COMPLEX USE OF MICROSILICA AND ACTIVE ASH AND SLAG MIXTURE OF THERMAL POWER PLANTS FOR THE PRODUCTION OF "GREEN" CEMENT COMPOSITES

Iskandarova Mastura[1], Mukhitdinov Dilshod Davronovich[2], Begzhanova Gulrukh Bakhtiyarovna[3], Yakubzhanova Zukhra Bakhtiyarovna[4], Makhsudova Nozimakhon Zhafarkhanovna[5]

Article History: Received: 12.12.2022 **Revised:** 29.01.2023 **Accepted:** 15.03.2023

Abstract

The results of studies on establishing the possibility of integrated use of microsilica of JSC "Uzmetkombinat" and ash and slag mixture of dry removal of the Angren TPP as components of hybrid additives and optimization of the compositions of Portland cements with their use are presented.

Keywords: microsilica, active ash and slag mixture (AASM), hybrid additive, Portland cement, hardening, cement composite, strength, physicochemical properties.

[1]Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan
[2]Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan
[3]Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan
[4]Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan
[5]Institute of General and Inorganic Chemistry of the Academy of Sciences of Uzbekistan

Email: [1]mastura.iskandarova@mail.ru, [2]mukhitdinov28@gmail.com, [3]gulrukh-begzhanova@rambler.ru, [4]farzona19@gmail.com, [5]Nazima-25@mail.ru

DOI: 10.31838/ecb/2023.12.s3.172

1. Introduction

Industrial waste is an inevitable result of any production and a serious threat to the environment. Every year, several billion tons of industrial waste are generated in the world, or up to one ton per year per inhabitant of the Earth. For example, in Russia, in the process of industrial production, more than 90% of the extracted natural resources go to waste [1]. At the same time, waste disposal and their use in the manufacture of various building materials promise economic and environmental incentives for production enterprises [2].

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 with the production of quality products at low production costs. In turn, the most promising direction of waste processing into building materials and products is the production of composite materials [3-6].

The Concept of Environmental Protection of the Republic of Uzbekistan establishes all aspects of maintaining the ecological balance in the country, the main trends of which are the improvement of the environmentally friendly waste management system, the development and implementation of waste-free and low-waste technologies in production, as well as technologies for processing waste from mining and processing industries [7].

It is known that the rise in prices for fuel, energy and material resources dictates the need to find their ways by saving the use of alternative energy sources and natural raw materials in all sectors of the economy, including the cement industry. In this regard, the direction of production and use of Portland cements with composite additives, including two or more ingredients of natural or technogenic origin, is currently developing all over the world [8-12].

At the same time, special attention is paid to the disposal and processing of solid waste from metallurgy, energy and the chemical industry. Many tonnage solid wastes include various types of steelmaking slags, microsilica, thermal power plant ash, phosphogypsum, with a rational approach to the processing of which, they can serve as valuable raw materials for the production of cement clinker, additional, pozzolanic and composite Portland cements, which has been proved by research [13, 14].

The purpose of the research was to determine the suitability of the use of microsilica (MC) and steelmaking waste in a composition with an active ash and slag mixture of dry selection as components of hybrid additives for the production of composite Portland cements.

Portland cement (PC) clinker of "Bekabadcement" JSC, microsilica (MS), slags of steelmaking production (reycled steelmaking-RS, bucket-BS, furnace - PS) of JSC "Uzbek Metallurgical Plant", ash and slag mixture of dry selection of Angren TPP-AASM and gypsum stone of the Kagan deposit were used as starting materials. The chemical compositions of the materials used are given in Table. 1.

2. Research Methods

The chemical compositions of clinker and additives are determined by standard methods of chemical analysis. The phase composition of the studied components was determined using the CHRONO-6199 diffractometer (Shimadzu, Japan), the hydraulic activity of the MS and AASM was established according to the Student's criterion (t-criterion). The physical and mechanical properties of composite Portland cements are determined on small samples-cubes of composition 1:0, the physical and mechanical indicators of their optimal compositions - in accordance with state standard 310.4 on standard samples-prisms of composition 1:3, the evaluation of the results obtained was carried out in accordance with the requirements of UzSS 2830:2014 "Portland cement with composite additives. Specifications".

