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Hydrophobization of Concrete Using Granular Nanostructured Aggregate

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Abstract. The possibility of giving hydrophobical properties to the fine-grained concrete matrix by using a granular nanostructured aggregate (GNA) with a hydrophobizing additive is investigated in this work. GNA is obtained by granulating the silica raw material with an alkaline component. The introduction of a hydrophobizing additive into the raw mix of GNA allows to encapsulate it reducing the negative effect on hydration processes, the intensity of migration of moisture and efflorescence in concrete and, consequently, improving the performance characteristics of fine-grained concrete products. The hydrophobizing ability of a solution of sodium polysilicates formed in the core of GNA during concrete heat and moisture treatment is proved. The analysis of IR spectra after the impregnation of cement stone samples with a solution of sodium polysilicates showed an increase in the degree of hydration and the formation of framework water aluminosilicates. Atmospheric processes modelling showed that the use of GNA on the basis of gaize with calcium stearate and on the basis of fly ash with GKZh-11 makes it possible to increase the resistance of fine-grained concrete to the atmospheric effect of the medium, namely, the outwashing of readily soluble compounds.

1. Introduction

Repeated exposure of moisture on concrete products during operation leads to rapid loss of esthetic properties as a result of efflorescence and premature failure. For products used in wet conditions, water absorption is one of the main factors determining the ability to maintain physical and mechanical properties for a long time. The task of its reduction becomes particularly important for fine grained concrete products, which, as a rule, are used for the production of various types of thin-walled products that are more subjected to aggressive environmental influences [1-3].

The solution of this problem is to provide the concrete matrix with water repellent properties due to the introduction of hydrophobizing additives. However, a side effect of their use is a reduction of hardening rate and ultimate strength of concrete products.

The following methods for introducing of hydrophobizing additives into concrete mixture are known: subsidence of a hydrophobisator on a mineral carrier by co-milling; saponification of water-insoluble products; emulsification; agglomeration into granules, briquettes, tablets, granulated powders. These methods are used to transfer water-insoluble additives to water-soluble products, as well as to reduce the negative effect of additives [4].

Of these methods, one of the promising is application of mineral raw materials, or industrial waste, as a factor in ensuring energy and resource saving [5-8].

Analysis of methods for reducing the negative effect of hydrophobizing additives on cement hydration processes and alternative ways to reduce water absorption of fine-grained concrete allowed us to formulate the hypothesis of this study, consisting in the possibility of providing a prolonged volumetric hydrophobization of the concrete matrix by introducing a hydrophobizing additive (HA) into the granular nanostructured aggregate. This allows to encapsulate the hydrophobisator and to reduce its negative effect on hydration processes, and in the future will lead to a decrease in the intensity of migration of moisture in the mass of concrete and efflorescence, and, consequently, to improve of the performance characteristics of products from fine-grained concrete [9-12].

The use of a granular nanostructured aggregate as a carrier of a hydrophobizing additive is promising for the production of products with increased hydrophobicity due to the fact that it, firstly, itself has a hydrophobizing effect on the concrete matrix due to its impregnation with solutions of sodium polysilicates during heat activation of the aggregate, secondly, its prolonged action is designed to minimize the negative impact of aggregate content on the process of concrete hardening [13-16].

The hydrophobing effect of solutions of sodium polysilicates, as an analog of liquid glass, is due to the formation of water repellent films of silicate composition on the surface of the pores and voids of the concrete matrix. These solutions can be prepared by reaction between silica and alkaline components [17]. In connection with the above, the effect of solution of sodium polysilicates on the water absorption of cement stone, its composition and resistance to outwashing of soluble compounds during repeated exposure of moisture will be determined in research.

2. Experimental program

2.1. Materials

As silica raw materials for the preparation of solutions of sodium polysilicates and the manufacture of the core of a granular nanostructured aggregate, silica raw materials of various origins were used: natural – gaize of Alekseyevskoye deposit (Republic Mordovia, Russia) (table 1, table 2); technogenic – fly ash of the Novotroitsk thermal power plant (Orenburg region, Russia) (table 1, table 3).

