

Improving properties of portland cement using new types of composite additives

MI Iskandarova, *FB* Atabaev*, *ZB* Yakubzhanova, *GB* Begjanova, *NA* Mironyuk, and *DU* Axmedova

Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan

Abstract. The possibility of improving the physical and mechanical properties of Portland cement with maximum clinker savings by optimizing the composition of hybrid additives is shown. It has been established that hybrid additives combining local mineral ingredients with the additive of artificial origin Phosfozol allow saving low-clinker Portland cement while maintaining its original grade 400.

1 Introduction

The urgency of the problem. At present, the issue of increasing the profitability of production is extremely important for the cement industry around the world. The solution to this issue is possible by reducing the cost of cement products through developing and implementing new technologies or using various types of secondary raw materials with improved product quality at a minimum cost. One of the possibilities for obtaining cement with optimal strength, performance, and cost characteristics, taking into account the use of rational options for solving the above problems, is the organization of the production of composite Portland cements, the advantage of which is, first of all, their composition, which contains special mineral additives, due to which the building mixture is calm withstands contact with aggressive environments. The undoubted advantage of this type of cement is its high resistance to low temperatures and a high degree of resistance to the negative effects of mineralized water since it contains special mineral additives. Thanks to these additives, this type of cement is characterized by high resistance to different temperature conditions and abnormal atmospheric phenomena. Such mineral additives significantly increase the properties of water resistance and frost resistance of cement.

In this regard, the share of composite cements in the world production of Portland cement is constantly increasing, which allows manufacturers to save expensive clinker, reduce CO₂ emissions into the atmosphere, obtain cements with a given set of properties, using additives of natural origin or additives that are by-products of metallurgy, energy and other industries [2-11].

* Corresponding author: atabaevfarruh@mail.ru

The latest Russian standard, GOST 31108:2020 "General construction cements. Specifications", harmonized with the European standard, only one type of cement without additives - CEMI; the rest contain up to 65% mineral additives. As for the varieties of mineral additives, the size of their particles is shifting to the region of ever smaller values; they are used and widely studied for the modification and filling of cement systems [12–18]. Caution shown by cement manufacturers when mastering the production of composite cements is primarily due to the poor knowledge of the combined effect of several simultaneously introduced mineral additives on the properties of the resulting finished product. In this regard, the main task of the industry is to find a simple technological application and relatively cheap ways to improve the efficiency of composite Portland cements and concretes based on them, each component of which plays a certain role in the processes of hydration and structure formation. In this regard, due to the high grindability and the ability to partially replace gypsum stone, preference is given to mineral additives in the form of limestone, dolomite, and phosphogypsum as ingredients of composite additives.

A large group of composite additives for cement are heat-treated aluminosilicate materials and volcanic rocks [19–23]. As naturally calcined natural and aluminosilicate ingredients of composite additives, gliezhs, various burnt rocks, tripoli, flask, oil shale ash, metakaolin, ceramic production wastes are used, and basalts, gabbro, diorites, diabases, tuff siltstones, pyroxenites are among the igneous aluminosilicate rocks. , andesites, spillites, etc.

According to the requirements of regulatory documents, additives of sedimentary origin are introduced in 20 to 30%, and additives of volcanic origin (claystone, glies, and ash) are from 25 to 40%. Additives with low activity are impractical to use since a large amount of a low-active additive necessary for the complete binding of lime significantly reduces the strength of cement and concrete. At the same time, the use of local additives, regardless of what type they are, reduces the cost of Portland cement by 0.2 ... 0.8% for each percentage of the additive.

An effective raw material for the production of active mineral additives is kaolinite clays, based on which metakaolin is obtained by heat treatment at a temperature of 750-800 ° C, using which, in combination with other types of additives of natural and technogenic origin, effective compositions of hybrid active mineral additives for composite Portland cements are formed [19, 20, 22].

