

Technological foundations for solving problem of metallurgy and TPP waste utilization for development of "Green" technology for composite cements production

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Abstract. The chemical-mineralogical compositions and physic-chemical properties of slag waste from the Angren TPP and Uzmetkombinat JSC were determined. A Conclusion was issued on their suitability for use as additives in cement and the possibility of using them for producing new types of hybrid additives for the production of composite Portland cements. With different combinations and ratios of Portland cement clinker, natural gypsum stone, and hybrid additives, the compositions of composite Portland cements were obtained and optimized, and Conclusions were issued on their compliance with the requirements of the Standard of the Republic of Uzbekistan Uz DSt 2830:2014 "Portland cement with composite additives. Specifications".

1 Introduction

To achieve the National Goals and Objectives in the field of sustainable development for the period up to 2030, the concept of environmental protection of the Republic of Uzbekistan establishes all aspects of maintaining the ecological balance in the republic, from "improving an environmentally friendly waste management system" to "economic incentives for the development and implementation of waste-free and low-waste technologies in production, as well as technologies for processing waste from mining and processing productions"[12].

The President of Uzbekistan, in his speeches, outlined the key areas of reforms being carried out in the country and shared his vision of the prospects for international cooperation in the field of green recovery. He emphasized that to make effective decisions on green and sustainable development, it is necessary to unite the efforts of the entire international community.

One of the most effective areas of waste processing is their use as components for the production of building materials and products since this direction allows you to dispose of almost all types of waste in large quantities to obtain high-quality products at low

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production costs. In turn, the most promising area of waste processing into building materials and products is the production of composite materials [1-6].

At the same time, special attention is paid to the disposal and processing of solid waste from metallurgy, energy, and the chemical industry. Large-tonnage solid wastes include various types of slags from metallurgy and thermal power plants, with a rational approach to the processing of which, they can serve as valuable raw materials for the cement clinker production pozzolanic, and composite Portland cements [7-18].

1.1 Purpose of the study

The aim of that research consists of the development of scientific and applied bases for the use of industrial waste from energy and metallurgy as ingredients of hybrid additives by examining their suitability and establishing compliance with the requirements of Uz DST 901-2020 for cement additives, optimizing compositions and developing technology for producing composite Portland cements using them

2 Methods

The determination of the chemical composition of the starting materials was carried out following the requirements of GOST 5382-91 "Cements and materials for cement production. Methods of Analysis". The physical and mechanical properties of highly filled Portland cements were determined on small cube samples 2x2x2 cm in size with a composition of 1:0. Portland cement without additives served as a base for comparison. The brand of new types of composite Portland cements with hybrid additives is determined following the GOST 310.4 methodology.

3 Results and Discussion

To study the effect of new types of hybrid additives on ordinary Portland cements' physical and mechanical properties, Portland cement clinker JSC Bekabadcement was used as a matrix; the chemical properties are shown in table 1.

Table 1. Chemical compositions of Portland cement clinker and gypsum stone.

Material name	The content of the mass fraction of oxides,%						
	p.p.p.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
Clinker JSC "Bekabadcement"	0.36	56.40	6.27	4.77	2.79	1.00	0.37
Gypsum stone	13.60 at 4000C	2.11	0.49	0.15	31.08	3.79	38.09

Portland cement "green" composites, the production of which was envisaged within the framework of the project, should contain hybrid additives from active ash and slag mixtures (AASM) of the Angren TPP and steel smelting wastes of Uzmetkombinat JSC: processed steelmaking slags (PSS), ladle (LS), furnace (FS) and waste from ferrosilicon – microsilica (MK) production. The chemical compositions of these wastes are shown in table 2.