Table 1. Chemical composition of silica raw materials.

Silica raw material	Content of oxides, mass %								
	SiO_2	AI_2O_3	Fe_2O_3	MgO	K_2O	CaO	TiO_2	Na_2O	other
Gaize	87.27	5.91	2.42	1.53	1.19	0.82	0.29	0.28	0.29
Fly ash	54.44	29.35	5.85	3.82	1.88	1.77	1.06	1.03	0.8

Table 2. Mineralogical composition of gaize.

Content of mineral, mass %				
Quartz	Cristobalite (low temperature)	Tridymite (low temperature)	Biotite	Amorphous phase
3.89	8.97	2.19	1.85	83.10

Table 3. Mineralogical composition of fly-ash.

Content of mineral, mass %				
Quartz	Mullite	Anorthite	Magnetite	Glassy phase
10.70	23.50	4.30	1.00	60.50

Sodium hydroxide according to Russian State Standard 55064–2012 was used as an alkaline component of the core of the aggregate. An aqueous solution of sodium silicate (liquid glass) according to State Standard 13078–81 (2005) with density of 1200–1300 kg / m^3 was used as a binding agent.

As a hydrophobizing component of the core of the aggregate the following additives were used: calcium stearate (powdered stearate – sal of stearic acid) and GKZh-11 BSP (hydrophobizing organosilicon alcohol free liquid) (sodium methylsiliconate solution).

As a binder, as well as for the creation of a shell of granular nanostructured aggregate, portland cement CEM I 42.5 N produced by ZAO "Belgorod Cement" was used.

2.2. Experimental procedure

To evaluate the hydrophobizing properties of solutions of sodium polysilicates with a hydrophobizing additive, model systems of pure solutions were obtained. When obtaining model systems, an express method was used, which was previously developed to determine the activity of silica raw materials [18]. Weighted amounts of gaize and fly ash were subjected to milling with HA and without them. Then the resulting materials were mixed with a solution of NaOH (10% for the gaize and 2% for the fly ash) and subjected to a heat and moisture treatment in the steam chamber for 2 hours at 80 ° C. The heat-treated suspension was filtered. Then, samples made of cement paste with normal density based on Portland cement were held in the filtered liquid for 8 hours.

The effectiveness of the impact of hydrophobizing solutions of sodium polysilicates was evaluated according to the degree of decrease of water absorption of cement stone treated samples [19] in comparison with untreated (control) (table 4).

The decrease of water absorption P_w was calculated from the formula [19]:

$$P_W = \frac{W_{control}}{W_{basic}} \tag{1}$$

$W_{control}$ – is the water absorption of samples of the control composition held in water to full saturation, % by mass; W_{basic} – water absorption of samples of basic composition held in water for 28 days, % by mass.

IR spectra of impregnated cement stone were obtained using a VERTEX 70 infrared Fourier spectrometer in a spectral range of 370 to 7500 cm^{-1}.

Simulation of atmospheric processes was carried out using a Soxhlet extractor. This device allows to reproduce the water circulation and prolonged washing of the samples placed in the main cylinder-extractor of the device (figure 1).

The extractor consists of a cooling compartment (1), an extractor cylinder (2), and a flat-bottomed flask (3), connected to each other by conical ground-glass joints (figure 1).

Samples of fine-grained concrete with a granular nanostructured aggregate were placed in the cylinder of the device (1). Distilled water in an amount of 500 ml was poured into the receiver flask of the filtrate (2). The filtrate receiver flask was placed on a heating element to intensify the evaporation of water. The cooling compartment (1) was connected by plastic pipes to the source of running water to cool the water vapor and form a condensate. The formed condensate got on samples of fine-grained concrete, filtered through them and was accumulated in the cylinder. After reaching a certain level in the cylinder, the infiltration water containing substances washed from the samples was drained through the side siphon tube into the lower receiver flask.

The device design allows simulating the processes occurring in three zones (see figure 1, c): “atmospheric” (non-watered) (NW) (4), in the upper part of the cylinder where the sample is in a constant moist environment in contact with air, water is constantly filtered through the sample; partially watered (PW) (5), where the state changes from full watering to a humid atmosphere; watered (W) (6), where most of the time the sample is immersed in water.

