



MAGNESIUM FINE-AGGREGATE CONCRETE BASED ON INTEGRATED USE OF TECHNOGENIC MATERIALS

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ABSTRACT

The opportunity of integrated use of skarn-magnetite ore concentration waste as a filler for magnesium binder and fine-aggregate filler has been determined. The formulas of fine-aggregate structure concrete on the base of blended magnesium binder and technogenic filler have been designed. The determining influence of the filler's fractional composition on the technological properties of molding materials, structure and physical-mechanical characteristics of composite material has been shown. By method of mathematical planning of the experiment the fractional composition of technogenic filler for fine-aggregate magnesium concrete has been optimized. The preferability of the molding material preparation method, implying the initial blending of the filler with saline gauging liquid and the subsequent introduction of the binder, has been substantiated. The technological scheme of wasteless processing of granular technogenic materials with obtaining artificial sands and fine-dispersed powders for binding composites has been developed.

Keywords: fine-aggregate concrete, magnesium binder, technogenic materials, filler, blended cement.

INTRODUCTION

The speed and efficiency of concrete production depend considerably on the state of mineral resources base of binders and fillers production [1-8]. The depletion of natural resources is accompanied with fundamental change of raw material base for building materials industry due to reclaiming of technogenic sources. The important source of new raw stuff is overburden rocks, ore extraction and concentration waste, ferrous slags. In spite of great amount and availability of technogenic materials, the level of their application in construction industry is low, which is due to low state of exploration and specific character of many types of waste, the absence of unified standards of evaluating the quality of new raw materials.

At the modern high-quality concretes production the principle of purposeful management of structure-formation processes at all technological stages is used. Production of fine-aggregate concretes implies using not only the optimal formula of the filler, but also introducing the active mineral fillers. The homogeneous fine-dispersed structure of fine-aggregate concretes provides the higher bending strength, high water-resistance and frost-resistance of composite material. The wide application of fine-aggregate concrete is hindered by the lack of resources of high-quality natural sands. The origin peculiarities of technogenic sands provide the higher resource of free internal energy due to dislocations, crystal lattice distortion, its defectiveness or destruction. This allows considering some kinds of technogenic granular materials as energy-saving raw stuff at producing fine-aggregate concretes.

The fine-aggregate concretes on the base of multicomponent blended binders are very promising [1, 2]. Lately the magnesium materials, characterized with intensive hardening and high strength of stone, have acquired a lot of interest. The low power consumption of its production provides the twofold reduction of magnesium binders production costs as compared to Portland cement [3].

The activating ability of caustic magnesite in comparison with other materials allows using a wider range of technogenic waste.

The magnesium materials production development is hindered by lack of sufficient theoretical base about the regularities of synthesis and properties of blended magnesium binders and composites.

The purpose of research is developing magnesium composite materials of fine-aggregate structure by optimizing the formula and technological methods of preparing multicomponent mixes, containing technogenic waste of various disperse composition.

METHODS OF RESEARCH

The preparation of initial materials included: grinding the solid raw stuff for the required state, drying wet materials at temperature 50-100°C, homogenizing of multicomponent fine-dispersed materials. To research the composition and structure of the substance the chemical, diffractometric, differential-thermal method and electron microscopy were used.

To grind materials the laboratory equipment, providing the multistage reduction of the initial particles size: roll-jaw crusher, vibration mill, high-speed ball crusher – were used. The vibration conical crusher «VKMD - 6» is aimed for grinding brittle materials of different hardness and provides fine grinding at the short duration of grinding. The high-speed ball mill «EMax» is equipped with two milling bowls, filled with balls 2 – 15 mm in diameter, made of zirconium oxide. The fraction of particles no bigger than 200 µm was obtained at the sifting machine «AS 200 control».

The granular composition of loose materials was evaluated by screen analysis. The dispersity of powders was evaluated with photometrical sedimentometer «FSH-6K» with scale range 0,1–300 µm. All the components of the blended magnesium binder were used in powdery condition with sieve residue percentage № 008 no more



than 5%.

To determine the special properties of composites the physical and mechanical tests of moulding and consolidated materials were used. Concrete mixes were characterized with fluidity, amounting to cone flow diameter in the interval 150–160 mm. The strength of composites was determined on cubic samples with edge 100 mm at the age 28 days of air-hardening. The «binder : filler» ratio – 1:1,5. The gauging liquid is magnesium chloride solution 1220–1250 kg/m³ of density. The samples were tested for compression resistance after the determined curing time on hydraulic press.