3. Results and its discussion

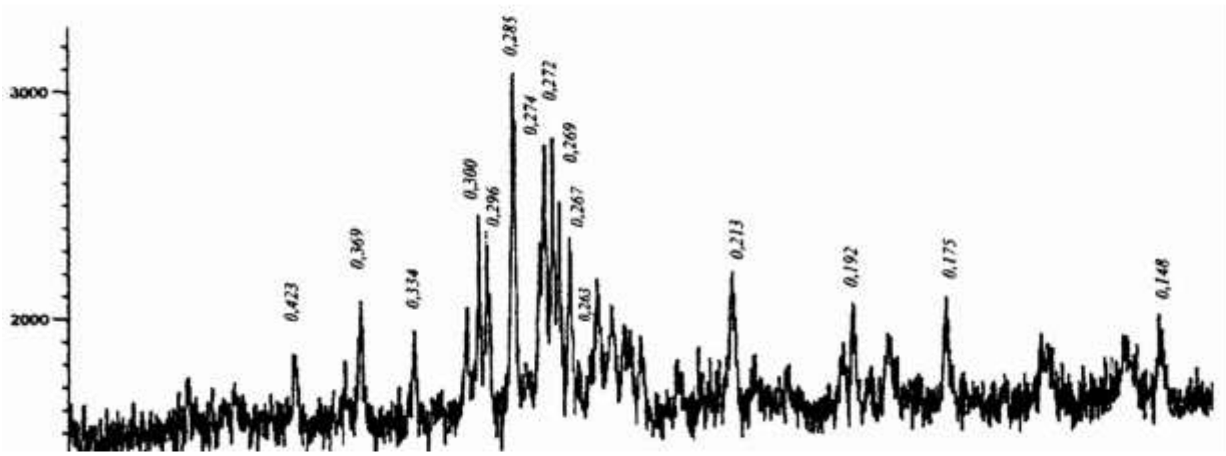
In accordance with the data of Table 1, the chemical composition of AASM is represented by a high content of silicon oxides SiO_2 (62.02%) and aluminum Al_2O_3 (23.55%). The content of other oxides (CaO, Fe_2O_3 and SO_3) is low. The total content of impurity inclusions is 0.8%. It was previously established that the chemical composition of ultrafine MC is characterized by a predominant content of SiO_2 (92.71%), impurities in the amount of 7.29% include oxides: Al_2O3, Fe_2O_3, CaO, MgO, R_2O and MnO_2. PSP slag, as well as furnace and bucket slags, are close to each other in the content of silicon and aluminum oxides, and they differ sharply in the content of iron and calcium oxides: bucket slag is a high-carbonate waste with a low content of Fe_2O_3 (Table 1).

Table 1
Chemical compositions of initial raw materials

Name of material	Content of mass fraction of oxides, %							
	determination of mass loss during calcination	SiO2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	others
PC clinker	0, 31	18, 03	6, 22	3, 94	58, 93	1, 98	5, 55	5, 04
active ash and slag mixture	3, 0	62, 02	23, 55	4, 32	3, 0	-	1, 28	0, 8
Microsilica	2, 79	90, 84	1, 51	1, 59	0, 56	1, 00	0, 23	1, 48
Recycled steel slag	9, 78	27, 92	9, 10	10, 93	25, 73	10, 43	1, 03	5, 08
Bucket 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
Gypsum stone	19, 10-at 400°C	1, 52	0, 13	0, 14	33, 04	0, 20	43, 46	2, 41