Table 2. Chemical compositions of ingredients for the formation of hybrid additives for cement

Material name	The content of the mass fraction of oxides,%							
	p.p.p.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	other
Waste JSC "Uzmetkombinat"								
Microsilica	2.79	90.84	1.51	1.59	0.56	1.00	0.23	1.48
Ladle slag	1.49	35.93	7.56	2.79	33.06	6.04	0.78	12.35
Furnace slag	-	31.34	9.57	20.78	15.97	4.23	1.19	16.92
Steel slag	9.78	27.92	9.10	10.93	25.73	10.43	1.03	5.08
Ash and slag mixture of Angren TPP dry removal								
slag part	0.39	67.09	22.29	5.1	3.06	Sl.	0.61	1.46
Ash part	0.92	63.08	21.27	4.83	3.10	1.01	1.31	4.48
Average sample AASM	3.0	62.02	23.55	4.32	3.0	-	1.28	0.8

Microsilica consists mainly (90.9%) of particles with a size of 0.1-0.2 microns (32.2%), 0.2-0.4 microns (34.1%) and 0.4-1.0 microns (24.6%). The rest, 9.1% of microsilica constituents, are particles with grain sizes less than 0.1 μm (3.7%), 1.0-2.5 μm (4.0%), and more than 2.5 μm (1.4%). The average sample of ultrafine microsilica contains 90.84% SiO₂. Impurities in the amount of 7.29% are Al₂O₃, Fe₂O₃, CaO, MgO, R₂O, and MnO₂ oxides. The high content of silica in ultrafine microsilica predetermines its activity in the composition of cement due to an increase in the contact surface of its particles with particles of clinker minerals and enhanced absorption of calcium hydroxide released during the hydrolysis and hydration of C₃S during hardening of Portland cement with the formation of hydrosilicates of the tobermorite group.

Figure 1 shows the results of the X-ray phase, DTA, and IR spectroscopic analyzes of ultrafine microsilica. Following the data in Figure 1, the main component of microsilica is X-ray amorphous silica - silicon oxide in the form of cousite - SiO, which gives it a high chemical activity in aqueous media.

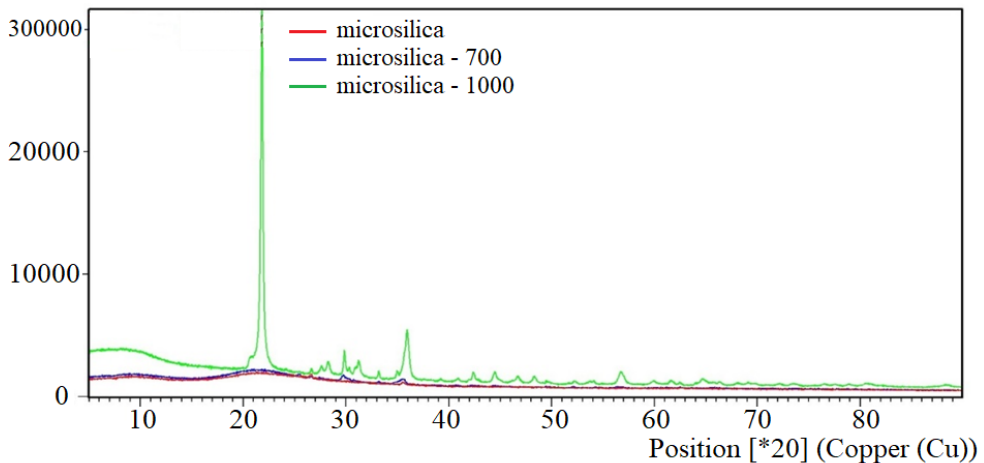


Fig. 1. X-ray diffraction pattern of ultrafine microsilica.

