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Cement concrete composites on the basis of by-passed stone and stone milling wastes[1]

Said-Alvi Yu. Murtazaev[2], Dena K.-S. Batayev[3], Magomed S. Saidumov[4], Madina Sh. Salamanova[4], Salambek A. Aliev[4]

Abstract. The analysis of an environmental situation of the region and results of research of the specified wastes for the purpose of their use in cement concrete production engineering, expansion of a raw-material base and upgrading of road surfacing on their basis is presented. The history of processes of structuring in the course of aging of a low-slump concrete mix with use of the compounded binding materials and a waste of crushing of a demolished concrete and rocks is founded. Character of distribution of pores by the sizes of a cement stone of compounded binding materials on the basis of a waste of sawing stones is revealed. Influence of the modified fine aggregate from screenings of crushing of a demolished concrete and rocks and micro-aggregates on structure formation and the basic physical-mechanical properties of the pressed concretes for construction of cement concrete pavements is also revealed.

Key words. By-products, by-passed stones, secondary fine aggregate, floured filler, compounded binding materials, pressed concretes, concrete strength, environmental safety.

1. Introduction

One of the basic criteria of a country development level is the condition of its street and road network. Now road pavements in Russia by their overall considerably drop behind the world level. Besides, on many roads volume of traffic for this class

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[2]Academy of Sciences of the Chechen Republic, Grozny, M. Esambaeva Avenue 13; e-mail: S.A.yumurtazaev2@gmail.com

[3]Comprehensive Research Institute named after H. I. Ibragimov of the Russian Academy of Sciences, Grozny, Staropromyslovskoye Highway 21a

[4]Groznensky State Oil Technical University named after Academician M.D. Millionshchikov, Grozny, H.A. Isaev Avenue 100

of road has increased almost in 3 times in comparison with the proof load which has been stipulated at their designing [1, 2].

The most promising solution of the problem according to Transport strategy of the Russian Federation for the period till 2020 is construction of road surfacing of a rigid type with use of cement concrete composites [3] that implies a significant increase in the volume of work. For this purpose the road-building industry should have a necessary raw-material base for production of cement concretes for arrangement of such pavements. The basic preconditions for production of effective road cement concretes are decrease in a water demand of designed compositions, raise in reactivity of binding materials with simultaneous reduction of its discharge, and also decrease in cost of produced concrete [4]. Therefore, application of especially low-slump concrete mixes with the reduced charge of cement in comparison with traditional compositions, and wide use of by-products and the compounded binding materials on their basis appear the most expedient.

Effective direction of use of industrial wastes for the solution of a problem of expansion of a raw-material base of the building industry is their complex use with provision of physical and service characteristics required for road surfacing [5–7].

2. Raw materials for cement concrete composites and research procedures

The methods applied in the course of carrying out researches within the frameworks of the study are based on known postulates of the theory of clinker minerals solidification with fillers of various composition, in particular, with by-passed stones and stone millings, mathematical logic, technology of composite materials, the theory of production processes and production automation and control. Researches were carried out taking into account state standards and recommendations.

Both macro and microscopic structures of concrete composites and chemical composition of a feed stock were studied by means of a power dispersion spectrometer (PDS) and raster electron microscope Quanta 3D 200i with integrated microanalysis system Genesis Apex 2 EDS from EDAX. Spectra processing was performed by means of software EDAXTEAM.

3. Secondary filler surface modifying with use of cation-active additive ADMAX

It was noted in proceedings of Pecheny that use of pulverous fraction in concretes reduces hardness of a contact area between filler and a cement stone due to a low adhesive bond between them. At the same time Bazhenov and Shishkin have carried out the researches which have proved that dust particles do not render influence on concrete strength if they are not mechanically connected with a filler surface and even raise it upon introduction of appropriate chemical additives.

Researches of influence of modified cation-active additive ADMAX included in a filler on structure formation processes and properties of the pressed fine concrete have found that in the course of processing the filler by cation-active surface active agent selective-oriented adsorption of its macro molecules is observed. Upon that, the polar terminal group of molecules is positively charged, and therefore in various media (neutral or alkaline) it is pulled to negatively charged surface of silicon dioxide. Simultaneously, hydrophobic hydrocarbon chains of molecules are aimed to be freed from a fluid phase and to join to each other forming the adsorptive monomolecular layer in the investigated medium whereby the surface becomes hydrophobic. These processes of adsorption provide the raised wetting and the best permeation of cement suspension in a micro relief of filler grains creating upon that the most favorable conditions for formation of the adhesive contact with the increased hardness. It is found that use of a filler modified with ADMAX improves compactness of an agglutinant sand, changes behavior of opened porosity and raises strength characteristics of the concrete (see Table 1).

