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DEVELOPING THE COMPOSITION OF FINE-GRAINED CONCRETE FROM THE WASTE OF THE MINING AND PROCESSING ENTERPRISE

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The object of this study is fine-grained concrete from the waste of mining and processing plants. These wastes are fine-grained dusty sands of polymineral composition. Their use as an aggregate for concrete is restrained by high water consumption, which does not make it possible to obtain sufficient strength for concrete. Therefore, the problem to be solved was the substantiation of the composition of fine-grained concrete from these wastes with mineral and chemical additives, which would ensure obtaining physical-mechanical and hydrophysical properties reasonable for the production of construction articles. The composition of fine-grained concrete from the waste at the Poltava Mining and Processing Plant and slag Portland cement in a ratio of 3:1 and additives of micro silica (15 % of the cement mass) and polycarboxylate superplasticizer (2 % of the cement mass) with W/C=0.5 was obtained. The compressive strength of this concrete reaches 40 MPa, which exceeds the strength of fine-grained concrete of a similar composition on natural fine-grained sand by 3 times. This is due to a greater degree of cement hydration, a greater number of formed hydration products, the presence of silica and quartz particles, a more uniform alternation of gel, silica particles, and crystal hydrates in the structure of cement stone. As a result, the structure contains a larger number of electro heterogeneous contacts between particles and grains that have negative (quartz, calcium hydro silicates) and positive (crystal hydrates of portlandite, hydro aluminates and calcium hydrosulfoaluminate) surface charges. This is what determines the achieved strength and water resistance of fine-grained concrete. The resulting composition of fine-grained concrete is recommended for the production of construction articles

***Keywords:** fine-grained concrete, waste from mining and processing plants, hydration products, compressive strength, water resistance*

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1. Introduction

For the production of concrete, structures and building articles from it, a high-quality raw material base is necessary – igneous rocks for coarse aggregate, coarse-grained, or medium-grained sand for fine aggregate. There are many regions in the world where there is a shortage of quality sands for fine aggregate, the available sands are fine-grained, and the nearest deposits of coarse-grained and medium-grained sands are located at economically impractical distances. For example, at the enterprise where one of the authors of this paper started his professional career, for the production of reinforced concrete supports for the contact network of railroads, the technological documentation involved the use of coarse-grained sand. But given its absence, only medium-grained sand was supplied to the region from a quarry located 700 km from the enterprise by rail.

Nowadays, fine-grained concrete, which is made without coarse aggregate and only from fine aggregate, sand, is becoming increasingly popular. Under the conditions of shortage of high-quality natural sands, the search for alternative inorganic dispersed materials becomes relevant.

For the production of building materials, production waste is widely used, mainly from metallurgical and fuel-energy plants. One of the industrial wastes that could become an alternative filler for fine-grained concrete is multi-ton waste from mining and processing plants (waste from mining and processing plants or "tailings") accumulated over decades. Its utilization in concrete would also contribute to solving a number of environmental problems. However, the wastes from MPP are characterized by a high content of dusty fractions, which prevents their use as aggregates. Therefore, research aimed at the creation of high-quality fine-grained concrete from the wastes of MPP is relevant.

2. Literature review and problem statement

In work [1], the possibility of replacing natural sand in the composition of fine-grained concrete with dispersed secondary construction materials based on cement, in particular, slabs of a specific brand and nomenclature, was investigated. The dependences of strength on the percentage of substitution were obtained. It is shown that, despite the decrease in strength with an increase in this percentage, even with 100 % replacement, the strength of fine-grained concrete remains sufficient for the manufacture of construction articles and structural elements. But the issues related to increasing the strength of fine-grained concrete with aggregate from dispersed waste remained unresolved. The reason for this could be the objective difficulties associated with the fact that the strength required for specific products from these wastes was achieved, which made the corresponding further studies impractical for the client.

An option to overcome the relevant difficulties may be to study the influence of cement content, additives, methods of preparation of the mixture on strength. This is the approach used in work [2], which shows that in order to achieve the necessary physical and mechanical characteristics such as strength, wear resistance, fine-grained concrete requires an increased consumption of cement. To achieve these characteristics, which are sufficient for arranging floors with a moderate cement content, superplasticizer additives such as polycarboxylate, basalt fiber, and high-speed mixing of the mixture were used. An almost two-fold increase in strength and wear resistance was achieved. In [3], a similar approach was used and the possibility of increasing the strength of fine-grained concrete on slag Portland cement with chemical additives and water activation was investigated. Acceleration of hardening by 60 % and increase in strength by 25 % were achieved. But in works [2, 3] the dependences are investigated only for a certain composition of fine-grained concrete on high-quality aggregate, so the influence of the proposed methods on the properties of concrete on various dispersed wastes remains unknown. In addition, paper [3] investigates the effect only on compressive strength, and therefore the material is not considered in the context of structural work. Fine-grained concrete for floors is considered in [2], in connection with which the impact on wear resistance indicators is also investigated. But in order to fully take into account the work of new materials in the design, it is necessary to study the indicators that determine crack resistance, deformability, water resistance, etc., such as tensile strength, modulus of elasticity, coefficient of water resistance.

In [4], this approach is used and fine-grained concrete is already considered in the context of work in structures. It is shown that due to the features of the structure, it can be used where the use of normal-grained concrete with coarse aggregate is difficult or even impossible – for thin-walled, lightweight, complex-shaped structures, etc. But precisely because of this, increased demands must be met for its deformable properties, which remain much less researched than for normal-grained concrete. The authors suggested improving these properties with the addition of mineral fibers, studied the static and dynamic modulus of elasticity of such concrete, found that the fiber increases them and improves the plastic characteristics of concrete. In [5], the effect of the addition of different types of fiber – steel, polypropylene, glass – on a wider range of strength and deformation characteristics of fine-grained concrete is also investigated. It was established that different types of fiber have different effects on these characteristics, and corresponding dependences were obtained. And in [6], comparative studies of the strength and modulus of elasticity of fine-grained and normal-grained concrete under complex loads were performed. Dependences were constructed, which, under the conditions of insufficient reference data, make it possible to evaluate these properties of fine-grained concrete based on the data of normal-grained concrete.