Gliezh is the most effective aluminosilicate additive in cement, which maximally replaces the clinker part of Portland cement without reducing strength and, at the same time, increasing its performance properties. Composite cements based on alite medium aluminate clinker, including 4% phosphogypsum and the optimal composition of the composite additive of 7% ash and slag and up to 15% gliège, are characterized by hydraulic activity, which ensures the grade of composite cement at the level of Portland cement without additives and its compliance with GOST requirements for setting time [24].

In modern ideas about the role of highly dispersed additives, there is a positive effect of the optimal amount of ash from the combustion of solid fuels on the structure and physical and mechanical characteristics of cement compositions: strengthening the contact zone between the cement stone and aggregates with the formation of clusters "binder - filler" due to the high surface energy of the filler particles; reduction of the total porosity of the cement stone in concrete with an increase in the volume concentration and dispersion of the filler; binding calcium hydroxide amorphous silica pozzolanic fillers; increase in the pozzolanic activity of the filler during its fine grinding, etc. The main advantage of ash compared with other raw materials is a significant proportion of vitreous phases of aluminosilicate composition and high dispersion in its composition. These two factors make it possible to obtain geopolymers based on ash with high technical characteristics without the thermal processing of raw materials and their grinding [15, 21].

Particularly high efficiency in terms of saving clinker and increasing the physical and mechanical properties of composite cements is shown by an active mineral additive of artificial origin, obtained by autoclaving a mixture of ash and slag and phosphogypsum, called Phosphozol, which has a dual effect in the process of hydration and hardening of the cement system and simultaneously plays a role as an active mineral additive and a cement setting time regulator, replacing natural gypsum stone [25, 26]. Studies of the physicochemical properties of cements containing the Phosphozol additive will make it possible to reveal the mechanism of action of this additive on the processes of hydration and hardening, followed by determining the possible composition of the resulting complex compounds and hydrate neoplasms and identifying the conditions for the formation of a solid structure of the hardened cement stone. The study of the hydration of cement stone over time makes it possible to determine the stability of emerging neoplasms and, in the case of the use of these cements for the manufacture of concrete, to predict their main properties (density, strength, weather resistance, frost resistance, etc.), which determine the durability of concrete under operating conditions. It has been established that with the introduction of the Phosphozol additive, the hydrated minerals present in its composition serve as a "crystalline seed", which accelerates the process of hydrolysis and hydration of clinker minerals, the formation of the structure and strength of the cement stone.

2 Research Methodology

The purpose of the research is to optimize the composition of composite additives with the participation of Phosfozol and develop a technology for producing Portland cements using them.

Research objects. The objects of study were the optimal compositions of new types of composite additives and Portland cements with their use. Gliege-like rock mass of the Angren deposit, basaltic andesites of the Shavazsai deposit, and modified Portland cements based on clinker of Akhangarancement JSC were chosen as the ingredients of composite additives.

The studies were carried out using a set of methods of chemical (according to GOST 5382-91), physicochemical (optical, X-ray phase, electron microscopic), and physical and mechanical (according to GOST 310.1-310-4, Uz DSt 2830:2014 "Portland cement with composite additives. Specifications") analysis of the additive "Phospozol", mineral ingredients of composite additives and Portland cements with composite additives.

3 Results and Discussion

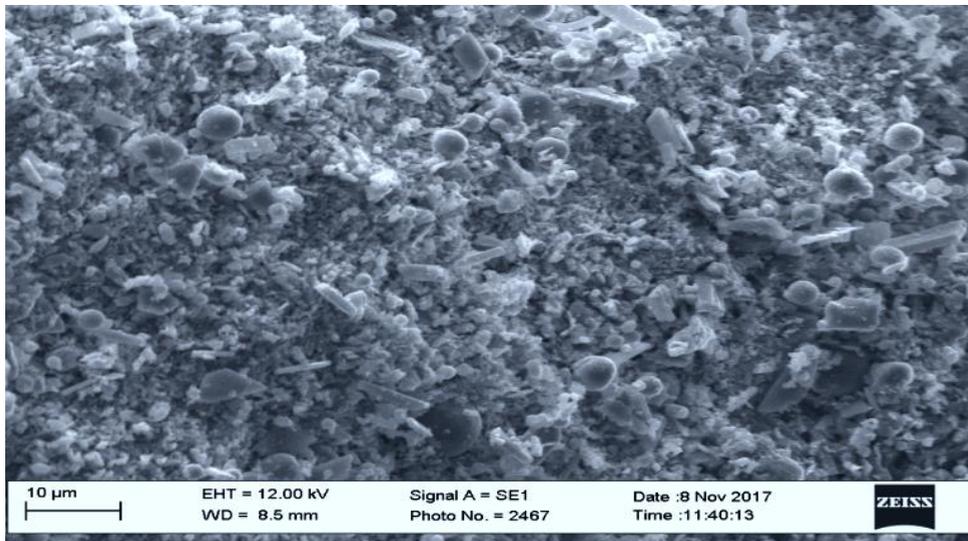
Analysis of the chemical analysis in table 1 shows that the Phosfozol additive, in addition to aluminosilicate minerals introduced into the additive by ash and slag waste, contains a significant amount of calcium sulfate introduced by phosphogypsum.

