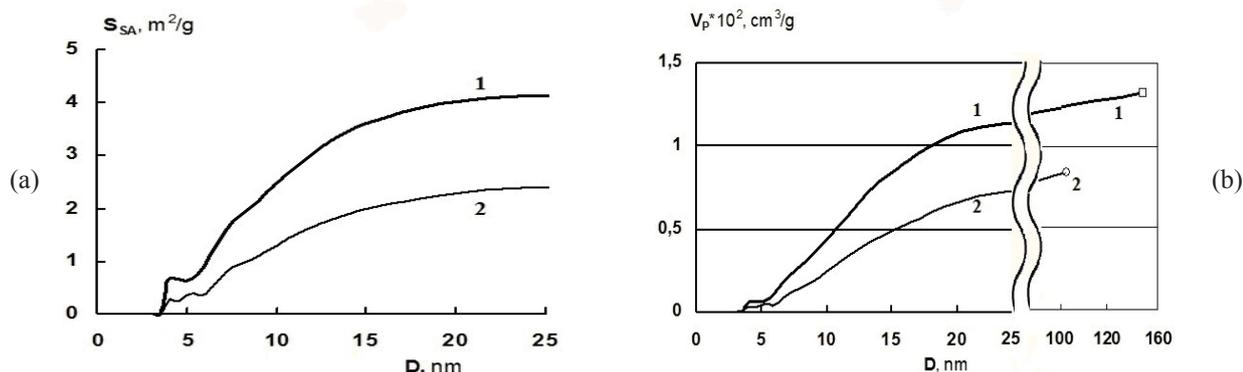


Fig. 4. Diagram of the specific surface area (S_{sa} , $sq.m/g$) (a) pore size distribution (D , nanometer) and the pore volume (V_p , m^3/g) (b) in samples of cement stones 1 and 2.

Table 1
Characteristics of the pore structure of exemplars of the cement stone

Exemplar number	Specific surface area, S_{sa} , $sq.m/g$		Bulk volume of pores, V_p , cm^3/g
	VET method	BJH method	
1	1.941	4.169	0.0130
2	0.869	2.485	0.0083

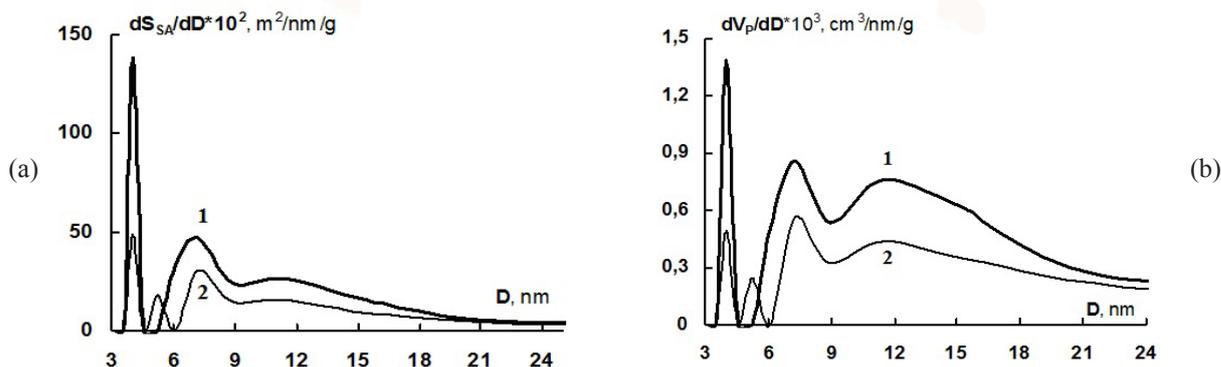


Fig. 5. Differential size curve distributions by the specific surface area ($dS_{SA}/dD, cm^2/nanometer/g$) (a) and the pore volume ($dV_p/dD, cm^3/nanometer/g$) (b) in samples of cement stones 1 and 2.

