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Regulation Of The Hardening Process And Structure Formation Of Portlandcement By Addition Of Modified Activated Ash Mixture Tpp

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Annotation. The paper presents the results of studies to determine the effect of dry removal modified with activated ash and slag wastes of the Angren TPP on the processes of hydration, structure formation and the formation of physical and mechanical properties of artificial conglomerate during hardening of Portland cement. It is noted that due to directional structure formation during hardening, replacing up to 20% of clinker does not reduce the quality indicators of Portland cement**.**

Key words: Portland cement clinker, activated ash and slag, addition to cement, degree of hydration, phase composition, structure, cement stone, strength

Introduction. In accordance with the Decree of the President of the Republic of Uzbekistan No. PP-4335 of May 23, 2019 "On additional measures for the accelerated development of the building materials industry", large-scale work is underway in the republic to build educational and preschool institutions, develop the road network and increase capital funds. directed to the construction of affordable and comfortable housing for the population and social facilities. This, in turn, led to an increase in demand for all types of building materials and, first of all, for cement and materials with its use. [1].

Over the years of operation of the power system, about 18 million tons of ash and slag from hydraulic removal have been accumulated at the ash dumps of the Angrensky TPP, and the issue of their utilization is relevant in terms of ensuring the ecological balance in the region. In order to improve the efficiency of the power units, a dry removal system was installed at the Angren TPP in 2018. In this case, the ash-and-slag mixture formed in the furnaces of coal-burning boilers is removed through a pipeline cooled by irrigation in the pipeline inside which it is located. Development and implementation of new technologies that provide a significant reduction in energy consumption in industrial production, the implementation of an economically sound policy of import substitution. The concept also provides for the implementation of investment projects with the introduction of advanced innovative energy-efficient technologies for obtaining building materials, in particular, high-quality and special types of cement. [2].

At the same time, special attention is paid to the issue of saving fuel and energy resources and waste disposal. One of the energy-efficient ways to increase the volume of production of many types of binders, including cement, is the complex use of active mineral additives and technogenic genesis. In this regard, the search for simple in technological execution and relatively cheap ways to increase the efficiency of composite binders and concretes based on them, each component of which plays a certain role in the processes of hydration and structure formation, is an urgent task [3]. Replacing part of the clinker in cement with a mineral additive contributes to a more rational consumption of natural resources, an increase in production, and also reduces production costs, while maintaining a high hydraulic activity of cement [4].

Formulation of the problem. The factors that determine the nature and rate of chemical reactions occurring in the system "ground clinker - active mineral addition gypsum - water", as well as the reasons for the greater or lesser reactivity of individual silica compounds in pozzolanic additives have not yet been sufficiently studied. Therefore, in each specific case, when a new type of active mineral additive, supposed as pozzolanic, is used, it is necessary to conduct a study to determine its suitability as an additive to cement and to study its effect on the physical and mechanical properties of Portland cement. In this regard, the purpose of the research was to determine the hydraulic activity of dry removal modified with activated ash and slag waste at the Angren TPP, their effect on the strength indicators of Portland cement and to establish their applicability at “Akhangarancement” JSC.

Research objects. The objects of research were the Tashkent region modified with activated ash and slag wastes of the Angren TPP of dry removal and Portland cements with its addition. Portland cement clinker of Akhangarancement JSC and gypsum from the Bukhara deposit were used as a matrix for the production of additional Portland cements.

Research methodology. The chemical composition of the components is determined in accordance with GOST 5382-91 “Cements and materials for cement production. Chemical analysis methods ". The suitability of activated ash and slag as an additive in cement is determined by its ability to absorb lime by the Chapel method and by the value of the Student criterion in accordance with the methodology GOST 25094-94 “Active mineral additives for cements. Test methods ". The physical and mechanical properties of Portland cements were evaluated in accordance with the requirements

of GOST 10178 Portland cement and slag Portland cement. Technical conditions ". The genesis of the formation of a stone structure based on cements with activated ash and slag was studied using a scanning electron microscope (SEM) with an INCA Energy 350 energy dispersive microanalyzer and an attachment for studying the texture and structure of polycrystalline samples HKL Basic.

Results and its discussion. In order to determine the possibility of using the modified activated ash and slag wastes of the Angren TPP as an active mineral additive in cement, studies were carried out to determine their chemical and mineralogical composition, chemical and hydraulic activity. The chemical composition of activated ash and slag and other components used as objects of study are shown in Table 1.

Table 1.

