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Man-made waste is the dominant component of knitting compositions

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Abstract. Improving the quality and durability of construction materials while simultaneously reducing the costs of their production and use remains a pressing issue in construction material science. Analyzing the industrial experience of using construction composites leads to the conclusion that new technologies are based on the dominant position of the active binder component, which is responsible for accelerating the hydration processes, targeted formation of the phase composition, and modification of the structure of the cement paste. Combining clinker and mineral components, incorporating chemical modifiers, and properly designing the formulation and preparation technology of the binder composition and concrete mix makes it possible to achieve the desired design strength, reduce cement consumption, and lower product cost.

This paper presents the results of studying a complex pozzolanic additive, whose material composition enables the formation of a denser stone structure due to an additional active source of unhydrated calcium silicates and sodium/calcium aluminosilicates. The resulting filled binder exhibits properties significantly superior to control samples. Using local inert materials and achieving a 25% reduction in clinker, concrete mixes of classes B20–22.5 were developed. These are widely used in the casting of foundations, floor slabs, stair flights, paving elements, and other concrete and reinforced concrete products.

Keywords: filled binders, concrete debris, ash, binder systems, technogenic waste, grinding, heavy concrete

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1. INTRODUCTION

Given the widespread changes in the construction industry aimed at increasing the speed of work and improving the quality and durability of construction materials while reducing costs, high-performance concretes are increasingly in demand [1, 2]. These include concretes that harden quickly, exhibit high strength, and have low permeability. Such materials ensure stability and resistance to various aggressive environments [3, 4].

Industrial application analysis confirms that high-performance composites [5, 6] are based on the dominant role of an active binder component, which accelerates hydration, forms targeted phase compositions, and alters the microstructure of cement stone [7, 8, 11]. Combining clinker and mineral parts, incorporating chemical modifiers, and using well-designed mix formulations help achieve target strength while reducing cement usage and overall cost [9, 10, 13].

The production of filled binder compositions has been a focus of research for many decades [12, 14, 17]. There is strong interest in using natural additives and industrial waste, such as blast furnace slag, fuel ash, high-silica sands, microsilica, zeolite-containing and volcanic rocks, marl, clay, limestone, diatomite, tripoli, etc. Mechanical or mechanochemical activation of these additives and mixing them with a portion of the main binder can result in new materials whose properties depend on the additives replacing clinker [15, 16]. A well-known classification of filled binders is presented below table 1 [18, 19, 24].

Table 1. Classification of filled binders.

№	Type of binder	Content, mass. %					
		Clinker	Slag	AMA	MC	Quartz sand	CP
1	Portland cement	95-100	-	до 5	-	-	-
2	Slag Portland cement	65-90	10-35	до 5	-	-	-
3	Puzzolanic Portland cement	65-90	до 5	до 5	-	-	-
4	Composite cement	65-88	6-29	до 5	-	-	-
5	Cement with ferrous metallurgy slag	20-64	36-80	до 5	-	-	-
6	Puzzolanic cement	> 60	до 5	до 5	-	-	-
7	Fine-ground binders	> 50	-	-	-	-	-
8	Low water requirement binders	30-100	10-25	-	0-70	0-70	до 3

Note: AMA- active mineral additives, MC – мicrosilica, CP – superplasticizer.

The given classification of clinker cements allows us to note the fact that by changing the qualitative and quantitative composition of the binder, it is possible to obtain various products that differ in properties, purpose and cost [20,21,23]. And depending on the activity, mineral additives (hydraulic, pozzolanic and microfillers) have their own effect on the processes of formation of the structure of cement stone and the physical and mechanical properties of the composite [22, 25, 26].

