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The Use of Additives Based on Industrial Wastes for Concrete

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Abstract
The efficiency of use of additives based on spent pickling solutions for concrete is justified. The results on the use of hydrochloric acid spent pickling solutions as nanomodified additives for products based on cement binder are given. The efficiency of the action of additives under consideration on the structure and strength of the concrete is shown. The efficacy of the considered additives on the structure and strength of the concrete is shown. When using such additives in an amount of 0, 32 % from the cement weight on the 28th day of hardening in the air-humidity conditions fine concrete compressive strength is increased in 1.8 times, and the tensile strength in bending – in 15 % compared to the control composition due to the additional formation of hydrosilicates, sealing of structure and the reduction of the overall porosity of cement system in 2 times.

Keywords: nanomodified additives, pickling solution, salts of iron (II) and (III), fine-grained concrete, structure, compressive.

INTRODUCTION

Modern trends in the development of construction industry are associated with the application of new high-performance materials when using resource-and energy-saving technologies of their production [1-12].

Therefore, the use of industrial waste as components that improve the performance of building units is the actual direction for research.

It is known that the use of nanomodified additives is very relevant, since it allows adjusting the structure of materials at the micro-and nanolevels purposefully [13-23].

In the manufacturing activity of steel rolling mills (SRM) in the process of removing rust from the steel surface it is treated with the solutions of sulfuric and hydrochloric acids.

Wherein more than 10 000 m^3 of unclaimed spent pickling solutions (SPS) containing up to 3000 tons of iron salts (II) are formed annually. Such SPS are utilized by calcium oxide neutralizing, the result of which is the formation of huge amounts of sludge and waste water. In order to do this, the mill annually consumes about 1400 tons of CaO and 1 million m^3 of industrial water, paying wherein enormous fines for the dumping of such wastewaters in the volume of 1500 m^3 and for placing 5000 tons of sludge in special storage facilities. As a result, about 2700 tons of sulfate and 320 tons of iron chloride (II), 100 tons of sulfuric and 20 tons of hydrochloric acids are irretrievably lost for one year [24].

In this regard, taking into account ecological and economic importance of the problem of disposing unclaimed spent pickling solutions actual and perspective direction both from the scientific and technical and ecological points of view are studies on their use as additives for concrete.

Currently, a large amount of scientific and technical information on various types and kinds of additives to concrete (more often complex) of wide profile of action is represented in literature [25].

Additives that increase the strength of concrete as this is achieved by sealing its structure should be recognized as the main ones among the great diversity. The hydration process is complex, multi-step and depends on many factors, including

the qualitative and quantitative composition and sizes of particles which are the centers of crystallization.
The aim of this research is to study the effect of additives based on spent pickling solutions containing iron salts, on the structure and strength of fine-grained concrete.

EXPERIMENTAL PART

A chemical composition of spent hydrochloric acid pickling solutions is determined by the combination of different instrumental methods of research. The research results are summarized in Table 1.

Table 1: Quantitative composition of the spent hydrochloric acid pickling solutions

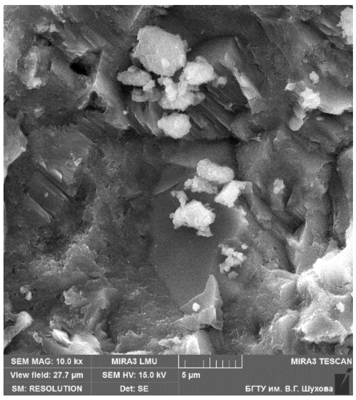
SPS component	$FeCl_2$	$FeCl_3$	HCl
Composition, g/l	325,0	12,0	16,7