Chemical compositions of the starting components

Material name	The content of the mass fraction of oxides, %								
	p.p.p	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	Прочие
Portland cement clinker	0,36	21,30	4,75	4,86	63,58	3,07	0,36	1,58	0,36
Gypsum stone	Pt 400^0C 19,57	1,59	0,49	сл.	31,45	0,49	44,00	-	2,41
activated ash and slag dry removal of Angren TPP	0,61	64,79	20,64	3,99	3,36	0,80	1,64	4,12	0,05

According to the chemical composition, the analyzed sample of АЗШС belongs to the acidic type (the content of SiO2 is more than 45%, CaO is less than 10% by mass), according to the content of combustibles, determined by the value of losses on ignition - to ash-and-slag materials with a low content (no more than 5%). In terms of chemical composition, the activated dry ash and slag of Angren TPP meets the requirements of the state standard for ash mixtures O'z DSt 2912: 2014. Consequently, in terms of the content of the main oxides, the activated ash and slag of dry removal of Angren TPP, which has sufficient pozzolanic capacity. The chemical activity of activated ash and slag for lime absorption is 242 mg / g, and the hydraulic activity for compression according to the value of Student's criterion (t) is 52.92, which is more than its regulated value 2.07 according to O'z DSt 901-98 “Additives for cements. Active mineral additives and additives - fillers. Technical conditions ". Based on the data obtained, it was concluded that the modified activated ash and slag waste of the Angren TPP for dry removal complies with the requirements of regulatory documents and can be used as an active mineral additive in cement.

To study the effect of the investigated activated ash and slag dry removal of Angren TPP on the physical and mechanical properties of Portland cement, joint grinding (55-85)% clinker, (10-20)% activated ash and slag in the presence of 5% gypsum stone was carried out. At the same time, it was

found that when activated ash and slag (10-20%) is added to the charge, the grinding process proceeds in the same way as when grinding non-additive cement: the fineness of grinding, determined by the residue on sieve No. 008 of cements with the addition of activated ash and without it, was 10-12%. The water-cement ratio of the test of normal density (TNG) of the test cements with the addition of activated ash and slag, depending on its content in the cement, is (0.69-8.4)% higher than the water demand of the control cement PC-D0, which is associated with a higher content in them mass fraction of oxides of clay minerals (SiO2, Al2O3, Fe2O3) than in cement PC-D0. Depending on the content of the additive, the beginning of the setting of the test cements is within 3 hours 20 minutes - 5 hours 45 minutes, the end - 5 hours 10 minutes. - 6 hours 45 minutes, moreover, the greater the amount of activated ash and slag introduced. This is due to the fact that with an increase in the content of the additive in the cement, its clay part also increases, which quickly soaks in water and envelops the cement particles, slowing down the process of hydration and hydrolysis of clinker minerals, inhibiting the process of release and transition of calcium ions into the liquid phase, which lengthens the setting period cement paste. Since, during the interaction of cements with water, hydration reactions of aluminate and aluminoferritic structures occur precisely at the initial time and determine the onset of the onset of setting of cements, and the time of the beginning of interaction with water of highly basic calcium silicates is the end of setting. Despite the slow progress of the hydration process, the setting time of all experimental Portland cements meets the requirements of GOST 22266-94.

The results of determining the physical and mechanical properties of cements with activated ash and slag are shown in Table 2.

Table 2

Changes in the physical and mechanical properties of Portland cement depending on the content of activated ash and slag

№	Composition and designation of cements, masses.%				Compressive strength, MPa, after (day) hardening				
	Designation	Clinker	Gypsum	AZShS	1	3	7	28	90
1	ПЦ-Д0	95	5	-	10,3	33,4	41,0	42,5	46,8
2	ПЦ-Д10	85	5	10	15,2	35,0	44,5	53,2	60,0
3	ПЦ-Д15	80	5	15	12,0	40,0	42,5	52,5	65,0
4	ПЦ-Д20	75	5	20	9,8	25,5	40,2	49,5	53,3

In accordance with the data in Table 2, Portland cements with activated ash and slag at the age of 90 have a compressive strength in the range of (40.6-44.2) MPa, which characterizes them as cements of general construction grade 400 according to GOST 10178-85. At the same time, the activity of cements with 10% activated ash and slag is 60.0 MPa, with 15% - 65.0 MPa, and with 20% - 53.3% MPa, which is higher than the strength of no additive cement having a strength of 46.8 MPa.