The use of the Soxhlet extractor allows continuous monitoring of the character of the transformation of concrete samples at different stages of the process. The use of this method makes it possible to create the most reliable “model” of surface erosion processes and study the behavior of the basic chemical elements under conditions closest to natural ones. After simulating atmospheric processes, both the solid residual erosion phase and the filtrate were studied.

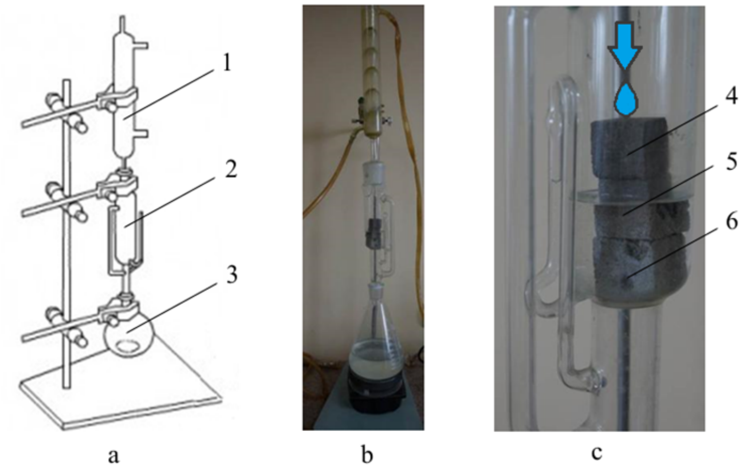

Figure 1. Appearance of the Soxhlet extractor (a, b) and the arrangement of the samples in the cylinder (c).

Samples of fine-grained concrete with a granular nanostructured aggregate (cement-sand ratio = 1:3, water-cement ratio = 0,5, granular nanostructured aggregate content – 30% of the dry mix volume), after 28 days of hardening after heat and moisture treatment were used for this experiment. A granular aggregate consisting of a core (a mixture of silica raw material and a hydrophobizing additive (co-milling), NaOH solution, and a liquid glass) and a protective cover (portland cement) was produced using a plate granulator.

3. Results

3.1. Effect of sodium polysilicate solution on the water absorption of cement stone

The obtained results show that impregnation with solutions of sodium polysilicates significantly reduces water absorption of cement samples in comparison with control (non-impregnated) ones (table 4). Despite the fact that fly ash contains less amorphous phase, sodium polysilicates based on it have high hydrophobic properties. This can be explained by the higher content of aluminum compounds in the fly ash that acts as solidifier of sodium polysilicates.

Table 4. Degree of decrease in water absorption of samples of cement stone after impregnation with solutions of sodium polysilicates of various composition.

Raw materials used for preparation of solutions of sodium polysilicates (all compositions have NaOH)	Water absorption, %	Degree of decrease in water absorption in comparison with control (non-treated) sample
Gaize	4.58	2.06
Gaize + GKZh-11 BSP	2.06	4.57
Gaize + calcium stearate	1.25	7.55
Fly ash	4.35	2.17
Fly ash + GKZh-11 BSP	2.09	4.52
Fly ash + calcium stearate	2.65	3.56
Control (non-treated))	9.43	–

The best results are observed in samples treated with solutions of polysilicate based on gaize with calcium stearate and fly ash with GKZh-11 BSP.

Therefore, to obtain highly hydrophobic building composites using granular aggregate based on silica raw materials, importance is not only in the activity, but also in the presence of compounds that promote the solidification of sodium polysilicates solutions that ensures the formation of water-resistant films on the surface of particles and in the pores of cement stone.

3.2. Effect of sodium polysilicate solution on the composition of cement stone

After steamed cement samples were held in solutions obtained from NaOH, water and, respectively, gaize and fly ash, the character of the IR spectra changes significantly with respect to the simply hydrated system (figure 2). Attention is drawn to the external similarity of the results obtained on two different solutions, which may indicate the identity of the occurring processes.