According to particle-size analysis by laser diffraction method on the analyzer Zetatrac, Microtrac (USA), an average particles diameter in additive is 0,2 mkm. Wherein the proportion of particles in the range from 0,01 to 0,1 mkm is 8.8 %; from 0,1 to 0,5 mkm – 76,2 %; from 0,5 to 1 mkm – 4,3%; from 1 to 3 mkm – 10,7 %.
The content of hydrosol with particles sizes 38-576 nm in additive is 85,1 %. Their coagulation occurs in an alkaline environment and nanoparticles distributing uniformly over the entire volume, act as centers of crystallization. The same effect have iron containing components forming the additive. They are engaged in the exchange interaction with the hydration products of the cement paste, resulting in the formation of crystals of insoluble iron hydroxides (II) and (III) at the molecular level [26].
Thus, additives based on spent pickling solutions containing iron salts can be referred to nanomodified.
The research of influence of additives on the structure and strength of cement products was carried out on the cement stone (CS) samples and concrete with various aggregates.
Samples of cement stone and concrete were produced on the basis of Portland cement CEM I 42, 5 N made in Kostyukovichi (Mogilev region, Republic of Belarus). Chemical composition (% by weight): CaO – 61,9; SiO_2 – 20,67; Al_2O_3 – 4,88; MgO – 5,71; SO_3 – 3,64; Fe_2O_3 – 2,4; Na_2O – 0,30; K_2O – 0,90; TiO_2 – 0,27; others – 0,29. Mineral composition (% by weight): C_3S – 19,8; C_2S – 35,0; C_3A – 4,6; C_4AF – 7,9. Specific surface area is 330-370m^2 / kg. Normal thickness is 27–28 %. Quartz sand of limited liability company "Agrostroyinvest" (Bryansk) with fineness modulus of 1,5, granite rubble of fractions (5-10):(10-20)=1:1 and the unfractionated expanded clay aggregate were used as concrete aggregate.
Additives were introduced with mixing water in a mixture which is necessary to obtain cement paste of normal consistency, in an amount of 0, 16-0, 64 % (on a dry basis) by the cement weight.
The definition and calculation of the strength of samples of fine-grained concrete were carried out in accordance with state standard (GOST) 10180-2012.
The structure of control and nanomodified samples of cement stone was investigated by scanning electron microscopy method (SEM) on the device TESCAN MIRA 3LMU and nitrogen porosimetry on the device Sorbi-M.
According to the SEM, it was found that sample of cement stone with additive based on pickling solution has more dense structure with reference to the control sample of cement stone [27].
When introducing the proposed nanomodified additive into cement stone in an amount of 0,32 % by the cement weight the volume of pores with a size of less than 94,6 nm is reduced from 0,008 to 0,004 cm^3 /g, i.e. 2 times because of the bridging effect of the additive. There is also a reduction of the specific surface of pores from 3,9 to 2,1m^2/g. The distribution of pores according to their sizes in accordance with the classification adopted by IUPAC in the samples of cement stone is presented in Table 2.

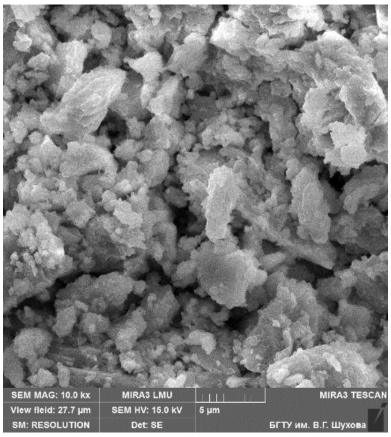
Table 2: Distribution of pores according to their sizes in the samples of cement stone

Distribution of pores	Sample,%	
	control	with the additive based on spent pickling solutions
Mesopores (2-50 nm)	7,6	76,6
Macropores (>50 nm)	92,4	23,4

According to the X-ray phase analysis, it was found that with the introduction of nanomodified additives based on pickling solutions the quantity of portlandite decreases, this is proved by a decrease of lines intensity specific to $Ca(OH)_2$ [27], which leads to the prevention of alkaline corrosion and contributes to the durability of products.
Analysis of mineral composition of control and modified samples showed that during the introduction of spent pickling solutions into the cement stone there occurs an increase in the content of hydrated silicate minerals C_3S и C_2S [27].
Platy structures which are characteristics of portlandite are clearly seen in the control sample of cement stone (Fig. 1a), whereas in the sample with the addition of hydrochloric acid spent pickling solutions (Fig. 1b) platy structures are not observed.



a) Control sample



b) Sample with the addition of spent pickling solutions (0,32 % by the cement weight)

Figure 1: The microstructures of cement stone (x 10 000)

Samples of the cement stone with different composition of additives on various periods of hardening in the in the air-humidity conditions have the following values of the compressive strength (Table 3).