CHARACTERISTICS OF TECHNOGENIC FILLERS

The blended cement was prepared on the basis of caustic magnesite and a fine-ground technogenic component – the filler. As the filler for blended cement and for fine-grained concrete mixtures the skarn-magnetite ore concentration waste and the granodiorites grinding screenings were used. The skarn-magnetite ore concentration waste is formed at dry magnetic separation (DMS) of polymineral rocks. The DMS tailings are presented by disintegrated mass with grains no larger than 25 mm. The mineral basis of waste is formed by silicates, mas. %: pyroxenes 20 – 25; epidote 10 – 13; feldspars 8–

12; chlorites – 10; scapolite 8–11; garnets 7–12; amphiboles 7–14. The waste includes also, mas. %: calcite 4–7; pyrite 4–8; quartz 2–4; magnetite 3–4.

The great variety of mineral composition and the range of grain sizes of DMS tailings are not corresponding to the properties of conventional fillers. This has excluded this waste from the list of raw stuff for granular components of concrete. But the indicated peculiarities of DMS tailings predetermine the possibility of their mechanical processing to obtain fractions of the required particle size.

Granodiorites are holocrystalline rocks of the medium composition between granite and quartz diorite. The granodiorites grinding screenings is formed at the break-stone production and is presented by the mass of particles no larger than 10 mm. The mineral composition of the grinding screenings includes, mas. %: plagioclase 35–40; potash feldspars 20–26; quartz 15–37; biotite – до 3.

The fractional composition of the initial technogenic materials is shown in Table-1. The grain composition of the waste under research predetermines the possibility of obtaining manufactured sand on its base. The ore concentration waste, as coarse-grained material, was ground in three stages.

Table-1. Fractional composition of technogenic granular materials.

Residue on sieves, %	Particle fractions, mm										
	40+	40 – 20	20 – 10	10 – 5	5 – 2,5	2,5 – 1,25	1,25 – 0,63	0,63	0,315	0,315 – 0,14	0,14 – 0
Skarn-magnetite ores concentration waste											
Partial	2,09	53,60	39,80	3,34	0,41	0,05	0,03	0,07	0,33	0,28	
Total	2,09	55,69	95,49	98,83	99,24	99,29	99,32	99,39	99,72	100	
Grinding screenings of granodiorites											
Partial	–	–	–	50,20	16,80	5,00	4,80	7,00	9,90	6,30	
Total	–	–	–	50,20	67,00	72,00	76,80	83,80	93,70	100	

The grain composition of DMS ground tailings and granodiorites grinding screenings is characterized by the presence of particles over 5 mm in size. That's why the materials' dispersal curves are located outside the range recommended for sand as the concrete filler (Figure-1).

The fraction larger than 5 mm allows obtaining from technogenic materials under research the sands with fineness modulus 3,8–3,9. But coarse-grained sands precondition the increase of binders' consumption in concrete due to the higher void ratio. The particle size of the crushed material depends on mineral composition. The

similarity of the mineral composition of some fractions of waste is the result of the consistent crushability and the high degree of mineral intergrowth. The hardness of the most minerals is 5-7 by the Mohs scale. The X-ray patterns analysis indicates the increased content of chlorites – the least hard minerals (hardness 2-3 by the Mohs scale) in the fraction «0,315–0,63 mm»; the concentration of pyroxenes in the fractions «0,14–0,315» and «0–0,14 mm»; the absence of epidote and actinolite in the finely-dispersed part of material.

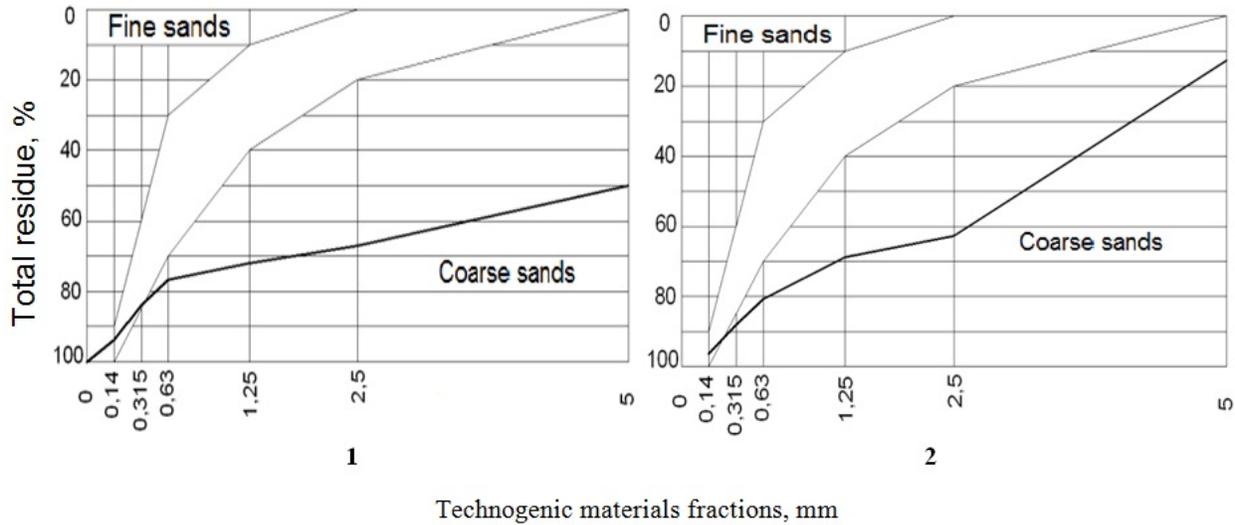


Figure-1. Grain composition of granodiorites grinding screenings (1) and of ground skarn-magnetite ores concentration waste (2).