Pozzolanic additives can be considered the most promising in the cement industry; they include ferrous metallurgy slag, thermal power plant fly ash, zeolite-containing rocks, opoka, clay, volcanic pumice, tuff, tripoli, etc. The effect of using pozzolanic additives in a binding system has been established, the presence of amorphous silica and alumina in the composition of which has a positive effect on the hardening active bond «C_3S – pozzolana – water». The acceleration of hydration processes in the initial stages of hardening is facilitated by the surface of the pozzolana particles, which, by adsorbing Ca^{2+} ions, facilitates the rapid dissolution of tricalcium silicate grains [14, 28]. Hydrate compounds accumulate in layers around C_3S and lead to a volumetric expansion of the layer of new formations on the grains of the clinker mineral. As a result, the hydration products, and in particular calcium hydroxide, are bound into strong hydrate compounds according to the following scheme: $xCa(OH)_2 + SiO_2 + nH_2O = xCaO \cdot SiO_2 \cdot mH_2O$. The basicity of the formed hydrosilicate compounds can vary within the range of 0.8–2, and will depend on the quantitative and qualitative composition of the pozzolanic additive, dispersion, hardening conditions, and other factors. It should also be noted that the presence of pozzolana stabilizes the amount of calcium hydrosulfoaluminates (ettringite) at later stages of hardening of artificial stone, neutralizing the possibility of sulfate corrosion [19,27] in concrete.

2. METHODS AND MATERIALS

To better understand the benefits of the "Portland cement – pozzolan" binder system, this study investigates new formula-technological approaches using industrial waste for environmental protection and resource conservation. Concrete scrap and thermal power plant ash were used as pozzolanic components. For the region of the Chechen Republic, the search for a real application of this man-made plant has long been discussed in many forums of the scientific community, since large-scale waste is filling agricultural areas, causing significant damage to the environment and in general, Image of the region. In addition, it is necessary to take into account that a full raw material resource is accumulated in landfills, because after transformation and enrichment it can be reintegrated into the technological cycle. What is important to note about the scarcity and non-renewable nature of mineral raw materials.

Of course, in the first phase of the studies, mineral stockings were prepared, since there is little use for this material in its original form (Fig. 1). Concrete scrap and thermal power plants ash were cleaned from unwanted inclusions, dried and processed.

Fig. 1. Industrial wastes.

The concrete scrap was crushed in a laboratory crusher DШ6S, to 5-20 mm fraction, for use as a major filler of concrete; a fine solvent fraction less than 5 mm was separated from the mass and ground into a laboratory carpet mill MLR-15. It is a fine fraction containing a certain proportion of the gemstone that is of interest to obtain filled binders, in the hope of showing activity from the previously unreacted part of the clinker background in the powder additive. Ash milling thermal power stations and fine fraction of concrete scrap were carried out within 30 minutes, the specific surface area of the resulting powders was determined on the instrument PCH-12, test results are presented in Table 2.

Table 2. Specific surface area of mineral powders.

Name additives	Specific powder surface area, m^2/kg, ground 30 min
Concrete scrap	630
Ash thermal power stations	790

The microstructure of the particles of the powders studied was examined on the raster electron microscope Quanta 3D 200i (Fig. 2), the microparticles of the concrete scrap are represented by loose grains of irregular geometric shape, and ash thermal power stations more dense, have a smooth spherical surface. Chemical composition of the product, % by mass:

– concrete scrap:: MgO = 1.22; Al_2O_3 = 5.03; SiO_2 = 52.8; Na_2O = 0,19; CaO = 34.52; Fe_2O_3 = 3.33; TiO_2 = 0.31; K_2O = 1.31; Na_2O = 0.51; SO_3 = 0.11; ппп = 0.38.

– ash thermal power stations: MgO = 1.44; Al_2O_3 = 10.31; SiO_2 = 55.41; Na_2O = 0,19; CaO = 12.62; Fe_2O_3 = 5.01; TiO_2 = 0.32; K_2O = 1.49; Na_2O = 1.72; SO_3 = 0.76; ппп = 10.97.

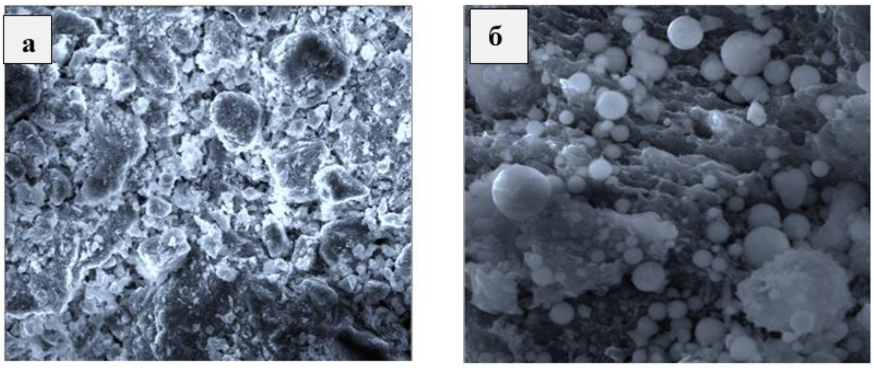

Fig. 2. Microphotography of Putsal Additive: a – concrete scrap; b – Microphotography of Putsal Additive: a – concrete scrap; b – ash thermal power stations.