Analysis of these works [4–6] reveals that precisely for fine-grained concrete, it is possible to adjust its properties by various technological techniques in a very wide range, including within the structure. This observation remained beyond the attention of the authors of those works. In [7], a study of the operation of gradient materials in structures was carried out. It has been proven that the production of structures from materials with gradients in physical and mechanical characteristics makes it possible to significantly increase their load-bearing capacity, minimize their mass and material consumption. We believe that it is possible to make fine-grained fiber-reinforced concrete with a gradient in a wide range of physical-mechanical, hydrophysical, and even electrophysical properties by adjusting the fiber dosage. But in the cited works, either certain specific compositions of fine-grained concrete on high-quality aggregate or abstracted fine-grained concrete without connection with its composition and structure, were investigated. Therefore, the influence of the proposed methods for regulating the properties of concrete on the wastes from MPP remains unknown.

In the works above, either certain specific compositions of fine-grained concrete on high-quality aggregate or abstracted fine-grained concrete without connection with its composition and structure, were investigated. In [8], a theoretical substantiation of the production of fine-grained concrete from the waste of a mining processing plant, in particular, Poltava MPP, slag Portland cement and micro silica additives, was performed. Its structure was substantiated taking into account the contacts between the angular aggregate grains, the possibility of increasing the strength by introducing mineral fillers and micro fillers with particles 5 times smaller than the aggregate grains and cement particles, respectively, was proven. The determination of the composition of fine-grained concrete from the waste of the Poltava MPP was justified by determining and ensuring the optimal value of the coefficient of displacement of the aggregate grains by the cement slurry with the inclusion of dusty fractions of the aggregate. The influence of the methods of compaction of the mixture in the products on their physical and mechanical properties was studied. It is proposed to form them by layer-by-layer pressing in layers with a thickness of 5 mm under a pressure of 12 MPa. Fine-grained concrete was obtained from the waste of the Poltava MPP and slag Portland cement with the addition of micro silica. Its strength exceeds the strength of concrete on natural quartz sand with the same ratio of aggregate and cement: in terms of compression – by 2 times, in terms of tension – by 1.9 times. However, in [8], the hydrophysical properties of fine-grained concrete, the influence of their dusty fractions and micro silica additives on the composition of hydration products of slag Portland cement and the structure of cement stone remained unexplored.

Thus, for the creation of fine-grained concrete from the waste of the Poltava MPP, the issues related to the insufficiency of experimental data on the influence of its composition on the physical-mechanical and hydrophysical properties, as well as the lack of data on the influence of MPP waste, Portland cement slag, micro silica on the structure of cement stone and composition of hydration products remained unsolved.

3. The aim and objectives of the study

The purpose of tour study is to establish the influence of the composition of fine-grained concrete from the waste of Poltava MPP (Ukraine), slag Portland cement and micro silica additives on its physical, mechanical, and hydrophysical properties, as well as the composition of slag Portland cement hydration products and the structure of cement stone. This will make it possible to start the industrial production of high-quality construction articles from fine-grained concrete on the waste from the Poltava MPP with the simultaneous disposal of the specified waste.

To achieve the goal, the following tasks were set:

– to conduct experimental studies to determine the compressive and tensile strength during bending, average density, water absorption by mass and volume, water resistance from the indicators of the composition of fine-grained concrete from the waste of the Poltava MPP with the addition of micro silica;

– to perform X-ray phase analysis of cement hydration products in fine-grained concrete from Poltava MPP waste with the addition of micro silica;

– to perform electron microscopic studies of the cement stone structure of fine-grained concrete from the waste of the Poltava MPP with the addition of micro silica.

4. The study materials and methods

The object of our study is fine-grained concrete from the waste of the mining and processing plant.

The main research hypothesis assumes that compressive and tensile strength during bending, water resistance, required for the manufacture of construction articles, can be provided by the use of slag Portland cement, micro silica additives and polycarboxylate superplasticizer. Portland cement slag will bind calcium hydroxide due to the pozzolanic reaction, micro silica particles will remain as a micro dispersed micro filler, which, together with quartz particles of the dusty waste fraction, will increase the number of electro-heterogeneous contacts in the cement stone structure.

Assumptions adopted in the study: compressive and tensile strength during bending – at least 30 MPa and 10 MPa, respectively, water resistance coefficient – at least 0.7 are required for the manufacture of construction articles.

Samples of fine-grained concrete with aggregates were studied: ore processing waste (tailings) from the Poltava mining and processing plant – experimental; fine-grained natural quartz sand – controls for comparison.

For the production of experimental and control samples of fine-grained concrete, slag Portland cement SPC III/A-400 DSTU B V.2.7-46:2010, similar to CEM III/A-32.5 EN 197-1:2011, with a slag content of 36–65 %, was used, with a specific surface area of 2800 cm^2/g, normal slurry density of 25 %, activity of 37 MPa.