The low-intensity lines present in the diffraction pattern at 30° and 35° characterize the presence in its composition of a small amount of crystalline silica and calcium-magnesium aluminosilicates $\text{Ca}(\text{Fe}, \text{Mg}, \text{Al})\text{Si}_2\text{O}_6$. The appearance of intense diffraction reflection in the region of $20\text{--}23^\circ\text{C}$ with a maximum at 22°C and 35°C ($d/n = 0.403$ and 0.249) nm during the firing of MC at 1000°C is associated with polymorphic transformations of the transition of silica from an amorphous state to a crystalline form with the formation, probably α -tridymite. The infrared spectra of ultrafine microsilica are characterized by the presence of three absorptions at wave numbers with maxima at 475sm^{-1} , 798 , 44sm^{-1} , and 1000 sm^{-1} (Figure 2). It is known that the IR spectra of multiple violations of the total internal reflection of MC coincide with the position of peaks and absorption bands in the transmission spectra in the range of $500\text{--}4500\text{ cm}^{-1}$ with orthosilicic acid sol. The absorption band, which is revealed at a wave number of 475 sm^{-1} , is characteristic of deformation vibrations of bonds inside silicon-oxygen joints and their groups. Due to symmetric vibrations of Si–O–Si bonds (vibrations of silicon-oxygen tetrahedra relative to each other), an absorption band appears at 798 sm^{-1} , which indicates their complete polymerization. In the spectral region $870\text{--}1250\text{ sm}^{-1}$ with a maximum at 1000 sm^{-1} , there is a deep absorption band associated with transverse, mixed, and longitudinal vibrations of Si–O–Si bonds, with a transmission minimum at 1080 cm sm^{-1} , which is revealed at a wave number of 475 sm^{-1} , is typical for deformation vibrations of bonds inside silicon-oxygen joints and their groups. Due to symmetric vibrations of Si–O–Si bonds (vibrations of silicon-oxygen tetrahedra relative to each other), an absorption band appears at 798 sm^{-1} , which indicates their complete polymerization. In the spectral region $870\text{--}1250\text{ sm}^{-1}$ with a maximum at 1000 sm^{-1} , there is a deep absorption band associated with transverse, mixed, and longitudinal vibrations of Si–O–Si bonds, with a transmission minimum at 1080 cm sm^{-1} , which is revealed at a wave number of 475 sm^{-1} , is typical for deformation vibrations of bonds inside silicon-oxygen joints and their groups. Due to symmetric vibrations of Si–O–Si bonds (vibrations of silicon-oxygen tetrahedra relative to each other), an absorption band appears at 798 sm^{-1} , which indicates their complete polymerization. In the spectral region $870\text{--}1250\text{ sm}^{-1}$ with a maximum at 1000 sm^{-1} , there is a deep absorption band associated with transverse, mixed, and longitudinal vibrations of Si–O–Si bonds, with a transmission minimum at 1080 cm sm^{-1} . Due to symmetric vibrations of Si–O–Si bonds (vibrations of silicon-oxygen tetrahedra relative to each other), an absorption band appears at 798 sm^{-1} , which indicates their complete polymerization. In the spectral region $870\text{--}1250\text{ sm}^{-1}$ with a maximum at 1000 sm^{-1} , there is a deep absorption band associated with transverse, mixed, and longitudinal vibrations of Si–O–Si bonds, with a transmission minimum at 1080 cm sm^{-1} . Due to symmetric vibrations of Si–O–Si bonds (vibrations of silicon-oxygen tetrahedra relative to each other), an absorption band appears at 798 sm^{-1} , which indicates their complete polymerization. In the spectral region $870\text{--}1250\text{ sm}^{-1}$ with a maximum at 1000 sm^{-1} , there is a deep absorption band associated with transverse, mixed, and longitudinal vibrations of Si–O–Si bonds, with a transmission minimum at 1080 cm sm^{-1} .