The strength indicators of Portland cement PCO-D20 with the addition of 10% activated ash and slag at the age of 7 and 90 days of hardening slightly exceed the strength indicators of the control cement.

In accordance with the requirements of GOST 10178-85, Portland cements containing an additive of sedimentary origin in an amount of up to 20% are general-purpose cements. Therefore, an experimental Portland cement containing an additive of activated ash and slag in an amount of 20% and having a compressive strength at the age of 28 days of 49.5 MPa is characterized by grade 400 with the symbol PC 400-D20. In terms of ultimate strength in bending and compression at the age of 28 days, Portland cements containing 15 to 20% of activated ash and slag additives correspond to grade "400" and, according to the requirements of GOST 2266-94, are classified as sulfate-resistant Portland cements with mineral additives with the symbol SSPTs 400- D20.

It is known that the performance properties of cements are determined by the structure forming in the cement stone, which is the result of the physicochemical features of the processes of structure formation in the "cement-water" system [5]. The main factor is the implementation of directional structure formation during hardening of cements, control of the formation of the structure of the cement stone at different stages of its hardening, which provides high physical and mechanical and high operational properties of cement stone and products with specified properties based on it.

It is possible to obtain effective materials and durable products by revealing significant reserves in managing the performance properties of concretes and other materials based on cement by purposefully shaping the structure and properties of cement stone during its hardening, including by introducing mineral and chemical additives. Revealing the regularities that allow to control the processes of structure formation and optimize the composition and properties of composites with waste requires extensive studies of the selected objects. This is especially true for the early period of hydration and hardening of cement with additives (from 1-3 hours to 1-3 days), when the hydration process is especially sensitive to the conditions of hardening and formation of cement stone. Therefore, various additives are proposed to ensure the rapid formation of primary hydrate phases, the composition of which determines the subsequent physical and mechanical properties of cement stone and concrete. Consequently, one of the ways to increase the activity and strength of the cement stone is the purposeful formation of its properties due to the introduction of additives that affect the process of hydration, structure formation and hardening of cement, which increase the early strength of the cement stone due to the rapid removal of Ca2 + ions from the liquid phase with the crystallization of hydrosulfoaluminates. calcium, the crystals of which reinforce the cement stone, and its brand strength and durability are due to the calcium hydrosilicates formed at a later date.

Proceeding from this, in order to clarify the correlation dependence "composition - structure - property", the "evolutionary route" of hardening with the formation of the structure of cements with activated ash and slag was investigated. The results of studies on the study of the genesis of the formation of the microstructure of a cement stone are shown in Figures 5 and 6.

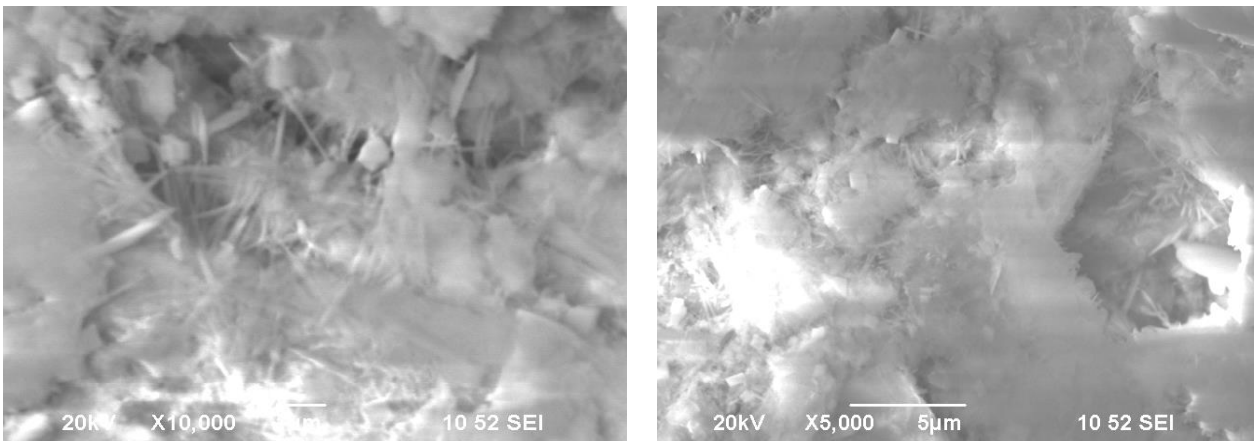

Figure 5 - Electron micrographs from the surface of a cleavage of a cement stone that hardened for 1 day.