The microstructure studies of the investigated additives have confirmed the presence of the necessary for the synthesis of the new formation of the oxide composition. And for the development of the Putzolin additive, the filled binders were considered to vary the quantitative composition in order to further investigate the chemical composition. In order to identify the optimal formulation, a large number of binder compositions were selected and tested, and as a result it was determined that the ratio of concrete scrap: ash thermal power stations = 75 : 25% is considered the most effective. In further studies, a complex additive was used in the indicated compound and milling at the proposed quantitative ratio was carried out jointly to produce more uniform and homogeneous powder powders. The grinding time was the same 30 minutes, the specific surface area was 726 m^2/ kg. The resulting additive based on binary powders was investigated using diffractometer «ARLX'TRA» (Fig. 3).

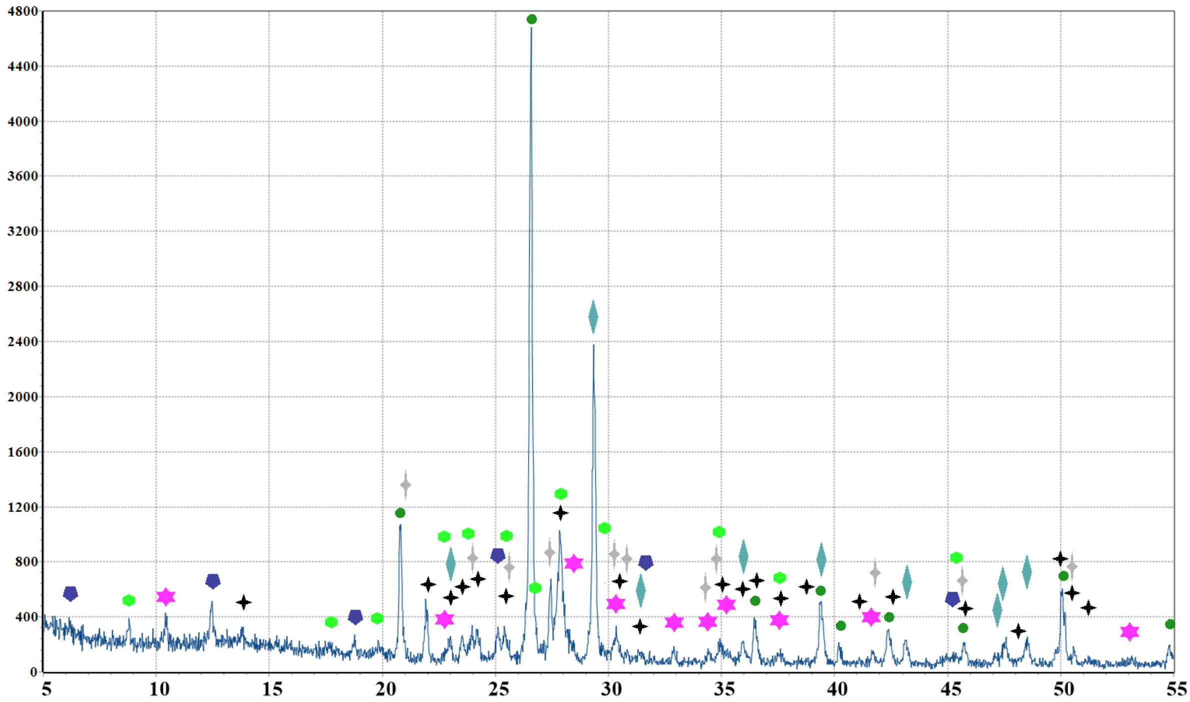

Fig. 3. X-ray diffraction pattern of a concrete sample according to PDF-2 database data. The given comparison phases: ● – quartz; ⬟ – chloritized dark-colored silicates; ⬢ – C_2S; ✦ – plagioclase (albite-oligoclase); ✦ – microcline; ♦ – calcite; ✶ – amphibole.

