Development of technology for "green" cement composites with new types of hybrid additives*

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Abstract. The article is devoted to the development and research of new types of "green" hybrid additives based on energy and ferrous metallurgy waste and composite Portland cements with their use.

Keywords: inorganic waste, disposal, silica fume, TPP ash mixture, dry removal, hybrid additive, composite Portland cement, strength, structure, efficiency.

Introduction. Due to the continuous rise in prices for fuel, energy and material resources and in order to save them, reduce carbon dioxide emissions, there is currently a worldwide trend for the production and use of composite Portland cements with hybrid additives that include two or more mineral ingredients of natural or man-made origin [1-3].

BioScience has published articles on climate change over the past year by researchers from the US, UK, France, Australia, Germany, the Netherlands and Bangladesh. According to their estimates, the number of natural disasters caused by climate change has increased sharply compared to 2019, with 2020 becoming the second hottest year in history (2016 remains the hottest year and all temperature records fall in the period after 2015). Three key greenhouse gases (carbon dioxide, methane, nitrous oxide) set records for atmospheric concentration last year. In April 2021, the carbon dioxide content in the atmosphere reached its highest monthly average of 416 ppm [4]. 2020 is the second hottest year on record, according to the International Group of Experts on Average Annual Temperatures. Scientists from the University of Colorado have named the most environmentally "dirty" power plants in the world. Scientists at the University of Cambridge believe that in places of tectonic faults, atmospheric carbon is converted into diamonds.

A group of researchers from the University of Colorado has estimated that 5% of the Earth's power plants emit 73% of greenhouse gases. Many power plants in the USA, Europe, East Asia, Poland and India are coal-fired and have low efficiency. Researchers at the University of Southern California found that reducing the amount of fine particulate matter PM in the air 2.5(roughly the size of coal dust) reduces the risk of dementia by 14% and slows down the rate of cognitive decline in older American women by 26%. Scientists from the University of California at San Diego have found that reducing the amount of the same fine particles reduces the risk of developing Alzheimer's disease by 17%.

Based on the results of such studies, at present all over the world there is a tendency to reduce the influence of harmful dust and gas emissions into the atmosphere of industrial enterprises, to fight against the formation of greenhouse gases and for a clean climate.

**Research is carried out within the framework of the joint Uzbek-Chinese project "Joint development of "green" composites using ash-and-slag mixture of power engineering and metallurgy slags. – Tashkent, 2021-2022*

In Uzbekistan, there are also many enterprises in the energy, metallurgical, processing sectors of the economy, which contribute to the deterioration of the environmental situation: these are enterprises of ferrous and nonferrous metallurgy, the cement industry, fuel and energy complexes that generate electrical energy by burning coal fuel, enrichment factories, etc.

Therefore, at present in our republic the problem of ecology is being solved at the state level, in this connection, consistent work is being carried out in the field of environmental protection, rational use of natural resources, improvement of sanitary and environmental conditions. 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, starting with "improving the environmentally safe 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 the processing of waste from mining and processing industries"[5].

In his speech at the second international summit "Partnership for Green Growth and Global Goals - 2030" (P4G), held in Seoul, the President of Uzbekistan outlined the key areas of reforms in the country and shared his vision of the prospects for international cooperation in the field of green recovery. The commitment of Uzbekistan to fulfill its commitments to reduce greenhouse gas emissions by 2030 under the Paris Agreement was reaffirmed. In this regard, it was noted that the widespread introduction of "green" technologies and the implementation of projects in the field of green energy in Uzbekistan will allow to increase the share of renewable energy sources by more than 3 times in the next ten years. In order to expand practical cooperation in this important area, the President declared Uzbekistan's readiness to join the P4G partnership and become its full-fledged participant 6].

The accumulated and current waste of mining and metallurgical production and heat power engineering, represented by overburden, enclosing rocks, poor, off-balance, substandard ores, tailings, man-made placers, ash and slag from thermal power plants, slags and sludge from metallurgical production, have significant resource potential and are increasingly considered as a promising reserve, stored mineral raw materials [7].