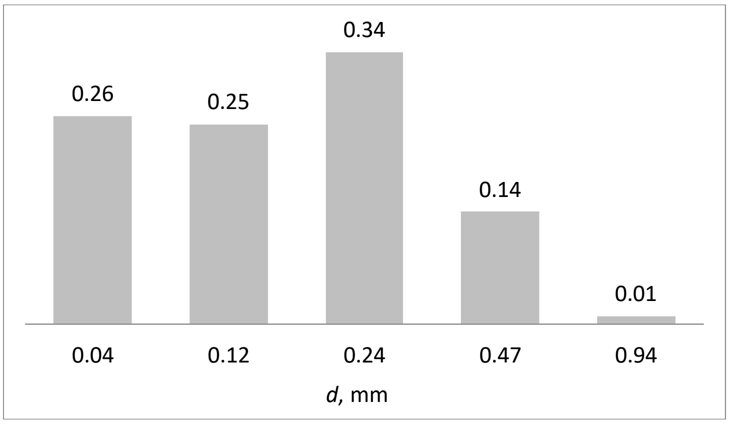
For the production of experimental samples of fine-grained concrete, the waste from the Poltava Mining and Processing Plant was used as an aggregate with a grain composition – residues on sieves: 0.63 mm – 1 %; 0.315 mm – 14 %; 0.16 mm – 34 %; 0.08 mm – 25 %; passing through a sieve of 0.08 mm (dusty fraction) – 26 %. According to this grain composition (Fig. 1, *a*), the fraction of 0.16–0.315 mm (34 %) with an average size of 0.24 mm is decisive, and the weighted average grain size is 0.2 mm. The specific surface area is 2700 cm^2/g, the true density is 2800 kg/m^3, the bulk density is 1700 kg/m^3, and the void factor is 0.41. Mineral composition: quartz – 65 %, carbonates – 14 %, magnetite – 3.5 %, other minerals – 17.5 %. The equilibrium electro surface potentials of these minerals in the medium of the pore electrolyte of cement stone with pH=12 are equal to [20]: quartz SiO_2 – (–1.26) V, magnetite – (–0.77) V; calcium carbonate – calcite $CaCO_3$ in its own environment with pH=7–(+0.2) V. Taking into account the mineral composition of the wastes from MPP, in the environment of cement stone at least 68.5 % by mass of their grains (quartz, magnetite) have a negative surface charge, at least 14 % (carbonates) – positive surface charge. Therefore, the waste from Poltava MPP has a dispersion close to natural very fine dusty sands but with a more developed surface, grains of irregular angular shape and polymineral composition. At least 68.5 % by mass of their grains have a negative surface charge, at least 14 % – positive.

For the production of control samples of fine-grained concrete, natural quartz sand from the Bezlyudivsky deposit (Kharkiv oblast, Ukraine) was used as an aggregate. Its grain composition – residues on sieves: 0.63 mm – 5 %; 0.315 mm – 20 %; 0.16 mm – 65 %; passage through a sieve of 0.16 mm – 10 %. According to this grain composition (Fig. 1, *b*), the fraction of 0.16–0.315 mm (65 %) with an average size of 0.24 mm is decisive, and the weighted average grain size is 0.3 mm. The specific surface area is 105 cm^2/g, the true density is 2630 kg/m^3, the bulk density is 1450 kg/m^3, and the void factor is 0.45.

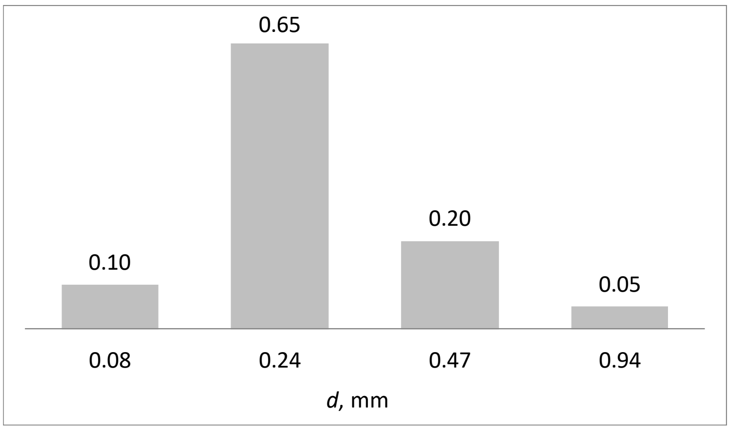
Micro silica with a SiO_2 content of 93–95 %, a specific surface area of 8500 cm^2/g was used as an active mineral additive in experimental formulations of fine-grained concrete, and Sika ViscoCrete 20HE polycarboxylate in an amount of up to 2 % of the cement mass was used as a superplasticizer additive.

Control and experimental compositions of fine-grained concrete are given in Table 1.

The physical and mechanical properties of fine-grained concrete were determined on beam samples 160×40×40 mm, which were made from uniform mixtures with a 1 cm cone slump. It is provided at W/C=0.5 for the mixture on natural sand – without additives, for the mixture on the waste from MPP – with the addition of a superplasticizer in the amount of up to 2 % of the cement mass. The samples were compacted by vibration (control samples), vibro-tamping, and layer-by-layer pressing in layers 5 mm thick with a pressure of 12 MPa (test samples) and subjected to natural hardening. The samples were tested by standard methods at the age of 7 and 28 days with the determination of the average density ρ, water absorption by mass W_m and volume W_V, the limit of tensile strength under bending f_t and compressive strength f, as well as the water resistance coefficient K_w. The coefficient of water resistance (softening) was determined as the ratio of the compressive strength of the samples in the water-saturated to constant mass state f_w to the compressive strength in the naturally dry state f – $K_w = f_w / f$.



a



b

Fig. 1. Histograms of distribution of grains by size: *a* — waste from Poltava MPP; *b* — Bezludivskyi natural quartz sand; *d* — the average size of the fractions

Physical-chemical studies of cement stone were performed as part of X-ray phase analysis and scanning electron microscopy.

For X-ray phase analysis, samples of fine-grained concrete at the age of 7 days were dried to a constant mass at a temperature of 70±3 °C. Then they were crushed to a particle size of 0.5÷1.0 mm, aggregate particles were carefully removed under a magnifying glass and ground in an agate mortar until they completely passed through a sieve with a cell size of 0.063 mm. The obtained powder was subjected to X-ray phase analysis using a modernized (computerized) X-ray diffractometer DRON-3, which is controlled, and X-ray patterns were recorded using DifWin1 software. The diffractometer was equipped with an X-ray tube 1.6BSV27-Fe with an iron cathode. Radiographs were recorded at a current of 20 mA and a voltage of 30 kV in the range of angles 2θ 7–80°.

Electron microscopic studies into the morphology of fine-grained concrete and its cement stone were performed at the age of samples over 1 year on the surface of their chips using a scanning electron microscope JEOL JSM-6390LV (Japan). Video shooting was carried out under an accelerating voltage of 15 kV with a magnification from ×100 to ×20000.