RSF-slag is presented in the form of sand and crushed stone fractions of 0-5 mm and 5-50 mm. Its diffractogram detects periclase reflections (MgO) at (d/n=0, 245; 0, 210; 0, 149...) nm; monticellite (CaO*MgO*SiO2) with (d/n=0, 540; 0, 387; 0, 298; 0, 268; 0, 182)nm; okermanite (2CaO*MgO*2SiO2) with (d/n=0, 288; 0, 237; 0, 228; 0, 205; 0, 191) nm; quartz (SiO2) (with d/n=0, 426; 0, 334; 0, 245; 0, 228; 0, 221; 0, 214; 0, 182)nm; bicalcium ferrite (2CaO Fe2O3) with (d/n=0, 366; 0, 279; 0, 274; 0, 268) nm; calcium carbonate (CaCO3) c (d/n=0, 302; 0, 245; 0, 228; 0, 209; 0, 191)nm; minerals of the transition series: tricalcium aluminate (3CaO*Al2O3) and mayenite (12CaO*7Al2O3) at (d/n=0, 480; 0, 426; 0, 408; 0, 279; 0, 268; 0, 221; 0, 214; 0, 191) nm; two-water gypsum (CaSO4×2H2O) with d/n=0.540 nm.The AASM diffractogram displays analytical lines at d/n=(0, 421; 0, 331; 0, 243; 0, 226; 0, 222; 0, 212; 0, 197; 0, 181; 0, 166; 0, 153) nm characteristic of quartz and mullite reflections (d/n= 0, 346; 0, 331; 0, 251 nm).The lines of CaOsb (d/n=0, 239; 0, 169) nm and CaCO3 (d/n=0, 301) nm are also marked. Lines detected at d/n=0, 291; 0, 285; 0.278 nm probably refers to low-base silicates formed during the combustion of coal as a result of firing its mineral part, consisting mainly of kaolin clay[13, 14].

According to the data in Fig. 1, calcium carbonate (d/n) predominates in the composition of furnace slag=0, 304; 0, 246; 0, 228; 0, 224, 0, 212; 0, 197; 0, 181 nm) and quartz (d/n=0.334; 0, 246; 0, 228; 0, 224; 0, 212; 0, 197; 0, 181 nm). Rather intense β-Ca2SiO4 c (d/n) lines were also noted. = 0, 283; 0, 281; 0, 278; 0, 269; 0, 228; 0, 220; 0, 217; 0, 197; 0, 187; 0, 183; 0, 176) nm. Iron is in its composition in the form of wustite (d/n = 0, 246; 0, 212) nm. In a small amount there is helenite (2CaO.A12O3.SiO2) with (d/n = 0, 378; 0, 306; 0, 283; 0, 278; 0, 256; 0, 246; 0, 239; 0, 236; 0, 224; 0, 217; 0, 212; 0, 209; 0, 197; 0, 191; 0, 187; 0, 176) nm.



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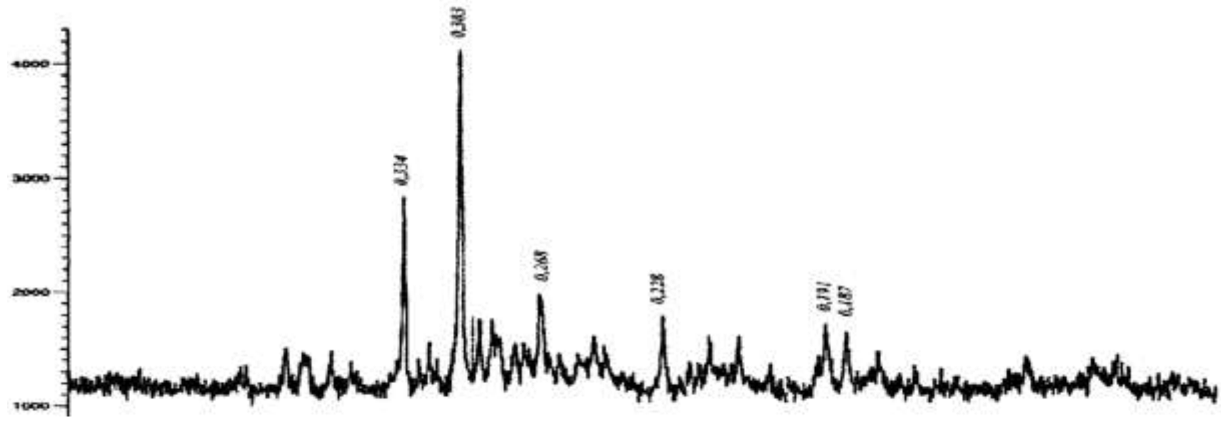