In TPP sludge plows, a huge amount of ash waste from hydro removal is accumulated, which has a negative impact on the environmental situation, and low hydraulic activity inhibits their large-scale utilization in the production of a wide range of construction products [8]. Therefore, preference is given to the dry method of removing them from the furnaces of coal-fired boilers. This method increases the degree of their useful consumption by developing resource-saving and environmentally friendly technologies for the production of construction products, in particular, cement. In this regard, in 2016, the Chinese company Harbin Electric International Company Ltd, based on the Angren TPP, upgraded and commissioned one power unit for dry ash disposal. The power unit will annually generate 1,050 million kilowatt-hours of electricity and 642.2 thousand Gcal of thermal electricity [9]. A new power unit with a capacity of 130-150 megawatts with a cogeneration extraction for burning high-ash coal was put into operation, in connection with which there was a problem of utilization of the dry ash-and-slag mixture (hereinafter ASM).

Disposal of industrial waste is also one of the most important problems at metallurgical enterprises all over the world [10]. Being potential resources capable of expanding the country's mineral resource base for ferrous, non-ferrous, noble metals, technogenic formations have a very aggressive effect on the natural environment, therefore, interest in their processing is due not only to commercial objectives, but also to increased environmental requirements. Of all the variety of technogenic formations involved in processing, the main volume is made up of metallurgical slags formed during the processing of ores of various genesis.

The Joint Stock Company "Uzbek Metallurgical Plant" is the leading enterprise of ferrous metallurgy in Uzbekistan. During the years of independence of Uzbekistan, the enterprise has

been dynamically developing. The enterprise increases its capacity every year, which naturally, along with an increase in the output of steel products, also leads to an increase in the output of "tailings" suitable for recycling and their waste, for use in the manufacture of various construction products. Currently, "Uzmetkombinat" JSC, in addition to the production of commercial steel products, also produces silicon alloys, where waste is formed in the form of ultrafine ash - microsilica, which is mainly represented by thermally activated aluminosilicates, which can be used as an additive in the production of cement to save expensive clinker with a simultaneous increase in the construction and operational properties of concrete based on it. When adding MC, the permeability of the cement stone will decrease by fifty percent, and the sulfate resistance will increase by one hundred percent, it gives low permeability to gases and water W12-W16, frost resistance F200-F600, increased durability [11]. The need to utilize the named man-made raw materials to ensure a "clean" climate, ensure the ecological situation of the population of industrial regions, preserve flora and fauna, determined the goal of research on the development of compositions of hybrid additives based on energy and metallurgy waste and technology for producing "green" composites using them.

Research objects and methods: To form the composition of new types of "green" hybrid additives (HA) and composite Portland cements (CP): ash and slag mixture of dry removal of Angren TPP (ASM-active component) and microsilica "Uzmetkombinat" JSC (MS-ballast component).

The matrix for obtaining Portland cements with hybrid additives was an ordinary Portland cement of JSC "Bekabadcement" according to O'z DSt 2801: 2013 "Portland cement clinker. Specifications "and gypsum stone of the Bukhara field according to O'z DSt 760-96" Gypsum and gypsum anhydrite stone for the production of binding materials". The chemical compositions of the components are determined in accordance with GOST 5382-91 "Cements and materials for cement production. Methods of chemical analysis", the definition of their hydraulic - according to GOST 25094-94 "Active mineral additives for cements. Test methods", evaluation of the results of hydraulic activity by the value of the Student criterion - according to O'z DSt 901-98 Additives to cement. Active mineral and filler additives. Technical conditions". The physical and mechanical properties of composite Portland cements were determined on small sample cubes with a face size of 4 sm with a composition of 1:0 (without sand). To assess the results obtained, the indicators of Portland cement PC400-D0, obtained by testing the same samples, were taken as an object of comparison.