Table 1. Influence of cation-active additives to properties of pressed cement concretes

Concrete additive name, content (%)	Stripping strength (MPa)	Compaction factor k_{comp}	Medium density (kg/m^3)	Water absorption (%w/w)	Compression strength R_{cs} (MPa)	Opened porosity (%)
ADMAX, 0.1 %	0.96	1.77	2312	2.51	55.8	7.6
Without the additive	0.84	1.71	2283	4.23	42.9	11.2

Besides, formation of an even number of modificator layers on a filler grain surface, as a rule, does not result in reaching the desirable results because the essential gain of compression strength R_{cs} is not observed thus. The maximum positive effect is observed upon introduction of surface active agent on a filler surface by odd quantity of layers, namely, 5 layers especially in researches within the frameworks of the present study (see Table 2).

4. Structure and properties of cement concrete composites with the modified filler

Studying of the pressed fine concrete structure with use of the filler which is superficially processed by the cation-active additive ADMAX was made by a method of radiography analysis and a raster electron microscopy (Figs. 1 and 2). It was found that use of the modified filler in the course of hydration of clinker minerals promotes synthesis of fine-crystalline new growths of low-base calcium hydro silicates.

X-ray analysis researches have shown that the microscopic structure of a cement stone in 28–day age (Fig. 2a, zoom $\times 5000$) samples without additives is presented by loosened matrix, there are no new growths with the expressed habitus of crystals. The microscopic structure of samples on the basis of the modified filler (Fig. 2b) is mainly presented in the same age by a dense mass and a fine-grained phase, and crystal hydrate which is a basic component of its microscopic structure is presented by the needle-shaped form. In such structures crystals of fibrous, needle-shaped and prismatic forms predominate to more extent. Formation of homogeneous structure due to effective intergrowth of hydro silicates in the entire matrix of solidifying system of a composite is observed.

Table 2. Key properties and hardness of the pressed cement concrete depending on a surface treatment type

No.	Quantity of monomolecular layers ADMAX on a filler surface	ADMAX concentration (%)	Water demand (%)	Water-cement ratio at equal place ability parameters	Compression strength R_{cs} (MPa)	
					7 days	28 days
1		10^{-2}, mixing with water	4.4	0.32	25.4	45.8
2	8	$1 \cdot 10^{-1}$	4.1	0.30	22.1	32.2
3	7	$7 \cdot 10^{-2}$	4.0	0.30	25.2	42.9
4	6	$5 \cdot 10^{-2}$	3.8	0.29	25.6	43.7
5	5	$1 \cdot 10^{-2}$	3.5	0.27	29.1	49.8
6	4	$5 \cdot 10^{-3}$	4.2	0.29	25.7	44.1
7	3	$3 \cdot 10^{-3}$	4.5	0.30	25.1	45.8
8	2	$1 \cdot 10^{-3}$	5.2	0.32	22.8	40.1
9	1	$6 \cdot 10^{-4}$	5.2	0.33	21.7	37.9
10			5.2	0.34	21.3	37.4

Structural particles (scales and plates) of low-base calcium hydro silicate penetrate into space between parts of the binding material that provides raise of hardness of a solidifying colloid system.

Besides, one instance of development of new highly effective technology for production of multicomponent compositions for construction of cement concrete pavements is mechanochemical activation of binding materials which allows synergistically to improve properties of components of the complex binding material with the highest filling level: hardness of cement increases by 2–3 grades, and the plasticizing effect of an organic component and the modifying additive increases approximately twice. Therefore the task in view in the study for production of the effective compositions intended for cement concrete pavements with improved properties is to develop the formula of cement concrete mixes with use of a secondary material for a road making.

Thus, filled binding materials (FBM) are received with filler from a waste of sawing of stones (see Table 3). A Portland cement TSEM I 42, 5 H is used in the capacity of a binding material in the course of their production.