Table 3: Strength of cement stone at different times of hardening

Sample	Composition of additive, %	Compressive strength, MPa	
		3 days	28 days
Control		51,5	62,0
With additive	-	45,8	96,5
	0,16	44,0	121,2
	0,32	47,6	96,9

It is found that the optimum composition of additive that provides maximum value of R is 0,32 % by the cement weight. Wherein in the early stages of hardening (3 days) it has a retarding effect on the hydration process in comparison with the control composition. However, on the 28th day of hardening in the air-humidity conditions value of the compressive strength of samples with the additive exceeds the control composition at about 2 times and is equal to 121.2 MPa.
Adhesion on the border of cement stone-aggregate is one of the determining factors of concrete strength. With good adhesion of cement matrix with aggregates and their high-strength the concrete strength increases. In this connection, research of the effect of additives based on SPS on the contact zone aggregate – cement stone was carried out.
SEM method demonstrated that when expanded clay and crushed granite are used as aggregates, there is a seal at the interface between aggregate – cement stone in comparison with control samples [27].
Samples of concrete with various aggregates and additives composition on various periods of hardening in the air-humidity conditions have the following values of compressive strength (Table 4).

Table 4: Strength of concrete with various aggregates on the 28th day of hardening in the air-humidity conditions

Aggregate	Sample	Composition, %	Compressive strength, MPa сжатие, МПа	Increase of compressive strength,%
Sand	Control	-	30,0	-
	With additive	0,16	41,4	38,0
		0,32	54,0	80,0
		0,64	37,5	25,0
Crushed granite	Control	-	50,5	-
	With additive	0,16	38,3	-24,2
		0,32	75,7	50,0
		0,64	63,3	25,3
Expanded clay aggregate	Control	-	6,2	-
	With additive	0,16	8,7	40,3
		0,32	7,81	26,0
		0,64	7,5	21,0

It was shown experimentally that value of the compressive strength of the samples where sand (the content of additives is 0, 32 %) was used as an aggregate on the 28th day of hardening increases by 1,8 times, crushed granite when the content of an additive is 0,32 %-by 1.5 times, expanded clay aggregate when the content of an additive is 0,16 %-by 1,4 times.
It was shown experimentally that dependences of the tensile strength in bending for samples of fine-grained concrete from the composition of an additive are of extreme character (Table 5).

Table 5: Tensile strength in bending of fine-grained concrete on the 28th day of hardening in the air-humidity conditions

Sample	Composition of additive, %	Tensile strength in bending, MPa
Control	-	6,70
With additive	0,16	6,94
	0,32	7,71
	0,64	6,90

The optimum composition of additive that provides maximum value of the tensile strength in bending is 0,32 % by the cement weight and on the 28th day of hardening in the air-humidity conditions samples of fine-grained concrete with additive exceed the control composition by 15.0 %.

CONCLUSION

It was found that structures of calcium hydrosilicates, sealing the system and promoting great increase of the compressive strength are formed when spent hydrochloric acid pickling solutions are present. It is proved that additive under consideration provides directional effect on the formation of cement stone structure by reducing the overall porosity of the cement system and redistributing pores towards the reduction of their size. It is experimentally proved that additive increases the adhesion of cement stone with such aggregates as sand, crushed granite and perlite. Wherein the compressive strength increases depending on the nature of the aggregate. The optimum content of additive which ensures maximum increase in the strength of fine-grained concrete samples was determined experimentally. When the content of additive is 0, 32 % by the cement weight the compressive strength increases from 21, 3 MPa to 38, 5 MPa, i.e. 1.8 times, and the tensile strength in bending increases by 15 %.

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