5. Results of research on fine-grained concrete with aggregate – waste from a mining and processing plant

5. 1. Results of experimental determination of concrete characteristics

Experimental studies of the dependence of the compressive and tensile strength during bending of fine-grained concrete with aggregate – the waste from Poltava MPP on the content of aggregate and active mineral additive – micro silica were carried out. The *W/C* of all mixtures was 0.5, the ease of laying of 1 cm was ensured by the introduction of a superplasticizer additive. The results of the study are shown in Fig. 2.

Fig. 2, *a* demonstrates that with an increase in the aggregate content from *A/C*=1:1 to 3:1, the compressive strength *f* and tensile strength f_t almost do not change and are in the range of 27–28.5 MPa and 9.5–9.7 MPa. With a further increase in W:C, *f* and f_t decrease sharply. The compressive and tensile strength during bending of the control composition on natural sand with *A*:*C*=3:1, *W/C*=0.5 was *f*=13 MPa, f_t=5 MPa, respectively. Analogous indicators of the experimental composition on the MPP waste exceed compressive strength *f* by 27/15=1.8 times, tensile strength at bending f_t – by 9.7/5=1.94 times. For further research and development of the composition of fine-grained concrete, *A*:*C*=3:1 was chosen, for which the influence of the content of an active mineral additive – micro silica – on the strength was investigated (Fig. 2, *b*).

Fig. 2, *b* demonstrates that with an increase in the silica content of *MS*:*C* from 0 to 0.15, the strength increases: for compression – from 27 to 39 MPa, therefore, by 1.44 times, for tension – from 9.7 to 11.6 MPa, therefore, by 1.2 times. With a further increase in the micro silica content, the increase in strength is within statistical error.

Thus, the composition of fine-grained concrete *A*:*C*:*MS*:*W*=3:1:0.15:0.5 was chosen for further research, and the control composition on natural sand – *A*:*C*:*W*=3:1:0.5. The results of a more detailed study of the specified compounds are given in Table 1. The nominal compositions (with dry aggregate) in kg/m^3 are specified taking into account the obtained average density of concrete ρ (Table 1):

$$A+C+MS+W=\rho; \quad (1)$$

$$A=C\times A/C; \quad (2)$$

$$MS=C\times MS/C; \quad (3)$$

$$W=C\times W/C, \quad (4)$$

where *A*, *C*, *MS*, *W* – consumption of aggregate, cement, micro silica, and water per 1 m^3 of concrete, respectively, kg/m^3; *A/C* – mass ratio of aggregate content to cement content; *MS/C* – mass ratio of micro silica content to cement content; *W/C* – water-cement ratio.

By substituting (2), (3), and (4) in (1), we get:

$$C\times A/C+C+C\times MS/C+C\times W/C=\rho. \quad (5)$$

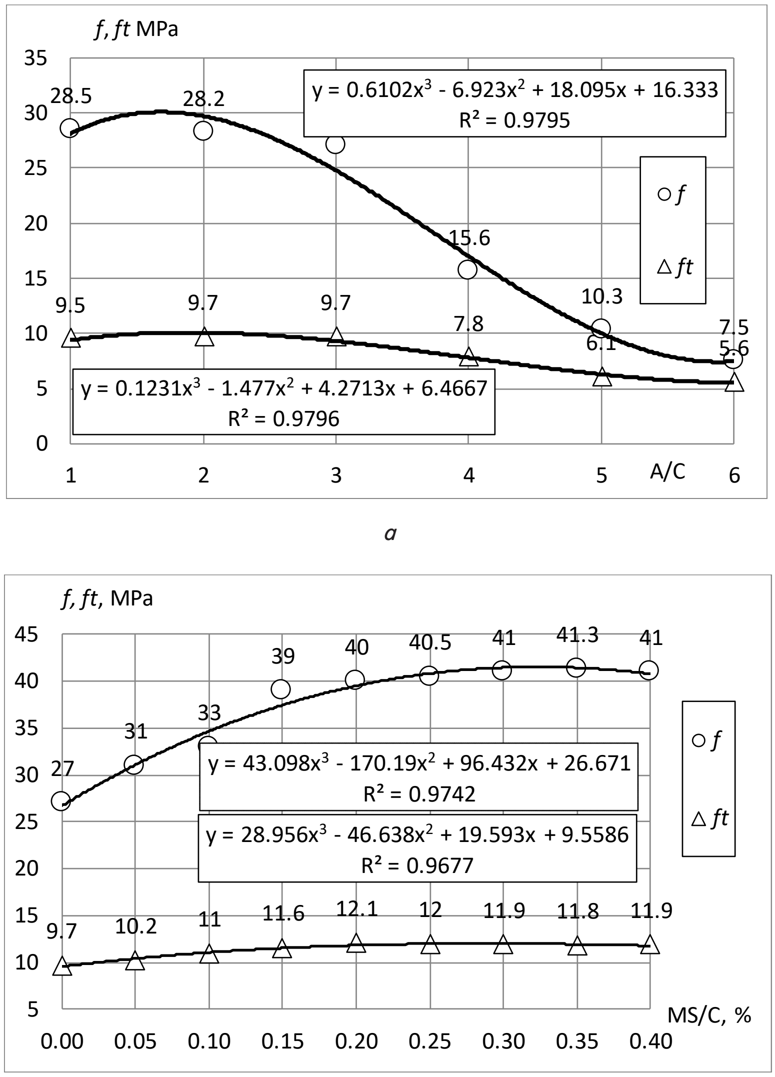


Fig. 2. Dependence of compressive strength f and flexural tension f_t at the age of 28 days of fine-grained concrete with aggregate – waste from Poltava MPP: *a* – on the mass ratio of aggregate content to cement content *A/C*; *b* – on the mass ratio of the content of the active mineral additive – micro silica – to the content of cement *MS/C* at *A/C*=3:1

Hence the formula for determining cement consumption:

$$C=\rho/(A/C+1+MS/C+W/C). \quad (6)$$

The consumption of components is determined according to formulas (6), (2), (3), and (4), according to the input data:

– control composition on natural quartz sand: ρ=2200 kg/m^3; *A/C*=3, *MS/C*=0; *W/C*=0.5;

– experimental composition on the waste from Poltava MPP: ρ=2350 kg/m^3; *A/C*=3, *MS/C*=0.15; *W/C*=0.5.