Mostly the granodiorites grinding screenings are composed by minerals, which are traditional for concrete fillers: plagioclases, feldspars, quartz. The high quality of breakstone, at the production of which the grinding screenings is obtained, predetermines the fitness of the technogenic material of the similar mineral composition to obtain the fine filler for concrete. That's why the material composition of fractions of granodiorites grinding screenings was not analyzed.

The influence of type of the filler on magnesium compositions' properties

To research the influence of the type and fractional composition of technogenic filler on technological properties of magnesium concrete mixtures and on properties of the magnesium composite there was

used a blended magnesium binder, containing 50% of fine-ground ore concentration waste.

The technological properties of moulding materials were implicitly evaluated by the «fluid: solid» ratio. The comparative analysis of the findings indicates the dependence of concrete mixtures' molding properties and of concrete strength on the filler's fractional composition (Table-2). Concerning the mineral composition influence no distinct dependence was found, though the preeminence of composites made of ore concentration waste was indicated. The findings of the preliminary tests have confirmed the dependence of properties of concrete and concrete mixes on the granular component's particle size.

Table-2. The influence of type and characteristics of the filler on magnesium concrete's properties.

Type of filler	Particle size, mm	Fluid : solid	Average density, kg/m ³	Ultimate compression strength, MPa
Grinding screenings	0,63 – 0,315	0,18	2233	29
	1,25 – 0,63	0,14	2332	43
DMS tailings	0,63 – 0,315	0,17	2273	35
	1,25 – 0,63	0,15	2380	47

The strength characteristics of magnesium concrete are mostly influenced by: the percentage of the filler in the moulding material and mechanical properties of the granular component particles. The highest strength values are achieved at using the coarse fractions of the filler, which is conditioned by the small specific surface of particles. With the reduction of the particle size and the subsequent increase of the specific surface of the filler the

binder's coats around the filler grains become less thick. Such moulding materials have the high demand for the tempering liquid and have relatively low strength after their hardening.

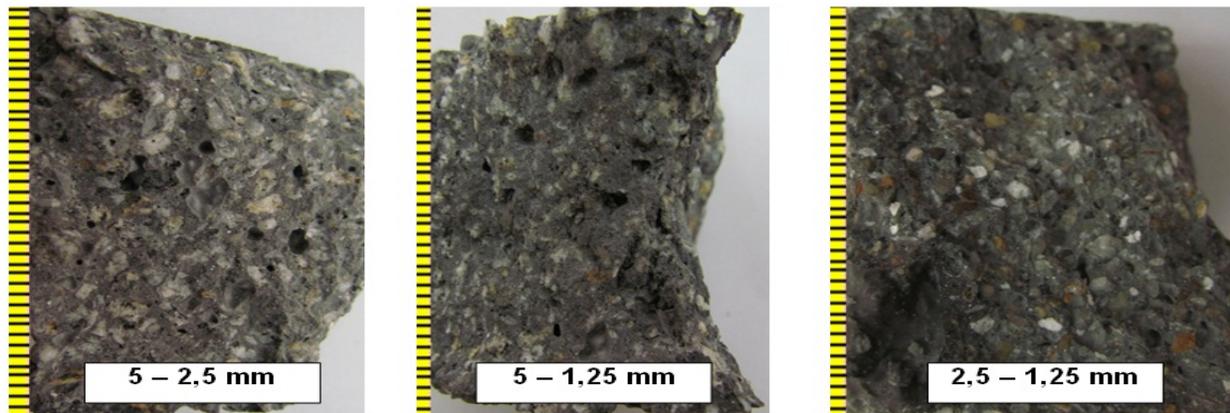
At the next stage of research the range of fillers' fraction was widened, and the share of the filler in the concrete mix is increased (Table-3).