Taking into account the fact that hydration continues in the samples immersed into solutions, we should note a further increase in the gross content of carbonates in the cement stone (figure 2). This should also contribute to the partial carbonation of the solution itself, which penetrating, including inside the sample, during subsequent drying and sample preparation increases the total content of carbonates in the system. It should be noted that it is rather difficult to clearly determine the material composition of these phases, namely the cations (Ca^{2+} or Na^{+}) and the anions (CO_3^{2-} or HCO_3^{-}) forming them.

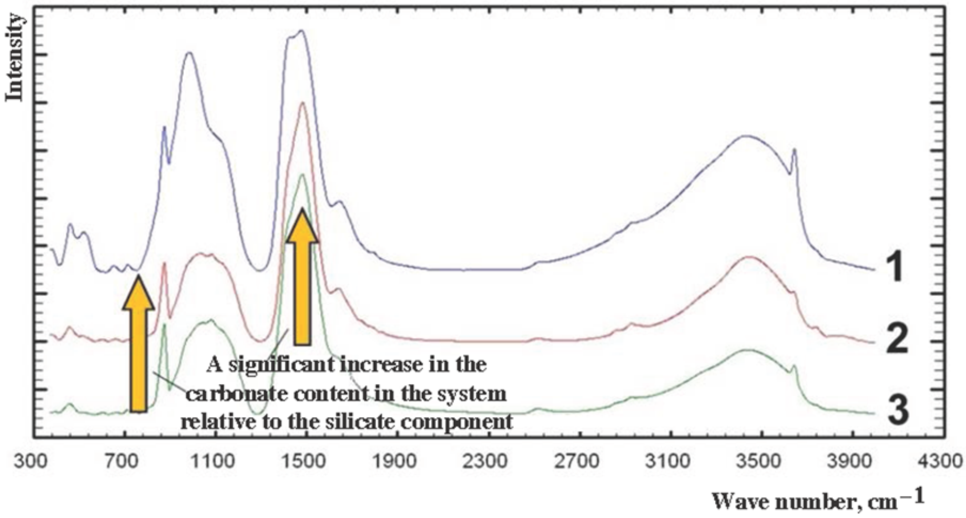

Figure 2. Influence of treatment with solutions obtained on the basis of NaOH, water and, respectively, the gaize (2) and the fly ash (3) on the IR spectra of hydrated cement stone (1).

Evidence of continuing hydration is a decrease in the intensities of the absorption bands at 984, 522, and 460 cm^{-1} [20] (figure 3). This can be characterized as a gradual decrease in the content of the silicon-oxygen ortho groups Q1, indicative for C_3S and C_2S. When they are bound during hydration, an increase in the degree of polymerization of the silicate motif takes place, with the formation of a C–S–H gel first, and following formation of calcium nanoscale hydrosilicates that are not recognized by X-ray diffraction. The increase in the Si–O polymerization is indicated by the shift in the maximum of the stretching band of the bridge-type Si–O–Si bonds from 984 cm^{-1} to the 1000–1100 cm^{-1} area with occurrence of two local maxima at 1033 cm^{-1} and 1082 cm^{-1} (fig. 3). The presence of the last peak can be explained by the appearance in the system during treatment at solution of water-soluble sodium silicates (both on the basis of a gaize and fly ash) of the framework water aluminosilicates - zeolites with a maximum degree of connectivity Q4 , which were also detected by X-ray phase analysis.