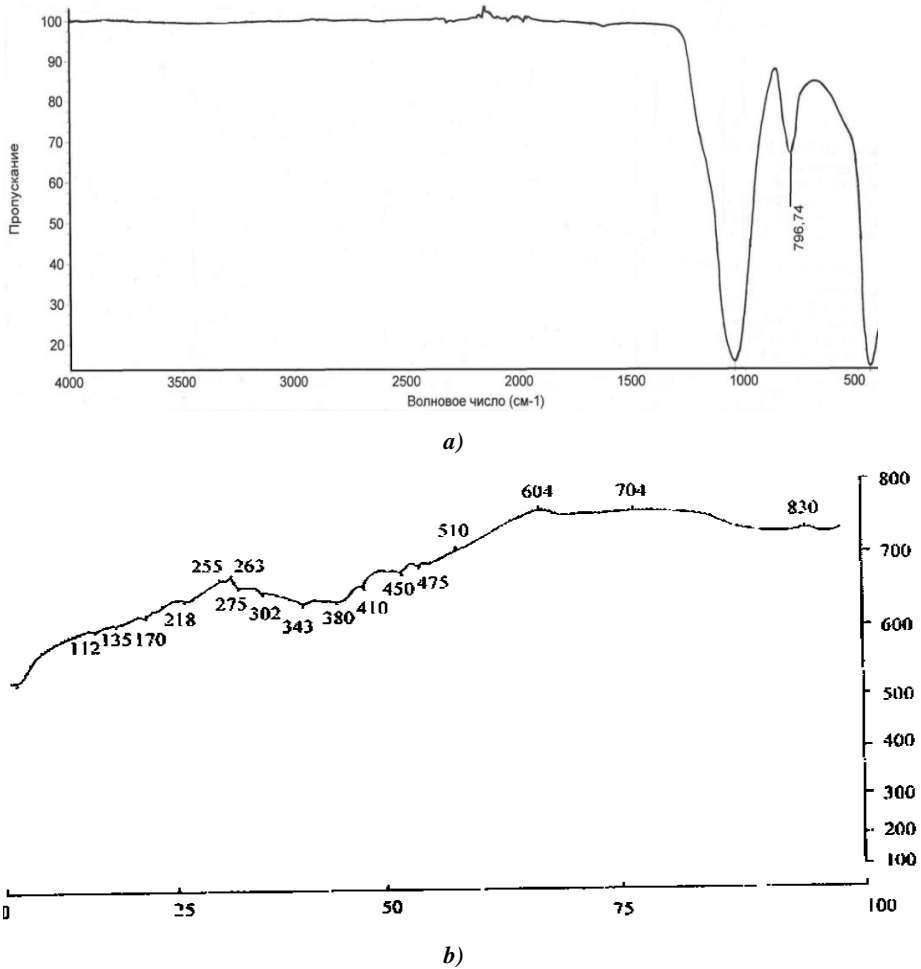
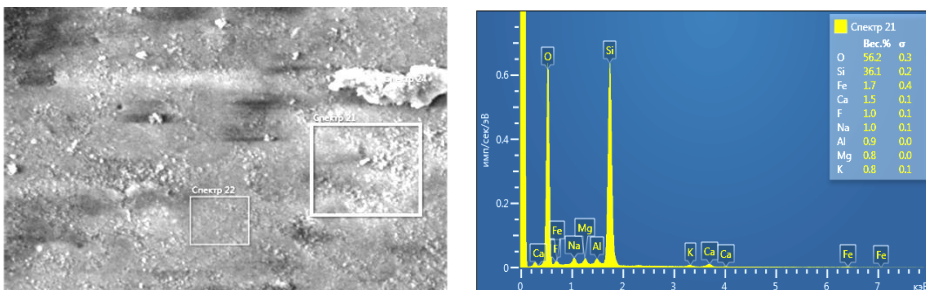


Fig. 2. IR - absorption spectra (a) and thermal curves (b) of silica fume JSC "Uzmetkombinat"

Microphotographs of microsilica obtained on an electron microscope SEM - EVO MA 10 with an analyzer, shown in Figure 3, show the percentage composition of each element of one and that section of the investigated microsilica with even a slight shift of the objective lens has a slight difference.



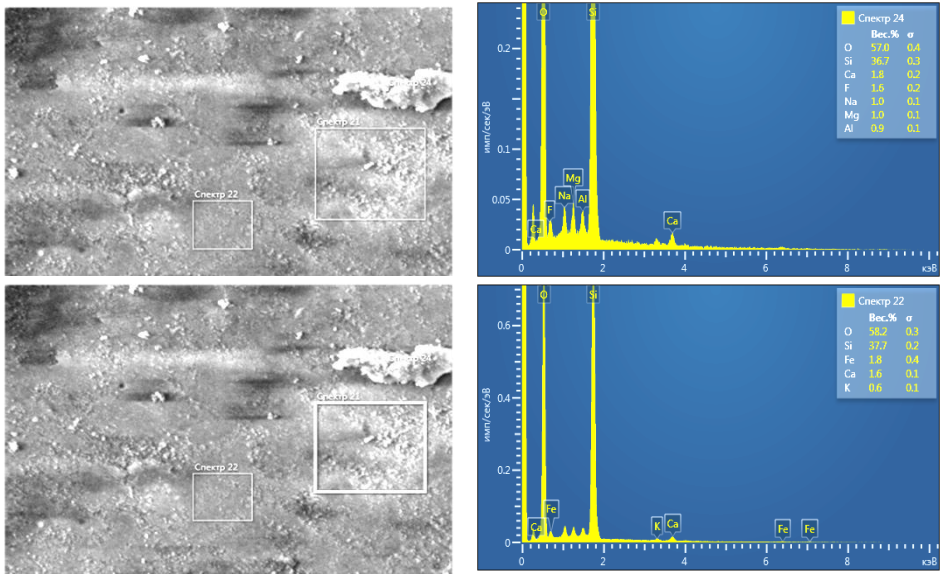


Fig. 3. Electron micrographs and spectra of microsilica elements taken with a scanning electron microscope. 25µm

The content of various elements in three sections of the same microsilica sample is Ca - (16; 15; 18)%, O - (58.2; 56.2; 57.0)%, Si - (37.7; 36 ;1; 37.7)%, etc., which is apparently due to the variability of the chemical composition of the raw material supplied for processing - quartz.