Table 2

Test data of exemplars of the cement stone on durability

Solution strength of $CaCl_2, mol/l$	Quantity of an additive, % of the mass of cement	Mechanical activation	Ultimate strength, MPa	
			during compression, $P_C \pm 0.5$	during bending, $P_1 \pm 0.2$
-	-	-	41.7	5.3
0.032	0.1	-	44.6	6.1
		+	48.6	7.4
0.48	1.5	-	46.8	6.8
		+	47.9	7.0
0.965	3	-	47.6	7.0
		+	48.0	7.2

Apparently, the dominating contribution in the control specimen is provided by pores with a diameter of 4 nanometers and also 7.0 ± 1.0 and 11.5 ± 1.5 nanometer. In the experimental exemplar emergence of a padding strip of the dominant pore size 5.0 ± 0.5 nanometer is observed against decrease in amplitude of the specified dimensional extremums.

Thus, use for obtaining cement mass of the mechanically activated solutions of calcium chloride provides decrease in integral indexes of porosity of the formed cement stone reducing the size of the maximal diameter of pores by 1.8 times and leveling the distribution of pores size of indexes of a specific surface area and the volume of pore spaces. Decrease of the deficiency of the cement stone structure and especially the amount of mesopores with large cross sectional dimensions (up to 160 nm) has to reduce probability of a stress concentration on the weakened structural places under the influence of an external loading up to 160 nanometers promote redistribution of efforts and increase of the mechanical stability of the material.

Validity of this assumption is confirmed by the

changes of indexes of the ultimate strength of exemplars of the cement stone presented in Table 2 during compression and stretching on a bend. The received results testify that presence of an additive in the liquid used for a cement mixing and carrying out its mechanical activation promote the unidirectional change of strength indexes of the cement stone towards their increase. In case of a small salt concentration (0.032 mol/l) the influence of the second factor prevails over the relative size of an increase of indexes for the option of non-activated solution using in 2.4 ... 2.6 times. Apparently the increase in quantity of crystallization centers as a result of the mechanically activated ultradispersion of the modifying additive in this system is shown to maximal degree. The equivalent changes of strength characteristics are reached by the extensive way when strengthening salt concentration almost 30 times more.

It is interesting to note that the contribution of the mechanoacoustic influence is reduced with increase in the maintenance of an additive and strength characteristics of the material are approximately the same. Perhaps it is bound up with competitive

manifestation of the secondary influence of the high concentrated solutions of the mineral modifier subjected to mechanical activation course of structural transformations, bound to excessive distribution in volume of cement dough and premature initiation of processes of concreting. The results of researches open relationship of cause and effect of the serial changes generated by carrying out mechanical activation of solution of a mineral additive to cement compositions and allow to create a scientific reserve for the development of technological approaches of perfecting of structure and strength properties of concrete materials and designs.

4. Conclusions

1. The interrelation between changes of a condition of the disperse phase as a result of the rotor-pulse impact on solutions of calcium chloride pore structure and strength indexes of the cement stone formed with the use of the mechanically activated systems is traced.

2. With the use of a method of the dynamic light scattering it is shown that in the activated CaCl_2 solution with concentration of 0.032 mol/l particles size decreases from 500 ... 900 nanometers to 0.5 ... 0.8 nanometers; it causes increase of 9 decimal orders of the quantity of the potential crystallization centers of cement composition.

3. With the use of the method of the low-temperature adsorption desorption of nitrogen for the analysis of porosity of the experimental exemplars of the cement stone received with the use of the mechanically activated CaCl_2 solution, decrease in the area of a specific surface area in 1.7 ... 2.1 times and the volume of pore spaces by 1.6 times that is caused by preferred decrease of the maintenance with the diameter over 6 nanometers and decrease in an upper bound of pore size from 160 to 90 nanometers is shown.

4. Decrease of the deficiency of the structure of the exemplars of the cement stone received with the use of the mechanically activated aqueous solutions of CaCl_2 for preparation of cement will be coordinated with the data of an increase of indexes of ultimate strength of compression of 15 ... 17% and for bending of 32 ... 40% in comparison with the traditional mode of the cement water mixing. The maximal distinction (in 2.4 ... 2.6 times) with the results of the use of non activated solution of salt is received for concentration of 0.032 mol/l; the effect corresponding to the results of 30-fold increase in the maintenance of CaCl_2 .

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