Results and its discussion: In accordance with the data in tab. 1, in terms of chemical composition, the activated ash-and-slag mixture of dry removal of Angren TPP belongs to the acidic type (SiO_2 content is more than 45%, CaO is less than 10% by weight), in terms of the fuel content, determined by the value of losses on ignition, it is ASM with low content (no more than 5%) and meets the requirements of O'z DSt 2912: 2014 "Ash and slag mixtures for the production of Portland cement clinker and Portland cement for ash and slag waste. Technical conditions".

Table 1

Chemical compositions of ingredients for forming hybrid cement additives

Material name	Content of mass fraction of oxides,%							
	p.p.p	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	others
Microsilica	2.79	90.84	1.51	1.59	0.56	1.00	0.23	1.48
ASM process test	3.0	62.02	23.55	4.32	3.0	-	1.28	0.8

After statistical processing of experimental data on the determination of the hydraulic activity of the ash-and-slag mixture of dry removal of Angren TPP for compressive strength, the value of Student's criterion t=52.92>2.07 was obtained, which, according to the requirements of the O'z DSt 901-98 standard, characterizes it as a mineral additive high hydraulic activity. The value of the t-criterion for microsilica was equal to t=13.47>2.07, which also characterizes it as a

mineral additive suitable for use in the cement industry as an additive in order to save clinker, electricity for grinding and improve technical and operational properties. cement and concrete.

Taking into account the previously obtained results of studies to determine ASM and MS (each separately) of the effect on the physical and mechanical properties of PC [12-15], during the formation of the component composition of Portland cements with new types of hybrid additive "ASM + MS", the content of ASM in the primex including "50-70% clinker + 5% "gypsum stone" was (15-25)%, MS - 10% (tab. 2).

Table 2

The substance composition of the charge for the production of PC with CP "ash-and-slag mixture of dry removal: silica fume

№	Conventional designation of cements	PC clinker	ASM	MS	∑ HA, %	Gypsum	Grinding time, min	Sieve residue № 008, mass. %
1	C–D 0	95	-	-	0	5	45	14
2	CP with ASM+MS	70	15	10	25	5	40	13
3	C–D ASM+MS	60	25	10	35	5	45	13,5
4	C–D ASM +MS	50	35	10	45	5	45	12

With such a ratio of components, the mixtures were ground to a fineness not exceeding the regulated value of not more than 15% in accordance with GOST 10178. Testing of samples of composite Portland cements with new types of "green" hybrid additives showed that at a HA content of 25% and 45% at a ratio of 15% ASM+10% MS and 35% ASM+10%, composite Portland cements reach the level of strength indicators PC400-D0 (tab. 3).

Table 3

Strength characteristics of Portland cements with new types of HA

№	Conventional designation of cements	w/c	Compression strength of specimens, kg/sm^2, after (days);			
			1	3	7	28
1	C – D 0	0.24	133	358	529	540
2	**C–D ASM+MS**	**0.24**	**83**	**279**	**400**	**525**
3	C-D ASM+MS	0.24	116	320	420	450
4	**C-D ASM+MS**	**0.24**	**120**	**245**	**450**	**500**

Taking into account the positive results of research, it is possible to replace up to 45% of the energy-intensive clinker component in cement with new types of "green" hybrid additives, consisting exclusively of technogenic waste, as optimal for their further technological tests in accordance with the requirements of GOST 310.1-310.4 and the issuance of practical recommendations for mastering the technology of obtaining "green" cement composites at JSC "Bekabadcement", selected compositions № 2 and № 4, containing 25% and 45% HA.

Conclusion:

1. The hydraulic activity of the ash-and-slag mixture of dry removal of Angren TPP and microsilica of JSC "Uzmetkombinat" was determined according to the value of Student's criterion, which ensures their use as ingredients of hybrid additives for Portlard cement.
2. Compositions of "green" cement composites containing up to 45% of hybrid additives "active ash and slag mixture + microsilica" have been developed and their compositions have been optimized to issue practical recommendations for mastering the technology of their production at JSC "Bekabadcement".

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