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Figure 1. Diffractograms of furnace (1) and bucket (2) slags

The quantitative content of larnite β-Ca2SiO4, wustite, pyrrhotite, helenite, magnesioferrite, determined at the request of JSC "Uzmetkombinat" in the laboratory of quantitative analysis of the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences, is 20, 0-30, 0%, impurities of other minerals are present in small quantities (Table 2).

Table 2
Quantitative mineral composition of furnace slag

№	Mineral phase	Formula Content	mass. %	
			KSH PSH	KSH PSH
1	Larnite (β-Ca2SiO4)	Ca_2SiO_4	40, 0-45, 0	20, 0-23, 0
2	Calcium silicates other than Larnite	Ca_2SiO_4	10-12	not found
3	Vustit	FeO	4, 0-5, 0	3, 0-4, 0
4	Pyrrhotite	$Fe_{0, 96}S$	3, 0-3, 5	4, 5-5, 0
5	Pyroxmangite	$Mn_{0.97}Mg_{0.03}SiO_3$	2, 0-3, 0	not found
6	Olivine (Fayalite)	$FeSiO_4$	5, 0 -7, 0	not found
7	Magnesioferrite	$MgFe_2O_4$	not found	10, 0-12, 0
8	Mineral with spinel structure	$MnCrO_4$	1, 0-2, 0	0, 5-1, 0
9	Gelenit	$CaAl(AlSiO_4)$	11, 0-13, 0	7, 0-8, 0
10	Mineral with garnet structure	$Me^{II+}3Me^{III+}(SiO_4)_3$	not found	4, 0-6, 0
11	Neiborit	$NaMgF_3$	0, 5-1, 0	not found
12	Sum of crystal phases		83, 0-87, 0	52, 0-56, 0
13	X-ray amorphous phase (glass)		16-20	42, 0-48, 0

The content of β-Ca2SiO4 c (d/n) is predominant in bucket slag=0, 369; 0, 353; 0, 274; 0, 233; 0, 229; 0, 213; 0, 18) nm, of gelenit 2CaO..A12O3.SiO2 (d/n=0, 423; 0, 371; 0, 306; 0, 285; 0, 272; 0, 253; 0, 243; 0, 241; 0, 230; 0, 213; 0, 204; 0, 175; 0, 152) nm. The lines of lower intensity of quartz SiO2 with (d/n) are marked=0, 334; 0, 228; 0, 224; 0, 212; 0, 197; 0, 181) nm and calcium carbonate CaCO3 (d/n=0, 304; 0, 290; 0, 249; 0, 228; 0, 191; 0, 187) nm. FeO lines of weak intensity were detected at (d/n=0, 246; 0, 212) nm. The amount of larnite (β-2CaO.SiO2) is (40, 0-45, 0)%, and other types of silicates are within (10, 0-12, 0)%, helenite - (11, 0-13, 0) %. The total number of crystalline phases is high and is (83, 0-87, 0)%, and the X-ray amorphous phase (glass) is about (16, 0-20, 0)%.

The structure of RSF-slag powder is represented by particles of various shapes, among which the content of dark gray grains predominates (Fig. 2). There are grains of white, pink and brown colors, which indicates the presence of calcium-containing, aluminosilicate and ferruginous mineral impurities in it. Bucket and furnace slags also have an identical structure: under an optical microscope, the initial bucket slag is presented in the form of round spherical grains, as well as grains without certain geometric shapes characterized by surface porosity. When ground into powder, the shape of the grains almost does not change.