3. RESULTS AND DISCUSSION

The results of the X-ray phase analysis of the complex Putzolan additive showed the presence of the following minerals: calcium, quartz, C_2S belite, chlorinated dark-colored silicates of calcium, albite. The most expressive reflexes belonging to plagioplasty, minerals of alpha-bit $NaAlSi_3O_8$ and amortite $CaAl_2Si_2O_8$, microcline $K[AlSi_3O_8]$ and crystallized crystals of bicalcium silicate C_2S have been recorded. The mineralogical composition of the Putzolan complex supplement will improve the properties of the binder system «Portland cement – Putzolan» due to the additional source of non-hydrated silicates calcium, sodium and calcium aluminosilicate. A higher dispersion of the additive will create a dense and impermeable structure of the concrete composite, which will positively affect the strength and durability of the material.

Topological model of the contact zone «Portland cement – integrated putzolane additive – water» (putzolane surface area 726 m^2/kg), presented in Fig. 4, provides a visual perception of the processes of fasoforming due to the formation of diffuse gel C-S-H from calcium silicate hydrates of low basal, developing strength characteristics of the composite.

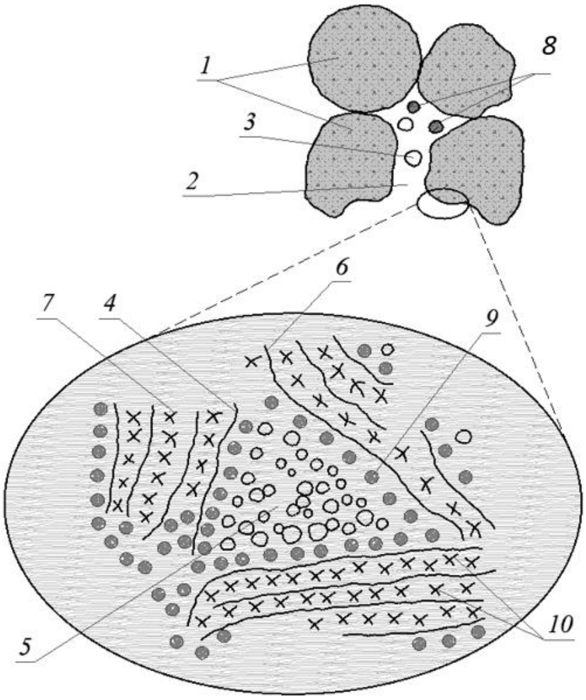

Fig. 4. Diffusion gel model C-S-H with the use of Putzolin additive: 1 – gel area C-S-H; 2, 4 – close contact; 3 – pores between the microparticles; 5 – intra-crystallization pores; 6 – water interlayers; 7 – Intercrystallization pores; 8-10 – Active additive particles (2–200) 10–9 м.

Formulations of the filled binder were selected experimentally, studies were conducted in accordance with GOST 310.4-81 Cements. Bending and compression strength methods; GOST 310.3-76 Cements. Methods for determination of normal density, latch times and evenness of change in volume; GOST 30515-2013 Cements. General technical conditions. The optimal formulation of the filled with complex putzolane binder additive has been established, the quantitative composition is Portland cement 75%, «concrete scrap -ash thermal power stations» 25%. As the main component of the binding system used Portland cement M500 without additional JSC «Chechen». The properties of the material obtained, in comparison with the control samples, are presented in Table 3.

Table 3. Results of cement studies.

№	Properties of cement	Indicators	
		Portland cement	Portland cement–pozzolana
1	Fineness of grinding, balance on bed 008, %	8.4	5.2
2	Normal density, %	25.0	26.3
3	Time to catch, hour-minute: beginning end	2 hours 21 minutes 3 hours 23 minutes	2 hours 52 minutes 3 hours 40 minutes
4	Activity, МПа	50.2	52.4

The test results showed that savings of clinker fraction up to 25% led to an increase in the water demand of the cement, which caused a higher dispersion of the filled cement. But the water-reactive particles of the com-plexient putzolans fill the intergranular space of the binding system, and they act as water channels to the defective points of the clinker particles, which contributes to the increased activity of the filled binder. Microphotographs obtained using the raster electron microscope Quanta 3D 200i allow to observe the effect of the application of binary powders, cement stone structure more dense, pores and voids filled with additional portion of neoplasms, This will affect the strength of the samples.