The calculation results are given in Table 1.

Table 1 demonstrates that fine-grained concrete from the waste of the Poltava MPP has physical, mechanical, and hydro-physical characteristics sufficient for construction articles: compressive and tensile strength when bending – 40 and 12.1 MPa, respectively, water resistance coefficient – 0.75. This exceeds the similar characteristics of fine-grained concrete of the control composition on natural sand by 3, 2.4, and 1.23 times.

Table 1

Composition and properties of fine-grained concrete

Indicator	Measurement unit	Value for fine-grained concrete on aggregate	
		Natural quartz sand	Poltava Mining and Processing Plant waste
1	2	3	4
The nominal composition of fine-grained concrete – the consumption of dry materials per 1 m^3:			
– aggregate *A*	kg/m^3	1,467	1,516
– cement *C*	kg/m^3	489	505

Continuation of Table 1

1	2	3	4
– micro silica *MS*	kg/m^3	0	76
– water	kg/m^3	244	253
– superplasticizer additive	kg/m^3	0	10.1
Relative composition of fine-grained concrete *A*:*C*:*MS*:*W*	mass fraction	3:1:0:0.5	3:1:0.15:0.5
Average density ρ	kg/m^3	2,200	2,350
Water absorption by mass W_m	%	8.14	8.5
Water absorption by volume W_V	%	7.62	7.8
Compressive strength f	MPa	13	40
Flexural tensile strength f_t	MPa	5	12.1
Water coefficient (softening) K_w	relative units	0.61	0.75
Crack resistance index f_t/f	relative units	0.39	0.30
Multiplicity of increase in the characteristics of fine-grained concrete of the experimental composition relative to the characteristics of the control composition:			
– medium density	relative units	1.07	
– compressive strength	relative units	3.08	
– bending strength	relative units	2.42	
– water resistance	relative units	1.23	

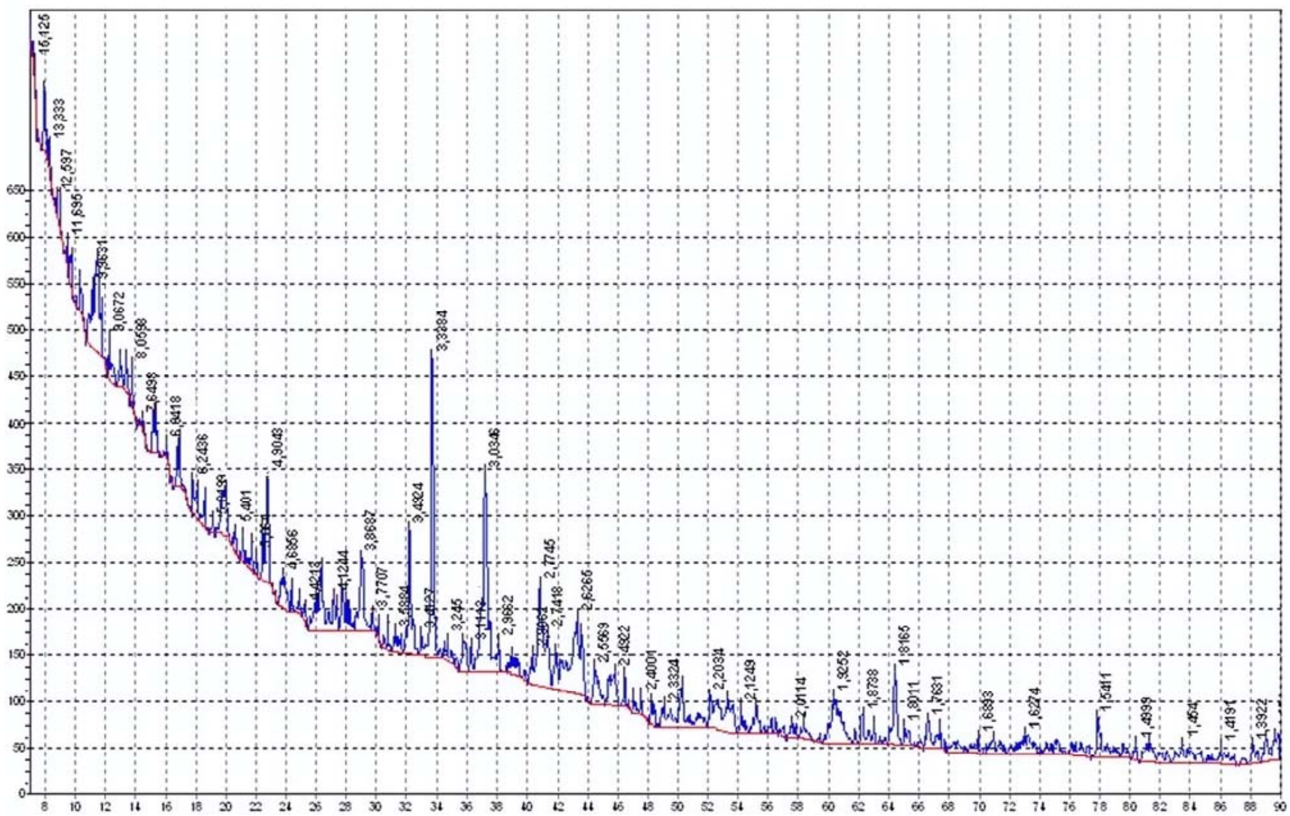
5. 2. X-ray phase analysis of cement stone

X-ray phase analysis of cement stone samples of control and experimental compositions was performed. The resulting radiographs are shown in Fig. 3. Taking into account that the cement consumption in the control and experimental compositions differs insignificantly – by 3 % (489 and 505 kg/m^3), the intensity of the diffraction maxima on their radiographs is comparable. The results of the analysis are summarized in Table 2.