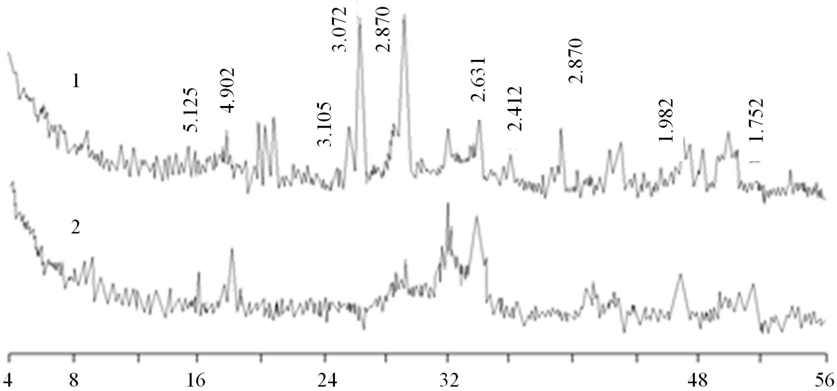

Fig. 1. Roentgenograms of contact areas of cement stone on the basis of modified fillers (1) and usual fillers (2)

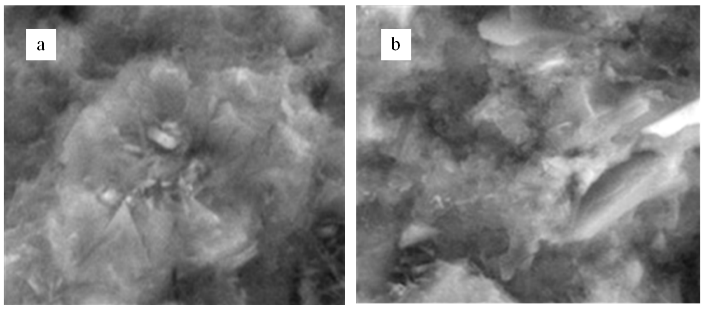

Fig. 2. Photomicrogram of contact area of usual (a) and modified (b) filler and cement stone (zoom ×5000)

Table 3. Formula of filled binding material on the basis of a waste of sawing of stones

Type of the filled binding material	Quantity of cement (%)	Filler level (%)	Quantity of the additive "Bio-NM" (% of FBM mass)	FBM specific surface (m^2/kg)	Compressive strength (MPa)
IA85	85	15	2	558	75.3
IA70	70	30	2	578	69.8
IA55	55	45	2	599	45.2

As is known, the main precondition for production of qualitative concretes is decrease of a water-cement ratio of a concrete mix and raise of binding material reactivity. From this point of view it is considered that the most actual directions use filled binding materials with fineness of grinding to $600\,m^2/kg$. Such approaches to formula designing allow composites to receive with high density and to upgrade a cement stone due to raise of cement hydration extent together with the filler and to provide a necessary reserve of anhydrate cement particles for embedment of the defects originating under the influence of various external factors.

Results of the comparative analysis of particle-size compositions of offered filled binding materials HB55 and HB70 with a floured filler produced from the waste of sawing of stones with specific area SSP $= 549$–$599\,\mathrm{m^2/kg}$ (see Table 4) have revealed essential difference in their granulometry.

Table 4. Particle diameters D (μm) falling into various fractions

Fraction	1	2	3	4	5	6	7	8	9	10
D (μm) from-to	0.20 0.25	0.25 0.30	0.30 0.36	0.36 0.44	0.44 0.49	0.49 0.58	0.58 0.75	0.75 0.90	0.90 1.05	1.03 1.31
Fraction	11	12	13	14	15	16	17	18	19	20
D (μm) from-to	1.31 1.50	1.50 1.80	1.80 2.21	2.21 2.61	2.61 3.22	3.22 3.81	3.81 4.53	4.53 5.46	5.46 6.54	6.54 7.83
Fraction	21	22	23	24	25	26	27	28	29	30
D (μm) from-to	7.83 9.42	9.42 11.4	11.4 14.1	14.1 15.9	15.9 20.2	20.2 24.8	24.8 28.2	28.2 34.5	34.5 41.5	41.5 49.9
Fraction	31	32	33	34	35	36	37	38	39	40
D (μm) from-to	49.9 58.9	58.9 70.2	70.2 84.6	84.6 100	100 125	125 150	150 175	175 210	210 260	260 300

Material HB55 has the quantitative content of more fine fractions that increase in the specified interval. The screening curve for HB70 is located in the interval of larger fractions. Thus, content of more fine fractions in HB55 is higher than in HB70. Such difference in granulometric properties upon equal specific surface of particles is caused by the fact that the filler presence promotes finer milling of the binding material.

Hence, it is necessary not only to increase the value of specific surface of the binding material, but also to be aimed to provide rational grain-growing composition by application of fillers of a various origin.

Electron microscope investigations founded more consistent character of the cement stone for samples with HB55 with specific surface of $599\,\mathrm{m^2/kg}$ (Fig. 3b) in comparison with a cement stone made from usual Portland cement (Fig. 3a).