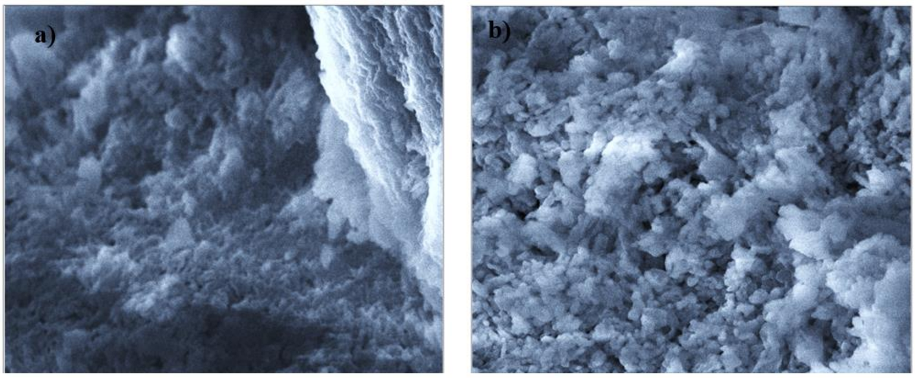

Fig. 5. Microphotographs of samples of cement stone based on teeming (a) and portland cement (b).

Using a filled thickening, natural fine and large fill of the local region, heavy concrete samples were selected and manufactured according to GOST 10180-2012 Concrete. Methods for determination of strength by reference samples; GOST 12730.1-78 Concrete. Methods for determination of density. Inert material – quartz sand module of 1.9 size, large aggregate limestone gravel fraction 5-20 mm, met the requirements of GOST 8736-2014 Sand for construction works. Technical conditions; GOST 8267-93 Gravel and gravel from dense rock for stripping works. Technical conditions. The compositions and properties of heavy concrete mixtures and concretes are given in Table 4.

Table 4. Concrete mixture and concrete test results.

№ composition	Water cement ratio	Material consumption per 1 m^3 of concrete, kg					Brand of mobility	Mixture density, kg/cm^3	Water consumption, % by mass	Compression ratio, 28 days, MPa
		Gravel	Sand	Filled knitting	Additive	Water				
1	0.42	1200	618	400	4,0	168	П3	2387	0.3	25.2
2	0.43	1190	613			172	П4	2383	0.4	25.8
3	0.46	1180	608			184	П5	2378	0.6	24.7
4	0,41	1170	622			164	П3	2389	0.1	26.9
5	0.49	1180	610	400*	4,0	196	П5	2380	0.3	22.5

Note: FK – filled knitting 75% filled with binder Portland cement: «concrete scrap – ash thermal power stations» 25%; composition 5* – Portland cement M500 without additives AS «Chemicum»; additive Sika ViscoCrete 5-600 SK based on polycarboxylate ethers, dosage 1.0% from the mass of cement.

As the studies showed, the technical properties of the concrete mixture and bitumen change depending on the quantitative composition of the inert material, since the discharge of the binder remained constant. Composition 5 showed a maximum strength increase of 26.9 MPa, minimum water separation of 0.1%, which indicates the correctly selected composition of the molding mixture on 1m3 concrete, the consumption of quartz sand 622 kg and the complex putzolin additive in 134 kg, superplasticizer Sika ViscoCrete 5-600 SK, prevents the concrete mixture from splitting and deterioration of the properties of the top layers of concrete.

The microstructure studies of samples from composition 5 give an idea of the structure of artificial stone (figure 6), the bulk of which is densely penetrated by the plate aggregates of aluminates and calcium silicates of various types. The chemical composition varies in aggregates with different structural-textural characteristics (Fig. 7, Table 5), there are massive cintolite-crystal aggregates of aluminosilicate and compounding mass crystallized cracked aggregates, Hydrolysed calcium silicates.