In accordance with the data in Figure 5, after 1 day. hardening in water, the surface of the grains of the hardening cement paste is completely covered with rapidly growing and chaotically located needle crystals of calcium hydrosulfoaluminates, which fill the micropores of the forming artificial conglomerate. The process of hydration and crystallization of calcium hydrosulfoaluminates also occurs in the entrained air pores of Portland cement with activated ash and slag: the figure clearly shows that both the surface of the cement particles in the pores and the side walls of the pores are covered with needle crystals (Figure 6).

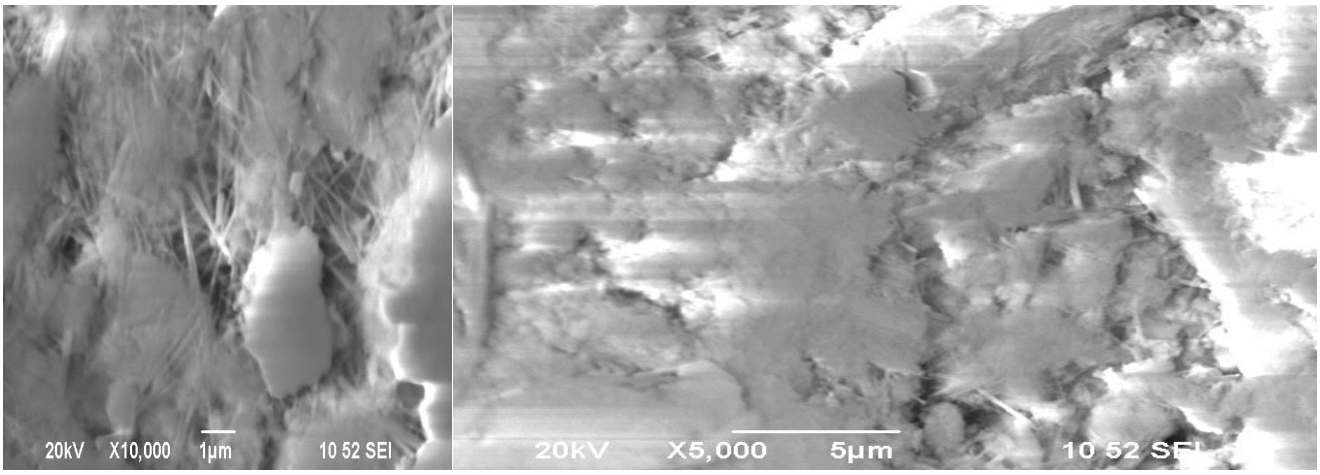

Figure 6 - Crystals and drusen of calcium hydrosulfoaluminates in the pores of the forming cement stone of 3 days of age.

From the smallest grains of clinker particles at the bottom of the pores, submicrocrystalline neoplasms grow in the form of needles and the thinnest plates, which, growing and increasing in size, form crystal aggregates in the form of druses, and they gradually fill the pores and microcracks of the cement stone. By the 7th day, the process of accretion of crystals of neoplasms accelerates both on the surface layers and in the pore spaces (Figure 7a). The number and size of lamellar crystals related to hydrated products of calcium silicates increase and, by narrowing the pore space in the hydrating cement-water system, contribute to the hardening of the cement stone. By the 28-day period of hardening, the cleaved surface of the cement stone is a rough plane with low porosity,

created by the intergrowth of crystalline products, a sufficiently high degree of pore filling and their homogenization (Figure 7b).