Furnace slag is a coarse-grained gravel fraction of dark gray color, consisting of fractions of pieces of various configurations with dimensions (54-0) mm.

The pieces are low-porous, sintered with a rough surface (Fig. 2).

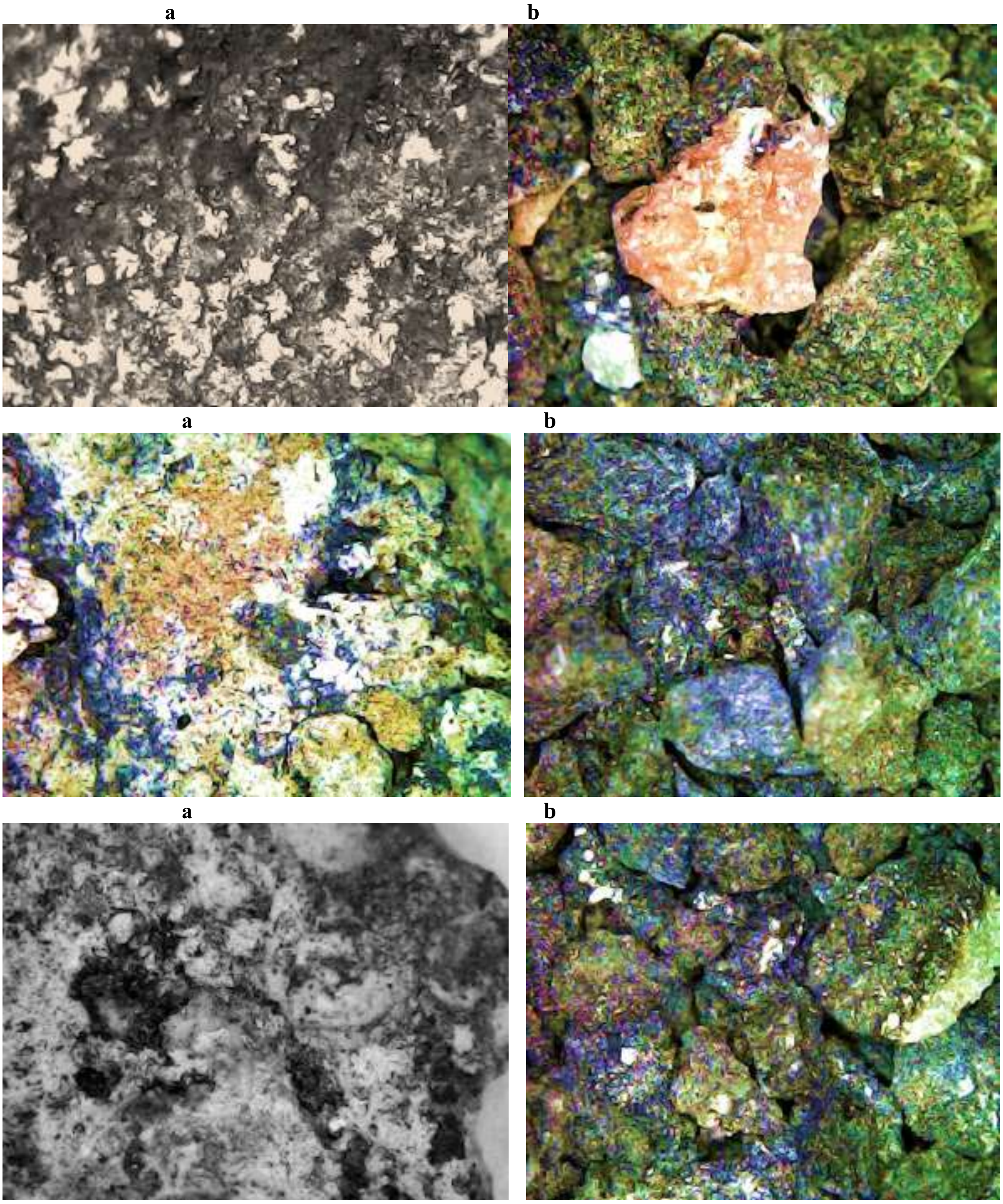


Figure 2. Structure of recycled steelmaking (a), furnace (b) and bucket (c) slags: 1-initial; 2- in powder

The hydraulic activity of additives according to Student's criterion was: for MS t=13, 47; RSF-slag t=2, 19; furnace slag t = 4.48; bucket slag t =5, 00; AASM t= 52.96.