Following the data in Table 5, the replacement of 25% of the clinker component in Portland cement by a hybrid additive, including AASM + MK, in the initial period of hardening (up to 7 days) slows down its strength development. By the 28th day, strength development accelerates, and the index of the cement composite reaches the index of the matrix Portland Cements-D0 (Figure 4). AASM+MK, an increase in the content of the additive has almost no effect on the rate of the process and curing of the Portland Cements up to 3 days. By the 7th day, the process slows down, and the hydraulic activity of the composite for 28 days is significantly lower than that of the matrix. Some slowdown in the hardening process of the modified Portland Cements containing 45% of the hybrid additive was also noted up to 7 days, then an acceleration of strength development is observed, and its indicators approach the strength indicators of Portland cements -D0 and C-D 25 (AASM + MK) by the 28 days.

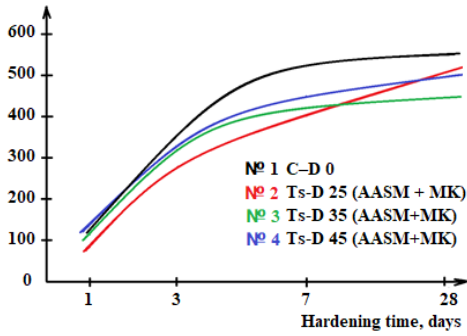


Fig. 4. The kinetics of the increase in the Portland Cements' strength depends on the dose of the hybrid additive "activated ash + microsilica".

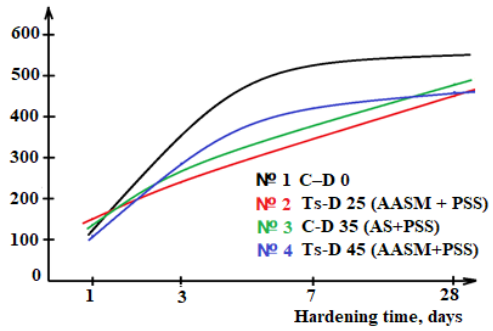


Fig. 5. The kinetics of the increase in the Portland Cements' strength depends on the dose of the hybrid additive "activated ash + steel slag".

According to Table 5 and Figure 5, the introduction of (25-45)% of the hybrid additive of the composition AASM + PSS contributes to the smooth flow of the hydration process of the binder composition and, consequently, the strength gain of "green" composites, the indicators of which by the 28 days are slightly inferior to the strength indicators of Portland cements-D0.

The same strength results were achieved with the introduction of 25-35% of the hybrid additive AASM + FS into the composition of Portland Cements -D0, an increase in the content of which to 45% significantly reduces the strength of the matrix during all hardening periods (table 4, figure 6).

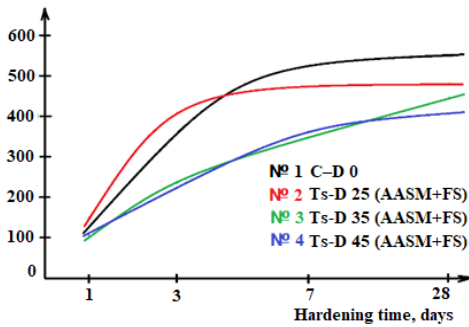


Fig. 6. Kinetics of portland cements strength increase depending on the dose of the hybrid additive "activated ash and slag + furnace slag".

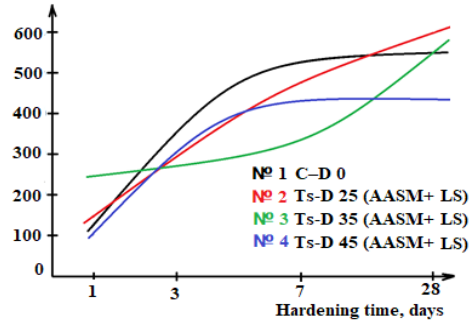


Fig. 7. kinetics of portland cements strength increase depending on the dose of the hybrid additive "activated ash + ladle slag".