**Table-3.** Basic characteristics of magnesium concretes with various fillers.

Type of filler	Particle size, mm	Binder: filler	Average density, kg/m ³	Ultimate compression strength, MPa	
				2 days	28 days
Grinding screenings	5 – 2,5	1 : 2	2175	35	51
Grinding screenings	5 – 1,25	1 : 2	2200	24	38
Grinding screenings	2,5 – 1,25	1 : 2	2266	21	32
Grinding screenings	1,25 – 0,63	1 : 2	1921	16	27
Grinding screenings	0,63 – 0,315	1 : 2	2106	11	25
Grinding screenings	0,63 – 0,315	1 : 2,5	2183	10	18
Grinding screenings	0,63 – 0,315	1 : 3	2201	9	17
Grinding screenings	0,63 – 0,14	1 : 2	2083	10	23
Grinding screenings	0,315 – 0,14	1 : 2	2065	8	21
DMS tailings	0,63 – 0,315	1 : 2	2134	15	27

The structure of magnesium concretes is presented in

Figures-2 and 3.

**Figure-2.** Magnesium composites with the grinding screenings of rocks.**Figure-3.** Magnesium composites with various amounts of fraction «0,63 – 0,315 mm» of the grinding screenings of rocks.

The structure of composites is characterized by the uniform distribution of filler's particles and firm adhesion of grains with the hardened binder. The presence of air-bubble voids in the structure of composites can be explained by the increased air entrainment into the low-ductile molding materials. For the concretes based on the

fractionated filler (Table-4) and at the ratio «binder: filler» amounting to 1 : 2, the highest strength values are achieved at the combination of fractions with various coarseness: «1,25–0,63 mm» with the finest fraction «0,63–0,14 mm» or with the largest fraction «5–1,25 mm». In the first case the fine fraction acts as filler and



contributes to the strengthening of cement stone, in the structure is achieved.
second case the highest compaction of the composite

Table-4. The influence of fractional composition of grinding screenings on concrete properties.

Content of fraction 1,25 – 0,63 mm, %	Content of fraction, %				Average density, kg/m ³	Ultimate compression strength, MPa	
	0,63 – 0,14 mm	0,63 – 0,315 mm	2,5 – 1,25 mm	5 – 2,5 mm		2 days	28 days
50	50	–	–	–	2140	10	21
50	–	50	–	–	2170	8	14
50	–	–	50	–	2170	10	18
50	–	–	–	50	2280	9	20

The influence of the binder's composition on the hardening of magnesium composites

The technological properties of molding materials and the physical and mechanical characteristics of composites depend on the magnesium binder's composition [1, 2, 6-9] (Table-5). The blended binders with the large range of technogenic filler content were used. The character of technological properties alteration indicates the reduction of a fluid component share in the moulding materials of the same flowability with the increase of share of the fine-ground magnetite ore concentration waste. The reduction of caustic magnesite share in the blended binder is accompanied with the increase of the composite density due to the increase of the «heavier» component and partially as a result of the reduction of liquid component share in the moulding material.

The comparative analysis of composite materials of various compositions indicates that replacing the caustic magnesite with a blended binder containing 30–50% of technogenic component virtually doesn't affect the strength properties of concrete. At using the coarse fractions of fillers the advantage of the strength properties

of composites on the base of blended binders was observed (Table-5). With the increase of the filler's share in the molding material the response to the material composition's alteration of the blended binder increases as well. To increase the high strength indices, comparable with those of caustic magnesite, the content of technogenic component at increasing the share of the filler in the blended binder should be limited.

The macrostructure of magnesium properties with various contents of technogenic filler in the blended binder is given in Figure-4.

The comparative analysis of the composites' structure indicates the close packing of components of various sizes in the structure of material. At carrying out the strength tests the samples are destroyed by the similar pattern: by the binder stone, and by the filler's particles. This indicates the uniformity of the stone structure and the high adhesion strength of components, as well as the comparable values of strength properties of the composite magnesium material's components.

Table-5. The influence of the binder's composition on magnesium concretes' properties.

The content of technogenic component in magnesium binder, %	Technogenic filler fractions, mm	Binder: filler	Fluid: solid	Average density, kg/m ³	Ultimate compression strength, MPa
0	2,5 – 1,25	1:1	0,28	2299	62
30	2,5 – 1,25	1:1	0,21	2424	67
50	2,5 – 1,25	1:1	0,29	2484	70
70	2,5 – 1,25	1:1	0,15	2504	45
0	1,25 – 0,63	1:1	0,29	2260	57
30	1,25 – 0,63	1:1	0,23	2441	54
50	1,25 – 0,63	1:1	0,19	2469	55
70	1,25 – 0,63	1:1	0,16	2468	38
0	1,25 – 0,63	1:1,5	0,24	2335	43
30	1,25 – 0,63	1:1,5	0,19	2482	42
50	1,25 – 0,63	1:1,5	0,16	2355	38
0	0,63 – 0,315	1:1	0,30	2135	38
30	0,63 – 0,315	1:1	0,22	2285	39
50	0,63 – 0,315	1:1	0,19	2303	36
0	0,63 – 0,315	1:1,5	0,24	1907	25
30	0,63 – 0,315	1:1,5	0,20	2137	27