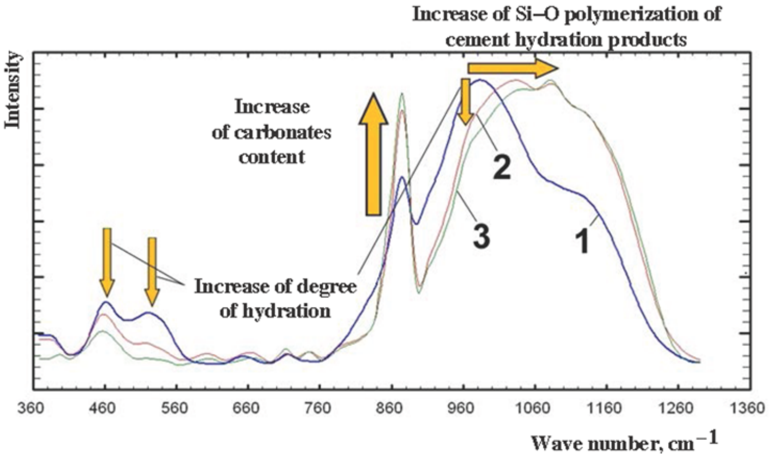

Figure 3. The area of “fingerprints” in IR spectra of hydrated cement stone (1) and after treatment in solution obtained on the basis of NaOH, water and gaize (2) and fly ash (3).

Thus, it can be concluded from the analysis that significant changes occur in the structure of the hydrated cement stone as a result of treatment the samples in water solutions of NaOH and the silica component (gaize or ash). These transformations, obtained on model systems, most likely are an explanation of the positive effect of the impregnation with the substance of the granules of the matrix of cement stone.

3.3. Influence of a granular nanostructured aggregate on the resistance to outwashing of water-soluble compounds of fine-grained concrete

Simulation of atmospheric processes of samples of fine-grained concrete with a granular nanostructured aggtegate was carried out for 30 days, after which the change in the mass and compressive strength of the samples after drying to the constant mass was determined (table 5), as well as the chemical composition of the residual solid phase (tables 6–8).

Table 5. Characteristics of fine-grained concrete samples after the test on Soxhlet device.

Characteristics	Type of sample	Concrete without GNA	Concrete based on granular nanostructured aggregate	
			Gaize + calcium stearate	Fly ash + GKZh-11 BSP
Weight loss of samples, %	NW	2,7	0,6	0,7
	PW	4,9	1,5	1,6
	W	5,6	2,3	2,5
Changes in compressive strength, %	NW	−1,7	11,4	2,0
	PW	−6,7	23,1	14,5
	W	−9,2	24,2	15,8

The reduction of samples mass after the test on the Soxhlet device is due to the removal of readily soluble compounds. The constant influence of the liquid medium on concrete causes corrosion of the first type, i.e. dissolution of cement stone components.

The greatest weight loss is noted for watered samples of fine-grained concrete without a granular nanostructured aggregate (table 5). The removal of readily soluble compounds is confirmed by a decrease in the content of oxides of alkali and alkaline-earth metals (CaO, MgO, Na_2O and K_2O) in the tested samples, and also of sulfur oxide (SO_3) (table 6). It is important to note that the chemical composition of the material is calculated in % of the total mass, and with a decrease in the content of one of the oxides, the content of the remaining increases. This results in an increase in the SiO_2 content of the samples after the test.

For samples with a granular nanostructured aggregate it is also possible to note a reduction in mass after testing the samples in a Soxhlet device. But it is much lower than for samples of fine-grained concrete without granular nanostructured agregate.

Table 6. Chemical composition of concrete samples without granular nanostructured aggregate before and after the test on Soxhlet device.

Material		Content of oxides, mass %										
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	P_2O_5	other
Before the test		61.50	3.79	1.66	27.23	2.24	1.59	0.38	1.13	0.19	0.12	0.17
After the test	NW	64.97	4.54	1.88	24.85	1.07	1.48	0.32	0.42	0.19	0.10	0.18
	PW	67.97	4.70	1.78	22.29	1.01	1.11	0.30	0.39	0.18	0.09	0.17
	W	68.69	4.74	1.71	21.73	0.98	1.07	0.27	0.39	0.18	0.05	0.18
Δ	NW	3.47	0.75	0.22	−2.38	−1.17	−0.11	−0.06	−0.71	0.00	−0.02	0.01
	PW	6.47	0.91	0.12	−4.94	−1.23	−0.48	−0.08	−0.74	−0.01	−0.03	0.00
	W	7.19	0.95	0.05	−5.50	−1.26	−0.52	−0.11	−0.74	−0.01	−0.07	0.01

Content reduction:	■	more than 1 %	▨	1−0,1 %	□	less than 0,1 %

Table 7. Chemical composition of concrete samples with granular nanostructured aggregate based on gaize and calcium stearate before and after the test on Soxhlet device.