Table 4. Change in the strength of portland cements depending on the type and dose of hybrid additives (samples-cubes 1.41x1.41x1.41sm, composition 1:0)

No	Conventional designation of cements	V/C	Ultimate compressive strength (MPa) of samples 2x2x2x cm in size with a composition of 1: 0, after (days):			
			1	3	7	28
1	C-D 0	0.24	13.3	35.8	52.9	54.0
2	Ts-D 25 (AASM + MK)	0.24	8.30	27.9	40.0	52.5
3	Ts-D 35 (AASM+MK)	0.24	11.6	32.0	42.0	45.0
4	Ts-D 45 (AASM+MK)	0.24	12.0	24.5	45.0	50.0
5	Ts-D 25 (AASM + PSS)	0.28	15.0	24.1	27.0	45.0
6	C-D 35 (AS+PSS)	0.28	12.9	26.6	37.0	48.0
7	Ts-D 45 (AASM+PSS)	0.32	10.8	28.0	43.0	45.0
8	Ts-D 25 (AASM+FS)	0.28	15.0	41.0	43.0	48.0
9	Ts-D 35 (AASM+FS)	0.32	10.5	23.7	32.5	45.0
10	Ts-D 45 (AASM+FS)	0.3	10.0	13.5	30.4	40.0
11	Ts-D25 (AASM+LS)	0.28	13.0	26.6	48.0	60.0
12	Ts-D35 (AASM+LS)	0.30	27.5	25.4	30.4	55.0
13	Ts-D45 (AASM+LS)	0.24	10.0	30.4	40.8	42.5

Note: AASM is active ash and slag mixture; MK is microsilica; PSS is processed steel-smelting slag; FS is furnace slag; LS is ladle slag

The introduction of a 25% additive from AASM + LS does not harm the hardening process of Portland Cements-D0, and the cement composite, after 1 day of hardening, has the same strength as it has (13.0 MPa). By the 3rd and 7th days, its value is slightly lower than that of Portland Cements -D0. By the 28th day, the process of strength development of the composite accelerates sharply, reaching 60.0 MPa against 54.0 MPa of the matrix Portland Cements, the indicators exceed its hydraulic activity at 6.0 MPa (Figure 7). At the content of 35% additive AASM + LS, the strength of the composite is almost 2 times higher than that of the matrix; however, by the 3rd and 7th days, a slowdown in the process of strength development was noted, which is much lower for a stone based on Portland Cements -D0. At the same time, by the 28 days, the process is observed to accelerate the process of hydration and hardening of the "Portland cements + AASM + LS" composition; as a result, the strength of the composite based on it will reach (55, 0 MPa) the level of strength index Portland Cements -D0 (54.0 MPa). Increasing the amount of added additive to 45% reduces the hydraulic activity of composite Portland cement during all periods of hardening [20, 21].

Because the strength indicators of composite Portland cements with new types of "green" hybrid additives are determined on small cubes made from cement paste with a composition of 1: 0, and to conclude their true brand and compliance with the requirements of GOST 10178 or GOST 31108-2003, the optimal compositions of modified cements were tested on prism samples with a composition of 1:3. The test results showed that in terms of hydraulic activity, the new types of developed composite Portland cements are superior to those of Portland Cements – D0 without additives.

4 Conclusion

The chemical-mineralogical compositions and physico-chemical properties of technogenic wastes of energy and metallurgy were determined: Angren TPP and Uzmetkombinat JSC, their hydraulic activity in terms of compressive strength, and the compliance of their values according to the Student's criterion with the requirements of regulatory document for active mineral additives were established. Based on the data obtained, a conclusion was made

about the possibility of their use as ingredients for producing hybrid additives for Portland cement.

The ratio gradient and optimal doses of "green" hybrid additives in composite cements have been established. Their fineness of grinding and hydraulic activity depended on the type and dose of hybrid additives introduced. It is noted that even though the proportion of high-temperature Portland cement clinker in their composition is 25-35% less than that of the matrix, the hydraulic activity of the developed composite Portland cements corresponds to the grade 400-450.

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