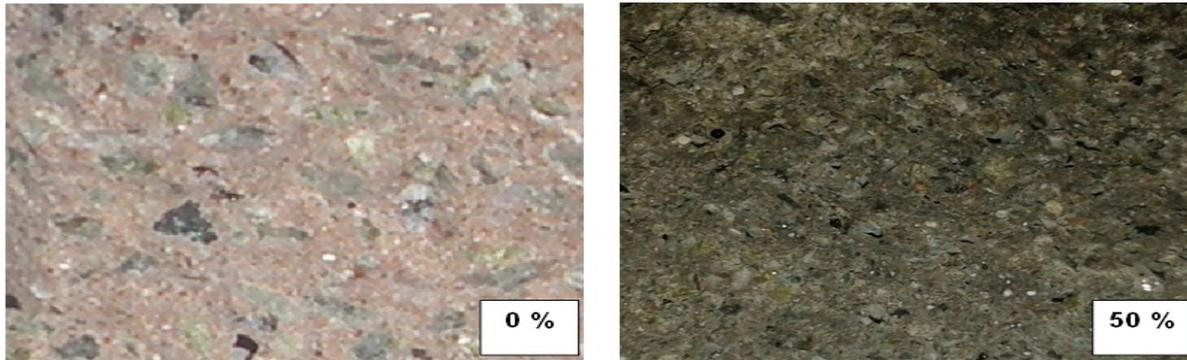


Figure-4. The structure of magnesium composites on the basis of blended binders with various content of DMS tailings (magnification x40).

The high strength properties of magnesium concrete based on waste are conditioned by the bonds forming at the contact between the binder stone and the filler. The more developed morphology of technogenic particles' surface contributes to the bond of concrete components. The contact strength of the filler with composite stone at the early stage of hardening is determined mostly by the mechanical interlocking due to rough surface, formed at the technological preparation of ore concentration waste. In the late stages of hardening the bond strength of concrete components is determined by the adhesion of the filler to the binder stone. At this the finely-dispersed mass of polymineral technogenic filler creates not only the concrete frame, but acts as the binding component at the artificial composite structure formation.

Optimization of technogenic filler's fractional composition

The findings, obtained by various researchers [10-14], show the feasibility of fractioning artificial sands

on the base of technogenic waste. The efficiency of combining artificial and natural fillers, providing the dense structure of fine-aggregate concrete, has been pointed out. The grain composition of the grinding screenings differ from the one recommended for the fine filler of concrete and needs altering by means of fractioning with the subsequent composing of grain mass of the required formula. To optimize the formula of technogenic filler the method of mathematical experimental design was used. At the formation of the fractionated filler the two-fraction mix of grain composition particles «1,25–5,0 mm» : «0,63–1,25 mm» in ratio 1:0,41; which was determined by calculation, was taken as basis. By method of step-by-step addition method of two-fraction mix with fine fraction «0,14–0,63 mm» the variations of fractionated filler were obtained. It was noted that with increasing the share of the fraction «0,14–0,63 mm» the pour density value is increased and the voidage is reduced (Table-6).

Table-6. Characteristics of the filler made of ore concentration waste.

Main fractional composition of the material, mm	Content of fine fraction «0,14 – 0,63 mm», %	The pour density, kg/m ³ , in the state		Voidage, %, in the state	
		loose	compacted	loose	compacted
«0,63 – 1,25» + «1,25 – 5,0»	нет	1268	1492	50,0	41,3
	5	1306	1484	48,6	41,6
	10	1308	1486	48,6	41,6
	15	1313	1488	48,4	41,5
	20	1317	1494	48,3	41,3
	25	1326	1498	47,9	41,2
	30	1332	1503	47,7	41,0
Initial		1373	1554	38,2	30,0

To optimize the grain composition of the fractionated filler of DMS tailings was used the method of mathematical planning of the experiment. With the help of «Statistica 6.0» application the matrix was solved, the available areas of fraction mixes are on the triangular diagram.

The mix under research consists of three

components – fractions of DMS tailings, mm: «0,14–0,63»; «0,63–1,25»; «1,25–5». Each mixture of these three components can be presented by point in a triangular coordinates system, determined by three variables. The sum of each mixture amounts to 1.0, so the values of the components in each mixture can be interpreted as proportions (Table-7).



Table-7. Experimental conditions of step-by-step addition method.