Material		Content of oxides, mass %										
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	P_2O_5	other
Before the test		67.76	3.96	2.16	20.52	1.66	2.25	0.28	0.78	0.22	0.12	0.28
After the test	NW	68.01	4.43	2.46	20.37	1.49	1.80	0.18	0.66	0.22	0.09	0.28
	PW	68.29	4.93	2.26	20.11	1.38	1.74	0.13	0.63	0.18	0.06	0.29
	W	68.81	5.80	2.18	19.05	1.28	1.69	0.08	0.61	0.16	0.06	0.29
Δ	NW	0.25	0.47	0.30	−0.15	−0.17	−0.45	−0.10	−0.12	0.00	−0.03	0.00
	PW	0.53	0.97	0.10	−0.41	−0.28	−0.51	−0.15	−0.15	−0.04	−0.06	0.01
	W	1.05	1.84	0.02	−1.47	−0.38	−0.56	−0.20	−0.17	−0.06	−0.06	0.01

Table 8. Chemical composition of concrete samples with granular nanostructured aggregate based on fly−ash and GKZh−11 BSP before and after the test on Soxhlet device.

Material		Content of oxides, mass %										
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2	P_2O_5	other
Before the test		66.89	5.56	2.37	20.85	1.99	0.66	0.14	0.99	0.20	0.14	0.22
After the test	NW	67.41	5.79	2.61	20.48	1.83	0.37	0.13	0.81	0.20	0.13	0.23
	PW	68.1	5.82	2.54	19.84	1.81	0.44	0.12	0.78	0.19	0.13	0.22
	W	69.23	6.02	2.50	18.83	1.79	0.33	0.12	0.69	0.15	0.10	0.23
Δ	NW	0.52	0.23	0.24	−0.37	−0.16	−0.29	−0.01	−0.18	0.00	−0.01	0.01
	PW	1.21	0.26	0.17	−1.01	−0.18	−0.22	−0.02	−0.21	−0.01	−0.01	0.00
	W	2.34	0.46	0.13	−2.02	−0.20	−0.33	−0.02	−0.30	−0.05	−0.04	0.01

At the same time, for samples with granular nanostructured aggregate the strength of watered samples has increased in comparison with control samples that have not been treated. This result can be caused by the formation of hydrate framework alumina-silicates – zeolites as a result of the interaction of a solution of sodium polysilicates with the products of cement hydration.

In concrete samples with granular nanostructured aggregate a significant decrease in the outwashing of oxides of alkali and alkaline-earth metals is observed (tables 9 and 10). This is due to two main factors: physical – reduction of water migration, chemical – binding of free lime and formation of water-insoluble new formations.

4. Conclusion

The possibility of reducing the negative effect of hydrophobizing additives as well as their consumption while maintaining low water absorption of products without additional surface treatment by creating conditions for temporary encapsulation of the additive in order to retardance the onset of interaction of the hydrophobizator with the cement matrix is proved. This is achieved by the use of a granular nanostructured aggregate of prolonged action as a carrier of a hydrophobizing additive. Impregnation of cement stone with a solution of sodium polysilicates with a hydrophobizing additive allows to reduce its water absorption and ensures the formation of water-insoluble compounds – zeolites. The use of granular nanostructured aggregate based on gaize with calcium stearate and based on fly ash with GKZh-11 makes it possible to increase the resistance to atmospheric effects of the medium, namely, corrosion of the first type cement stone. The resistance to outwashing of readily soluble compounds when using granular nanostructured aggregate is caused by a number of factors, namely, a decrease in the migration of water as a result of the formation of a system of closed pores with hydrophobic walls; binding of free lime by products of the reaction of the core components of granular nanostructured aggregate; formation of slightly-soluble new formations as a result of the reaction of sodium polysilicates with the products of hydration of cement; decrease in portland cement content as a result of its partial replacement with granular nanostructured aggregate.

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