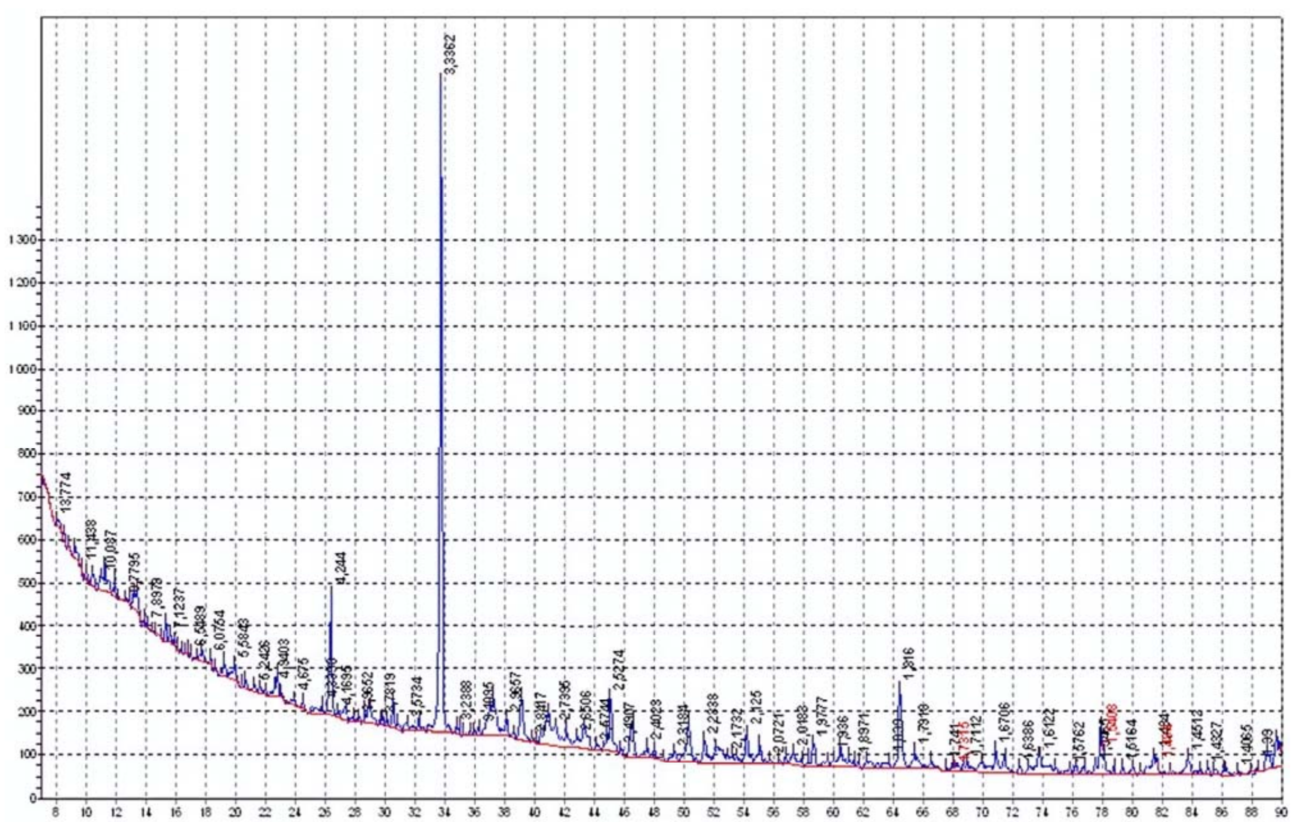
Table 2

Results of X-ray phase analysis of cement stone of fine-grained concrete on quartz sand and waste from the Poltava MPP with the addition of micro silica

Mineral		Plane-to-plane distance, Å	Intensity of diffraction maxima, imp./s, of cement stone in fine-grained concrete on aggregates:		I_e/I_c	
			quartz sand I_c	mining and processing plant waste with the addition of micro silica I_e		
Alit	C_3S	2.78	100	70	0.70	0.46
		2.61	70	15	0.21	
Tricalcium aluminate	C_3A	2.70	25	20	0.80	0.90
		1.91	10	10	1.00	
Portlandite	$Ca(OH)_2$	4.93	70	65	0.93	0.87
		2.63	95	85	0.89	
		1.93	45	35	0.78	
Low-basic calcium hydro silicates LBCHS	CSH(I)	12.50	50	50	1.00	0.63
LBCHS, HBCHS	CSH(I), $C_2SH(II)$	3.07	200	50	0.25	
High-basic calcium hydro silicates HBCHS	$C_2SH(II)$	9.80	110	0	0.00	0.38
		2.80	110	50	0.45	
		1.83	25	20	0.80	
Calcium hexahydrate hydro aluminate	C_3AH_6	5.14	20	20	1.00	1.89
		2.30	35	110	3.14	
		2.23	25	60	2.40	
		2.04	20	20	1.00	
Sulfoluminate *AFt* phase – ettringite	$C_3A{\cdot}3CaSO_4{\cdot}H_{32}$	9.73	130	50	0.38	1.00
		5.61	45	50	1.11	
		3.88	50	30	0.60	
		2.56	50	100	2.00	
		2.21	65	60	0.92	
Sulfoaluminate *AFm* phase	$C_3A{\cdot}CaSO_4{\cdot}H_{12}$	8.92	115	75	0.65	0.99
		2.87	25	20	0.80	
		4.46	20	10	0.50	
		3.99	20	40	2.00	
Quartz	SiO_2	3.34	330	1600	4.85	3.46
		1.81	85	195	2.29	
		1.54	40	130	3.25	



a



b

Fig. 3. Radiographs of cement stone of fine-grained concrete on aggregates: *a* – quartz sand; *b* – wastes from the Poltava Mining and Processing Plant with the addition of micro silica

Table 2 demonstrates the following:

1) diffraction maxima are present on the X-ray images of the control and experimental composition:

– clinker minerals – C_3S, C_3A (others were not considered);

– typical hydration products – portlandite $Ca(OH)_2$, low-basic and high-basic calcium hydro silicates CSH(I), $C_2SH(II)$, calcium hydro aluminate C_3AH_6, sulfoaluminate AFt- and AFm-phases;

– quartz SiO_2;