Factors	Variation levels			
	code appearance	-1	0	+1
Share of fraction «1,25 – 5,0 mm»	X ₁	0,44	0,54	0,64
Share of fraction «0,63 – 1,25 mm»	X ₂	0,24	0,34	0,44
Share of fraction «0,14 – 0,63 mm»	X ₃	0,12	0,22	0,32

As a result of processing the experimental data we have obtained the dependence of the strength (R) and average density (ρ) on the factors under research – content of the filler fractions, in the form of regression equations of the full quadratic model:

$$R = 35,8 - 5,9x_1 - 5,4x_2 - 4,8x_3 + 31,86x_1x_2 + 28,32x_1x_3 + 25,92x_2x_3 + 34,81x_1^2 + 29,16x_2^2 + 23,04x_3^2 \quad (1)$$

$$\rho = 2204 - 16,7x_1 - 15,8x_2 - 14,3x_3 + 263,86x_1x_2 + 238,81x_1x_3 + 225,94x_2x_3 + 278,89x_1^2 + 249,64x_2^2 + 204,49x_3^2 \quad (2)$$

The geometrical interpretation of regression equations is shown in Figure-5.

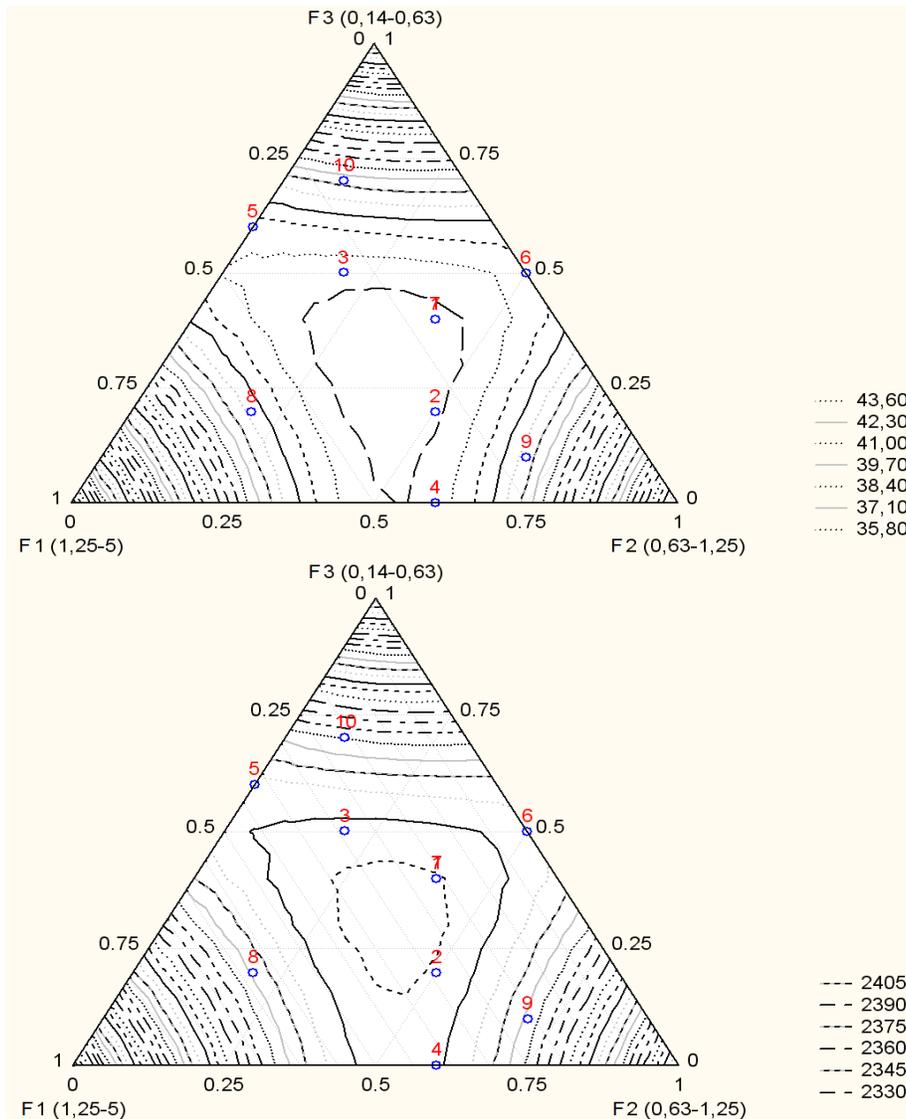


Figure-5. Response surfaces of fine-aggregate concrete properties' dependence on the fractional composition of the filler.



The highest values of strength and density of fine-aggregate concrete are achieved at the prevalence of the coarse fraction in the mixture «1,25 – 5,0 mm» – no less than 50%; at the fraction ratio «0,63–1,25 mm» : «0,14 – 0,63 mm», amounting to 1,1–2,0 : 1,0.

To optimize the grain composition technogenic filler – manufactured sand on the base of DMS – the method of rotatable two-factor experiment was used (Table-8). In accordance with the full planning matrix 9 formulas of concretes and concrete mixes were researched.