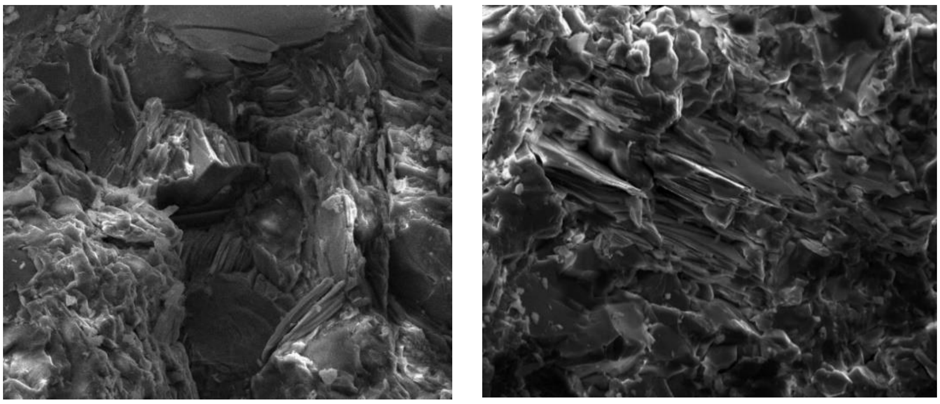

Fig. 6. Microphotographs of concrete samples of composition 5 magnified 2500 crt.

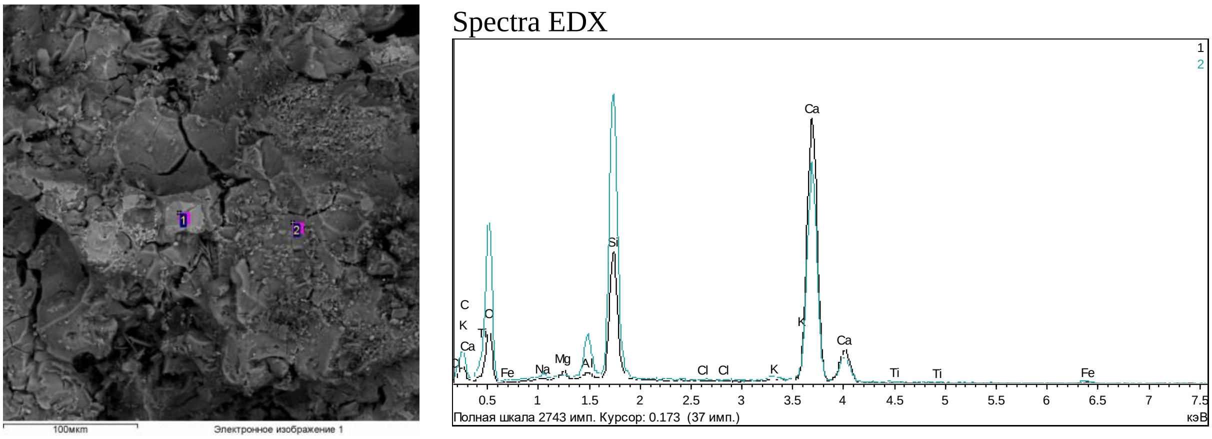

Fig. 7. Example of variation of hydrated silicate calcium compositions.

Table 5. Results of the analysis of the plots shown in Fig. 7.

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	Итог
1	0.90	1.55	4.37	29.50	0.31	45.46	0.00	2.46	84.55
2	0.65	0.12	5.15	40.52	0.41	34.99	0.21	1.17	83.22

4. CONCLUSIONS

Thus, the results of the X-ray phase analysis of the complex powdery powder confirmed the presence of minerals: calcium, quartz, C_2S belite, calcium nucleate silicates, albite, anodite, microcline. The material composition of the binder system «Portland cement - putzolan» will allow to create a more dense structure of the stone, and due to the additional active source of non-hydrated silicates calcium, sodium aluminosilicate and calcium increases the strength of concrete composites.

The topological model of the contact zone «Portland cement - integrated putzolan additive - water» allows visual perception of fasoforming processes due to formation of diffuse gel C-S-H from low-basal calcium silicate hydrates, developing strength characteristics of the composite.

The optimal formulation of the filled binder has been established, the quantitative composition of Portland cement is 75%, «concrete scrap – ash thermal power stations» 25%. The properties of the material obtained are much higher than those of the control samples. Using local inert material and saving 25% of clinker fraction developed heavy concrete compositions classes B20-22.5, widely used in the filling of foundations, slabs, stairways, tiles and other concrete and reinforced concrete products.

Finally, it should be noted that the results of the studies will allow to expand the raw material base for the cement industry and building materials in general. Even a small saving of expensive and resource-intensive material will have a positive impact on the environment, since the problems of decarbonization of the economy are urgent and require a global response.

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