2) diffraction maxima of C_3S and C_3A clinker minerals in the experimental composition compared to the control composition are smaller: C_3S by 30 %, C_3A by 79 %, which indicates a correspondingly higher degree of their hydration;

3) the diffraction maxima of portlandite $Ca(OH)_2$ and crystalline calcium hydro silicates – low-basic CSH(I) and high-basic $C_2SH(II)$ in the experimental composition compared to the control, are smaller: $Ca(OH)_2$ – by 23 %, CSH(I) – by 37 %, $C_2SH(II)$ – by 62 %. Taking into account the 30 % smaller amount of C_3S (higher degree of its hydration) may indicate a larger amount of X-ray amorphous hydro silicate gel (CSH-gel);

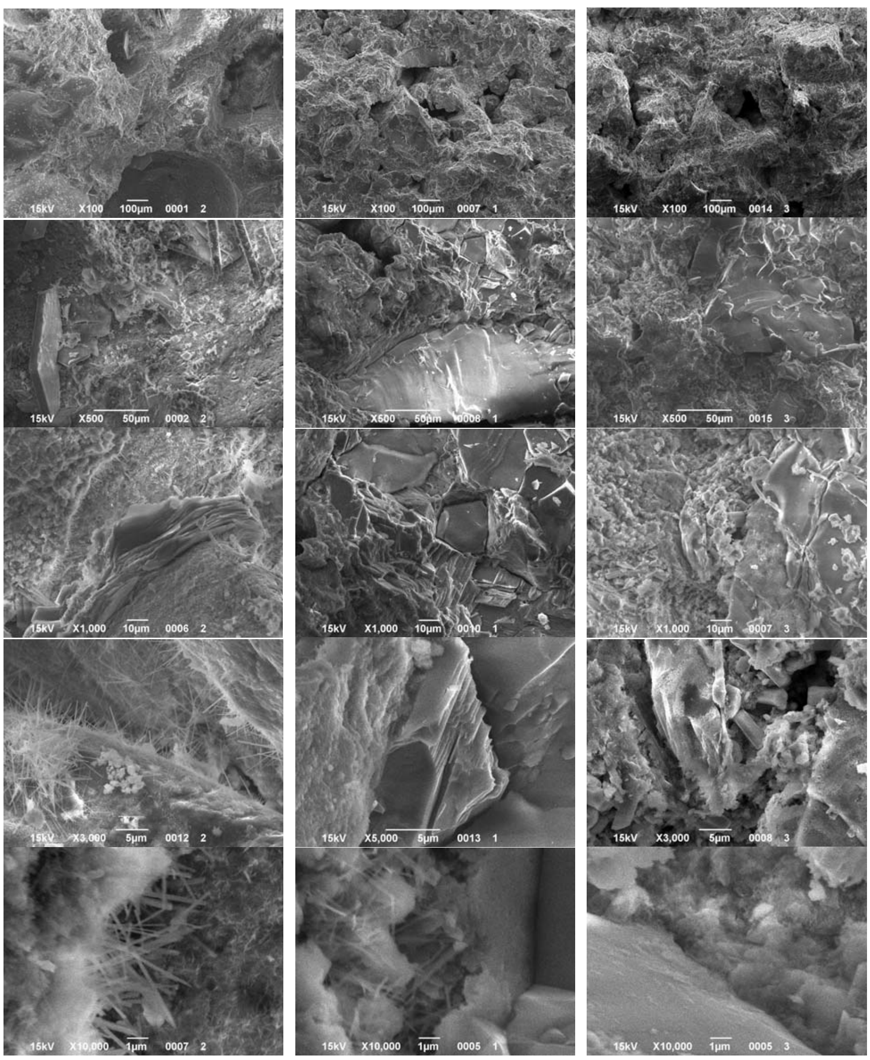
4) the diffraction maxima of calcium hydro aluminate C_3AH_6 in the experimental composition are on average 89 % higher in comparison with the control composition. This confirms the conclusion of point 1 about the corresponding increase in the degree of hydration of C_3A (the diffraction maximum of C_3A is 79 % lower);

5) the diffraction maxima of sulfoaluminates AFt- and AFm-phases in the test and control composition are the same, which indicates their equal amount, limited by the content of gypsum cement;

6) the diffraction maxima of quartz SiO_2 in the experimental composition are 3.46 times greater than in the control composition, which indicates its correspondingly greater amount, due to the presence of dusty fraction in the wastes from MPP.

5. 3. Electron microscopic studies of fine-grained concrete

Electron-microscopic studies of chipping of control and test samples of fine-grained concrete were also performed. The most characteristic of the obtained electron microscopic images are shown in Fig. 4. The results of the analysis of these pictures are given in Table 3.



a *b* *c*

Fig. 4. Electron microscopic photographs of fine-grained concrete at magnification from ×100 to ×10000 on aggregates: *a* – quartz sand, the mixture is compacted by vibration; *b*, *c* – waste from a mining processing plant with the addition of micro silica, the mixture is compacted by tamping (*b*), layer-by-layer pressing (*c*)

Table 3

Results of the analysis of electron microscopic images of samples of fine-grained concrete on quartz sand and waste from the Poltava MPP with the addition of micro silica

Image at magnification	Features of the structure and objects observed on electron microscopic images of samples:	
	Control	Experimental
×100	Pores with a size of 200–500 μm	Pores less than 100 μm in size
×500	Granular products of hydration, among which several individual hexagonal plates of portlandite crystals with a size of 50–100 μm are visible	Granular products of hydration, among which several quartz particles with a size of 50–100 μm are visible
×1000	Granular products of hydration, among which a loose layering of lamellar portlandite crystals up to 500 μm in size is visible	Granular hydration products or dense layers of portlandite plates, among which several quartz particles 10–30 μm in size are visible
×3000–5000	A large pore in which needle-shaped crystals of ettringite 5 μm long have sprouted	Hydration products: hydro silicate gel, dense layers of portlandite plates, several columnar crystals 5 μm long, apparently calcium hydro aluminate C_3AH_6
×10000	A large pore in which needle-shaped crystals of ettringite 5 μm long have sprouted	Hydration products: hydro silicate gel on the quartz surface, portlandite crystals and needle-shaped ettringite crystals up to 5 μm in size

Table 3 demonstrates that in the fine-grained concrete of the experimental composition on the waste from the Poltava MPP with the addition of micro silica compared to the concrete of the control composition on natural quartz sand:

– pore sizes are significantly smaller;

– a larger number of quartz particles, hydro silicate gel and crystal hydrates of calcium hydro aluminates;

– more uniform alternation in the structure of hydration products of crystal hydrates and gel.