As a result of processing the experimental data by methods of mathematical statistics we have obtained the dependence of fine-aggregate concrete strength on the content of certain fractions in the form of regression equation:

$$R = 16,389 - 0,283x_1 - 0,638x_2 - 0,505x_1x_2 + 1,536x_1^2 + 1,882x_2^2. \quad (3)$$

Table-8. Conditions of rotatable two-factor experiment.

Factors		Variation levels				
Real aspect	Coded aspect	-1,414	-1	0	+1	+1,414
Percentage of fraction «2,5 – 5,0 mm», %	X ₁	50,00	53,66	62,50	71,34	75,00
Ratio of fractions, mm: «0,63 – 2,5» : «0,14 – 0,63»	X ₂	1,50	1,94	3,00	4,06	4,50

The regression equation for the dependence of size modulus on the fractional composition of the filler:

$$M_K = 2,541 + 0,002x_1 + 0,003x_2 - 0,008x_1x_2 + 0,002x_1^2 - 0,001x_2^2. \quad (4)$$

The regression equation for the dependence of pour density on the fractional composition of the filler:

$$\rho_{II} = 1420,61 + 2,91x_1 + 20,24x_2 - 23,97x_1x_2 + 52,45x_1^2 + 14,66x_2^2. \quad (5)$$

The analysis of regression equations has allowed determining the optimal area of the filler's fractional composition: «2,5 – 5,0 mm» 62,5 – 75,0%; «0,63 – 2,5 mm» 16,7 – 22,5%; «0,14 – 0,63 mm» 8,3 – 15,0%.

The analysis of the experiment findings, obtained by using various mathematical methods, has shown the comparability of optimization areas of the technogenic filler's fractional composition.

The method of electron microscopy has confirmed the close coalescence of components of the complex composite material. The structure of magnesium fine-aggregate composites is of the contact type: the particle contact through thin layers of the binder at keeping the continuity and integrity of structure. Such structures for the conglomerate are formed as a result of capillary structure formation and optimal distribution of cementing agent.

The influence of the moulding material preparation method on the properties of the composite

The role of the initial contact of granular component at preparing moulding materials is often very important. It is conditioned by the influence of the

character of concrete mixed preparation on the formation and state of contact layer between the filler particles and binder's stone. The structural peculiarities of the contact layer determine the strength characteristics of composite materials and influence the durability of products. The following methods of preparing magnesium fine-aggregate compositions on the base of technogenic filler were researched: 1 – concurrent blending of all the components of the mix; 2 – initial contact of the filler with the gauging liquid within 2 – 3 minutes of mixing and the subsequent introduction of blended binder.

It has been determined that the method, implying the separate treatment of the filler with gauge saline solution, is more preferable, which is confirmed by electron microscopy research findings (Figure-6), which show the reduction of contact areas defectiveness in composite microstructure and the increase of crystalline hydrates' share in the border layer.

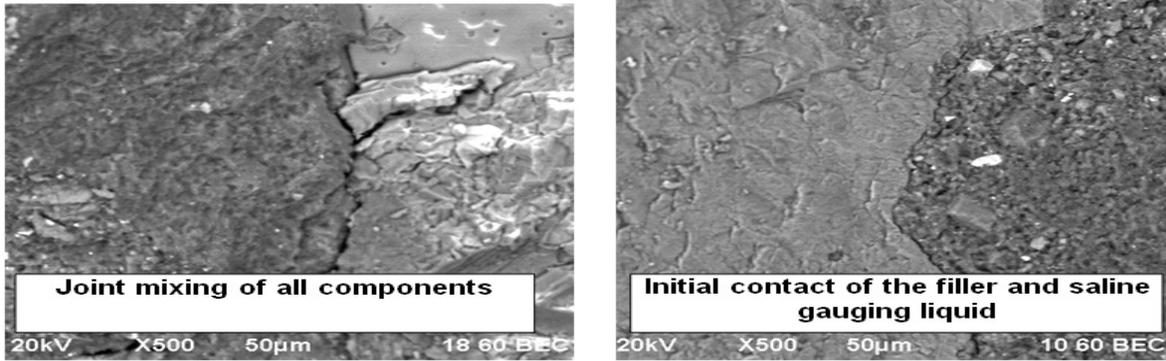


Figure-6. Microstructure of magnesium composites of various formulas.

The process scheme of ore concentration waste processing

To implement the technology of producing composite materials on the base of technogenic raw stuff, a process scheme of obtaining fractionated material by additional grinding and classification of the ground ore concentration waste has been developed (Figure-7).

The classification of the ground material was suggested to be performed by the dry method on oscillation screens. The particles with higher strength and hardness, separated from the bulk of the material, are

feasible to be used as concrete filler.

The coarse particles are presented by silicates, formed in early geological periods. The fine fractions of waste are the component of the blended magnesium binder. The feasibility of the integrated use of technogenic materials for concrete components production is confirmed by the maximal application of the advantages of the initial state of waste and minimal technogenic treatment of raw stuff, as well as high performance characteristics of the product.