The structure of samples with HB55 represents a close packing of clinker grains in a cement stone that is caused by presence of the thinnest films of water between grains and the secured formation in the constrained volume of enough quantity of low-base calcium hydro silicates. Selective point distribution of a surface active agent on cement grains (Fig.3 d) is noted. Therefore, the charge of the additive "Bio-NM" upon production of the filled binding material makes a small share from a total surface of cement grains. Among the factors influencing structure formation and properties of both newly compressed mixes, and matured concretes it is possible to select the main ones: the water content, compacting pressure, charge of the binding material, conditions of preparation and subsequent concreting of a composite. Water content influence in moldable mixes on properties of concretes was studied on the samples obtained with use of a filler made from screening of crushed materials in the Argunsky quarry and HB70. Pressing of samples was carried out at pressure about 30 MPa which have been tested at the age of 28 days (see Table 5).

By the conducted researches it is proved that the concretes made from sand with the water content 6.5 % (Fig. 4) have the greatest strength and therefore, further properties were investigated for concretes with this initial water content.

Studying of influence of the binding materials charge and compacting pressure on properties of investigated cement concretes (Fig. 5) was carried out with use of sands made on the basis of screening of rubble crushing in Argunsky quarry with the charge of binding materials 20–35 % from mass of the prepared mix and the initial water content in a mix of 6.5 %. Samples were pressed within the interval of pressure 20–50 MPa, and then stored in normal conditions for 28 days.

Raise of the cement charge promotes increase in physical-mechanical characteristics of green composites. At the same time the increase in the charge of cement at 25 % and more does not result in a notable gain of concrete strengths (see Table 6).

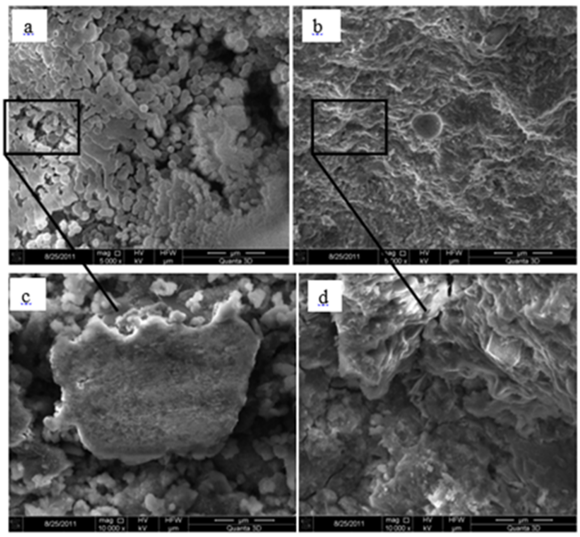

Fig. 3.
Photomicrography of a cement stone made from portland cement (a, c–zoom ×5000) and the binding material HB55 (b, d–zoom ×10000)

The increase in compacting pressure more than 30 MPa makes insignificant impact on properties both newly compacted, and green composites (see Table 7), therefore, in the further research there was accepted compacting pressure 30 MPa as the most effective (see Figs. 4–5).

So, possibility of cement concrete composites manufacturing on the basis of a secondary material made from by-passed stones is proved. Influence of a type and grain-growing composition of a filler to cement concrete properties is investigated. Influence of filler made from a waste of sawing of stones on processes of structure formation and physical-mechanical properties of a green composite is studied.

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Table 5. Properties of cement concretes depending on initial water content in a sand

No.	Initial water content (%) from mass of dry components	Compaction factor k_{comp}	Medium density of a concrete mix (kg/m^3)	Medium density of cement concrete (kg/m^3)	Compressing strength (MPa)
1	5.5	1.52	2302	2276	51.1
2	6.5	1.73	2328	2294	56.0
3	7.5	1.81	2316	2288	55.1
4	8.5	1.84	2294	2264	52.0
5	9.5	1.87	2272	2252	50.7

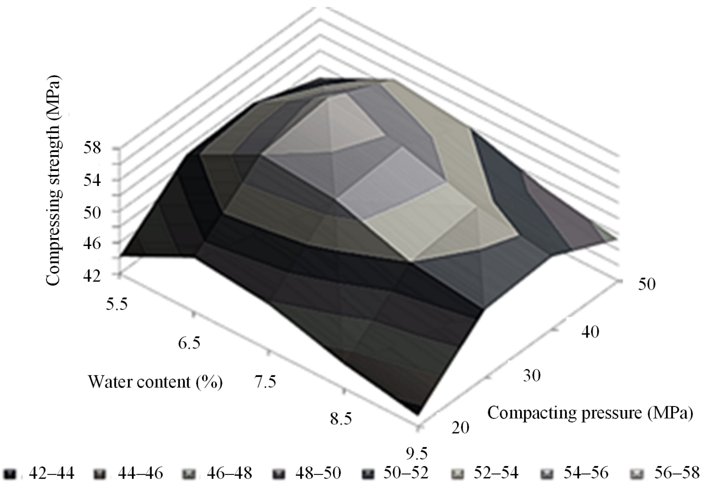

Fig. 4. Dependence of hardness pressed cement concrete from the initial water content and compacting pressure