6. Discussion of results of research on fine-grained concrete with aggregate – the waste from the mining processing plant

As can be seen from the Table 1, the physical and mechanical characteristics of the samples of the experimental composition on the waste from the Poltava MPP with the addition of micro silica significantly exceed the characteristics of the samples of the control composition on natural quartz sand:

– compressive strength – 3 times;

– tensile strength during bending – 2.4 times;

– water resistance coefficient – by 23 %.

However, the water absorption of samples of the experimental composition slightly exceeds the water absorption of samples of the control composition. This may indicate that, despite the fact that the porosity of the samples of the experimental composition is slightly higher than the porosity of the control samples (Table 1), there are much more electrically heterogeneous contacts in the structure of the samples of the experimental composition. These contacts are implemented between elements of its structure with different surface charges:

– negative – particles of quartz, silica, calcium hydro silicates;

– positive – crystal hydrates of portlandite, calcium hydro aluminate, AFm- and AFt-phases.

This is consistent with the results reported in [9].

It is also obvious that the formation of dense contacts between particles contributed to the greater number of these contacts, especially with the participation of angular aggregate grains according to the schemes proposed in [8]. This shows the positive role of dusty fractions of quartz in the wastes from MPP, which is consistent with [10], and the simultaneous use of slag Portland cement, the positive role of which for fine-grained concrete is shown in [3], and micro silica. Obviously, slag Portland cement slag is primarily involved in pozzolanic reactions, and part of the micro silica, instead of dissolving as a result of the pozzolanic reaction, remains as an ultra-micro filler that seals the contacts according to [8]. The primacy of pozzolanic reactions of slag aluminosilicates compared to amorphous silica can be verified by thermodynamic calculations, but obtaining initial data for such calculations has certain difficulties.

These conclusions are confirmed by the results of X-ray phase analysis and electron microscopy:

– larger volume in the samples of the experimental composition compared to the samples of the control composition of quartz, hydro silicate gel (with negative surface charges) and calcium hydro aluminates (with positive surface charges);

– more uniform alternation in the structure of the hydration products of samples of the experimental composition of crystal hydrates and gel (clearly visible on EMC at magnifications of ×1000 and more). In the samples of the control composition, on the contrary, loose layers of portlandite and large masses of hydro silicate gel are visible, as well as needle crystal hydrates of ettringite, which have grown into air pores without forming contacts with other particles.

Our research is limited to the waste from the Poltava Mining and Processing Plant. The results are applicable to wastes from other MPP in the case of their close grain (Fig. 1, *a*) and mineral composition. In the case of a significant difference in grain and mineral composition, it is necessary to conduct similar studies.

The resulting composition of fine-grained concrete is recommended for the production of construction articles such as hollow wall stones, paving slabs, side stones. However, high frost resistance must be ensured for such products as paving tiles and curb stones. The disadvantage of this study is the lack of frost resistance tests. In the future, this shortcoming can be eliminated – the production of the specified products and the development and approval of technical conditions for them should be preceded by a study of the composition for frost resistance.

The development of this research is to conduct physicochemical studies of hydration products by other independent methods, for example, infrared spectroscopy, thermal analysis, scanning electron microscopy with micro probing. This could increase the reliability of identification of hydration products. But there are certain difficulties for such a study, related to the difficulty of reproducing samples from materials available in the market, which would require repeating the determination of physical-mechanical and hydrophysical properties and physical-chemical studies in full.

7. Conclusions

1. As a result of our experimental studies, it was established that with an increase in the content of aggregate A – waste from Poltava MPP up to 3:1 from the mass of cement C, the compressive and tensile strength almost does not change, and with a further increase it sharply decreases. With an increase in the content of micro silica MS up to 15 % of the mass of cement, the compressive and tensile strength increases, with a further increase – the strength does not increase. The composition of fine-grained concrete from the waste of the Poltava MPP was obtained: A:C:MS:W=3:1:0.15:0.5, the compressive and tensile strength of which is 40 MPa and 12.1 MPa, respectively, the coefficient water resistance – 0.75. This exceeds the similar characteristics of fine-grained concrete of the control composition on natural sand by 3, 2.4 times and 23 %, respectively. The resulting composition of fine-grained concrete can be recommended for the production of construction articles that do not require frost resistance. For products operated under atmospheric conditions, it is necessary to carry out additional research, including testing for frost resistance.

2. As a result of X-ray phase analysis, it was established that the degree of hydration of cement in the experimental composition exceeds the degree of hydration of cement in the control composition. The amount of portlandite and crystalline calcium hydro silicates CSH(I) and $C_2SH(II)$ in the experimental composition compared to the control is smaller, which, taking into account the greater degree of hydration, may indicate a larger amount of X-ray amorphous hydro silicate gel (CSH-gel). The amount of calcium hydro aluminate C_3AH_6 in the experimental composition is greater compared to the control, and sulfoaluminates AFt- and AFm-phases are the same. The amount of quartz in the experimental composition is significantly higher compared to the control composition due to the dusty fraction of the waste from MPP.

3. As a result of electron microscopic studies, it was established that in the fine-grained concrete of the experimental composition on the waste from the Poltava MPP with the addition of micro silica, compared to the fine-grained concrete of the control composition on natural quartz sand:

– pore sizes are significantly smaller;

– a larger amount of silica (quartz and amorphous), hydro silicate gel (with negative surface charges) and calcium hydro aluminates (with positive surface charges);

– more uniform alternation in the structure of hydration products of crystal hydrates and gel.

Together, this provides a greater number of electrically heterogeneous contacts in the structure of cement stone and fine-grained concrete as a whole.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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