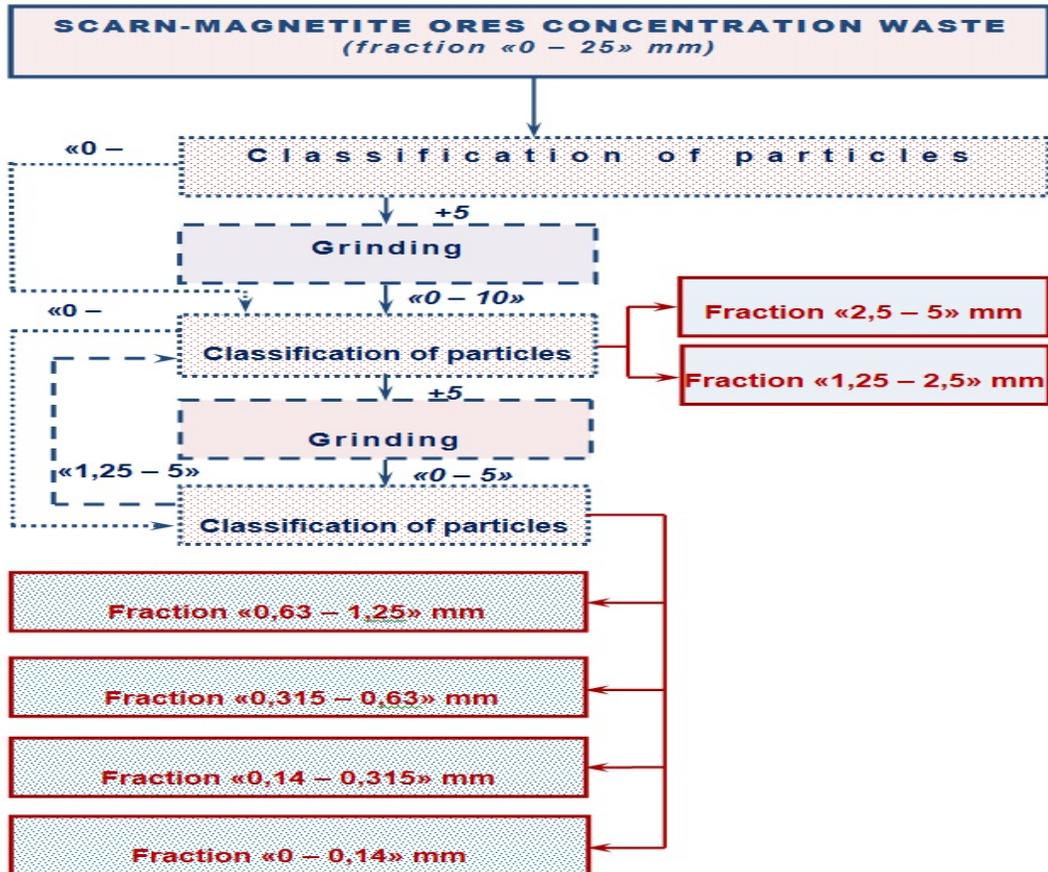


Figure-7. The scheme of obtaining fractionated technogenic material.



CONCLUSIONS

The granular composition of most of the technogenic materials differs from the fine filler, recommended for concrete, and requires correcting by means of additional grinding and classification of the ground material.

The polymineral composition of skarn-magnetite ore concentration waste conditions its multifunctional application for concrete.

The activating influence on the hydration capacity of minerals and the high adhesive ability of magnesium stone to granular materials provide the formation of contact structure of the conglomerate of skarn-magnetite ore concentration waste of different fractions.

INFERENCES

There were designed magnesium composites with regulated fine-aggregate structure on the basis of integrated use of skarn-magnetite ore concentration waste by means of activating influence of magnesium binder on the technogenic component.

The determining influence of the filler's fractional composition on technological properties of molding materials, structure and physical-mechanical properties of the composite material has been identified.

The fractional composition of technogenic filler has been optimized and the content of fine-dispersed filler for the formation of contact structure of concrete has been determined. To achieve the highest values of fine-aggregate concrete strength the prevalence of coarse fraction with particle size no less than 1,25 mm in the filler is feasible at the fractions «0,63 – 2,5» mm: «0,14 – 0,63» mm ratio amounting to 1,5 – 2,5. To increase the share of the filler in the composite material the blended binders should be used, containing no more than 50% of technogenic filler.

Предложен a method of preparing the molding material, which provides the initial contact of granular component with of granular component with magnesium chloride solution. This determines the possibility of washing the ground material and removing flour particles from the surface of grains. The activation of technogenic filler surface under the action of saline gauging liquid, which increases the adhesion of concrete components is possible.

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