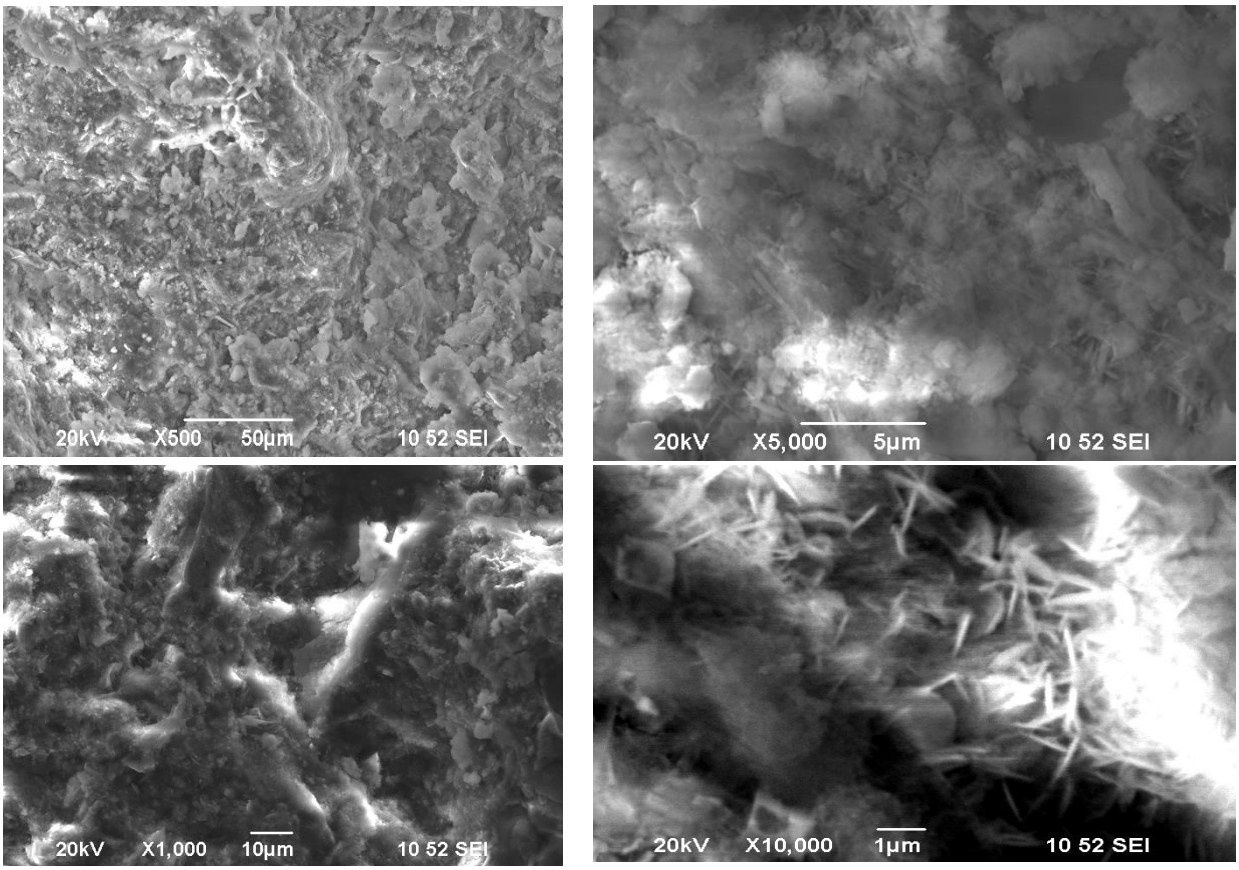

Figure 7 - Chipped surfaces of Portland cement with the addition of 20% activated ash and slag, hardened for 7 (a) and 28 (b) days in water

Thus, the positive effect of the activated ash and slag of dry removal of Angren TPP on the process of hydration and structure formation during hardening of Portland cement, which manifests itself in the intensification of the hydrolysis of clinker minerals, accelerated binding of Ca (OH) 2, accelerated crystallization of the products of new formations filling the pores and microcracks of the cement stone, has been established. and by the very ones contributing to the formation of an artificial conglomerate, the strength indicators of which are at the level of no additives Portland cement.

To organize the production of Portland cements with activated ash and slag wastes of the Angren TPP for dry removal for the purpose of their subsequent use for the production of dry building mixtures of a wide range, JSC "Akhangarancement" developed and registered with the Uzstandart Agency TS 18388312-01: 2019 "Activated ash and slag mixture. Technical conditions "

Conclusion

The favorable chemical and mineralogical composition of activated ash and slag contributes to the creation of optimal conditions for physicochemical transformation in the system "ground clinker - dihydrate gypsum - activated ash and slag - water", which manifests itself in the intensification of the process of hydrolysis of clinker minerals and intensive crystallization of new formations filling the

pores and microcracks of the cement stone , and thus, provides the synthesis of the optimal structure of the artificial conglomerate.

Unlike traditional Portland cement without additives, in Portland cement containing 20% activated ash and slag, the process of hydrolysis of tricalcium silicate begins at an earlier time of hardening. As a result of a decrease in the size of macropores and total porosity due to their filling with crystals and crystal aggregates of acicular crystals of ettringite, fibrous and lamellar crystals of calcium hydrosilicates, a cement stone is formed, the strength of which is at the level of no additive Portland cement.

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