To forecast strength of cement concretes with use of the modified filler and application of a floured micro filler made from a waste of sawing of stones researches with use of the mathematical experiment design apparatus were carried out. In the capacity of variables there have been selected water-to-binding material relation (W:BM) from 0.20 to 0.40; a type of a compounded binding material and a relationship between quantity of screenings after crushing (CS) and the compounded binding material in concrete (CS:BM) from 2:1 to 4:1.

For the investigated compositions of concretes with the charge of binding materials 435–585 kg/m^3 without additives, compression strength at the age of 28 days varied within the range of 34.2–42.3 MPa. Analogous compositions with application of the filler modified by ADMAX have compression strength 46.6–61.4 MPa and a prism strength 40.8–54.0 MPa. So, use of the filler processed by the cation-active additive ADMAX in the proposed effective compositions allows compression strength and a prism strength to raise approximately by 20–30 %. Values of static and dynamic elastic moduli have also increased.

Table 6. Influence of the binding material content in a sand on properties of cement concrete composites

No.	Relative content of binding materials in a sand (%)	Medium density of a concrete mix (kg/m^3)	Medium density of the cement concrete (kg/m^3)	Compressing strength (MPa)
1	20	2232	2223	50.2
2	25	2323	2294	56.0
3	30	2345	2312	57.6
4	35	2354	2325	59.2

Table 7. Influence of compacting pressure on properties of cement concretes

No.	Compacting pressure (MPa)	Compaction factor k_{comp}	Medium density of a concrete mix (kg/m^3)	Medium density of cement concrete (kg/m^3)	Compressing strength (MPa)
1	20	1.56	2245	2215	48.9
2	30	1.77	2330	2294	56.0
3	40	1.82	2350	2320	57.0
4	50	1.83	2360	2325	53.2

5. Conclusion

We developed and investigated cement concrete construction composites with complex utilization of by-passed stone and stone milling waste.

It was proved that compounded binding materials with filler from a waste of sawing of stones, which are partially amorphized in the course of milling, in the case of their hydration rate up a formation process of clinker mineral scatting as subcase upon obtaining of new growths and promoting binding of a lime hydrate in insoluble calcium hydro-silicates with fine-crystalline structure and various basicity factors.

The character of distribution of pores depending on the sizes of cement stone of compounded binding materials on the basis of stone sawing wastes is revealed. The grain size curve for particles of the compounded binding material made from stone sawing wastes has more intermittent character due to the polymineral composition which intensifies milling that has a positive impact on formation of a microscopic structure of a cement stone owing to more consistent spatial arrangement of particles and, therefore, production of stronger cement stone. Influence of the modified fine aggregate made from screenings of a demolished concrete and rocks crushing and micro fillers on structure formation and the basic physical-mechanical properties of the pressed concretes for construction of cement concrete pavements is revealed.

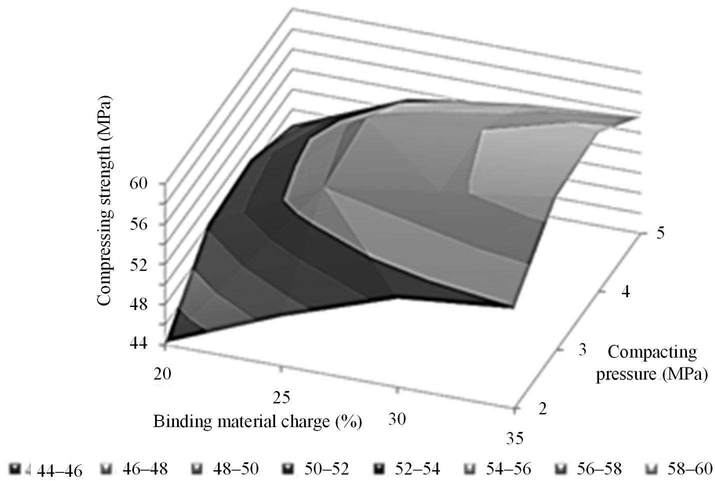

Fig. 5. Dependence of strength of pressed cement concretion the binding material charge

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