To obtain "green" cement composites, which are not inferior to traditional Portland cement PC-D0 in terms of quality, raw mixtures were compiled, including PC clinker, gypsum stone and hybrid additives, including AASM in composition with MS, RSF-slag, furnace and bucket slag at various combinations and ratios of ingredients (table 2). When the hybrid additive contains (25-35)% AASM with 10% MS, the process of grinding the charge is accelerated, and for the same grinding time (45 min), the passage of cement powder through a No. 008

sieve is 87%, which is 1% more, than in PC-D0 (Table 2).

Table 2
Substantial composition of charges with new types of hybrid additives and indicators of grinding of "green" composite cements

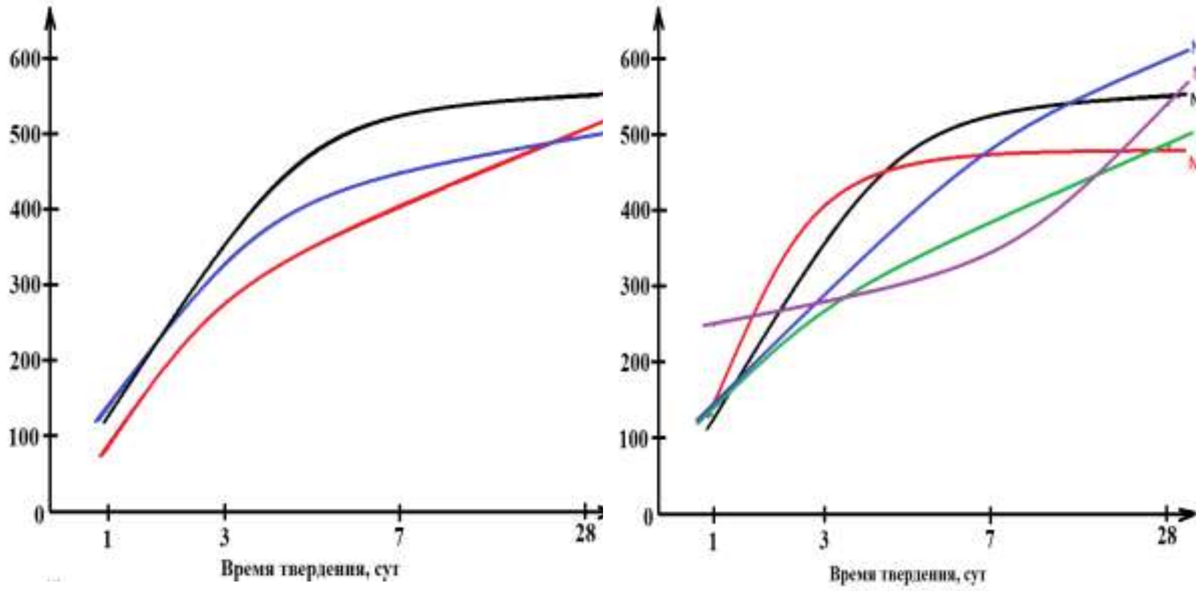
№	Conventional designation of cements	Clinker	AASM	MS	Gypsum	Grinding time, min	Residue on sieve №008, %
1	PC–D 0	95			5	45	14, 0
2	PC–D 25 (AASM+MS)	70	15	10	5	45	13, 0
3	PC–D 35 (AASM+MS)	60	25	10	5	45	13, 0
4	PC–D 45 (AASM+MS)	50	35	10	5	45	12, 0
		Clinker	AASM	RSFS	Gypsum		
5	PC–D 25(AASM+RSFS)	70	15	10	5	40	10
6	PC–D 35(AASM+RSFS)	60	25	10	5	40	10
7	PC–D 45(AASM+RSFS)	50	35	10	5	40	10
		Clinker	AASM	FS	Gypsum		
8	PC–D 25 (AASM+FS)	70	15	10	5	40	10
9	PC–D 35 (AASM+FS)	60	25	10	5	40	11
10	PC–D 45 (AASM+FS)	50	35	10	5	40	12
		Clinker	AASM	BS	Gypsum		
11	PC–D 25 (AASM+BS)	70	15	10	5	45	13
12	PC–D 35 (AASM+BS)	60	25	10	5	45	10
13	PC–D 45 (AASM+BS)	50	35	10	5	45	11

According to Table 2, when the hybrid additive contains (25-35%) AASM with 10% MS, the process of grinding the charge is accelerated: for the same grinding time (45min), the passage of cement powder through sieve № 008 is 87%, which is 1% more than that of PC-D0. With an increase in the dose of the additive to 45%, the dispersion of the crushed charge worsens somewhat and the patency of the powder through the sieve № 008 is 88%, which is 1% less than that of the previous compositions of composite PCs and 2% less than that of PC-D0. However, according to the fineness of grinding, all compositions of composite PC with hybrid additives "AASM+MS" correspond to the indicators (at least 15% of the residue on sieve No. 008) regulated by State std. 10178.

Charges, including "Clinker-AASM-RSFS-Gypsum" and "clinker-FS-gypsum" are characterized by a higher grinding capacity: for 40 min of grinding, their fineness is much higher (pass through sieve No. 008 - 90%) than that of PC with a hybrid additive "AASM + MS" and PC-D0.

The presence of a hybrid additive "AASM-BS" in the clinker-gypsum charge (35-45%) also significantly increases its grinding capacity: after 45 minutes of grinding, the amount of residue on the sieve № 008 was (10-11%).

Determination of physical and mechanical parameters of composite PC on small samples showed that the replacement of 25% of clinker in Portland cement with a hybrid additive, including AASM+MS, in the initial periods of hardening slows down the set of its strength, which accelerates by 28 days, and its indicators reach the PC-D0 index (Fig. 3a). The increased dosage of the additive reduces the strength of the PC during all periods of hardening.



a **b**

Figure 3. Change in strength of optimal compositions of "green" cement composites with hybrid additives:

a) "AASM+MS": №1 PC-D0; № 2 PC-D25 (AASM+MS); № 3 PC-D45 (AASM+MS)

b) №1 PC-D0; №2 PC- D25 (AASM+FS); No.3 PC-D35 (AASM+RFS); №4 PC-D25 (AASM+ FS). №5 PC-D35 (AASM+ FS).

Hybrid additive AASM+RSFS accelerates the process of hydration and durability gain of "green" composites, the indicators of which by 28 days are almost equal to those of PC-D0 (Fig. 3b).

The same effect on the physical and mechanical properties of the PC is exerted by the hybrid additive AASM + FS at a dose of (25-35%). An increased dosage of this additive (45%) reduces the strength of the PC. A hybrid additive, including AASM + FS, slows down the process of hydration and hardening of PC at all its dosages (25-45%). By the 28th day, there is an acceleration in the durability gain of the composite, which reaches the PC-D0 index. An increase in the amount of the additive to 45% reduces the hydraulic activity of composite Portland cement during all periods of hardening (Fig.3b).

4. Conclusion

The fundamental possibility of complex application of the ash and slag mixture of the Angren TPP of dry removal and waste of steelmaking production of JSC "Uzmetkombinat" for the production of hybrid additives of high activity has been established. To achieve optimal dispersion of composite Portland cements, the recommended dose of hybrid additives is 25-35%. The developed hybrid additives are able to replace 25-45% of the high-temperature clinker component and obtain "green" cement composites that are not inferior in strength to the matrix - Portland cement grade PC400-D0.

5. Literature

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