Table 1. Chemical compositions of initial components and additives "Phospozol"

Material	loss when calcined	Content of mass fraction of basic oxides, %							
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	SO ₃	other
Phosfozol	14.34	39.56	17.01	2.34	10.69	1.18	2.00	10.38	4.10
Mountain mass-gliezh andesitebasalt	2.16	74.15	16.79	0.79	1.95	0.60	-	traces	3.56
andesitebasalt	6.17	57.30	21.10	5.17	2.51	1.80		1.55	4.40
Portland cement clinker	1.43	20.59	5.76	4.77	63.32	1.80	-	traces	2.33
	Parameters and mineralogical composition of clinker (%):								
	saturation factor 0.88	n 1.95	p 1.25	C ₃ S 50.07	C ₂ S 14.39	C ₃ A+ C ₄ AF 14.76		CaO _{cb} 0.78	

Visually, the additive "Phospozol" is represented by a dispersed material of a gray polyfractional composition, containing particles less than 0.63 mm in size with inclusions of large grains with a size of (0.63 - 5.0) mm.

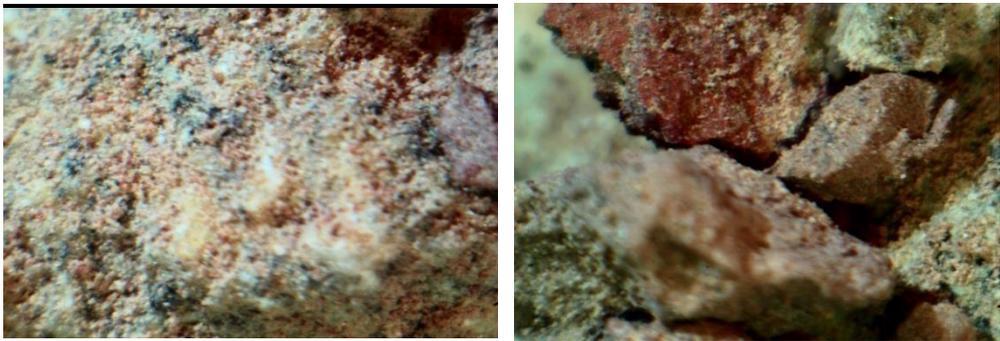
The microstructure of the "Phospozol" additive is represented by a granular mass of many particles of various shapes, among which short prismatic, long fibrous, thin needle-shaped crystals and round spherical grains predominate (Fig. 1). Short prismatic forms of crystals are calcium hydrosilicates, and gypsum-containing compounds, fibrous and acicular crystals indicate the formation of low- and high-sulfate forms of calcium hydrosulfoaluminates during hydrothermal treatment of the ash-and-slag + phosphogypsum mixture, and spherical grains are characteristic of quartz particles.

**Fig. 1.** Structural structure of the additive "Phosfozol"

Indeed, on the diffraction pattern of the Phospozol additive, there are clear reflections of hydrates of both sulfate-containing and calcium silicate minerals: CaSO₄·2H₂O at $d/n = (0.315; 0.305; 0.286; 0.278; 0.259; 0.214; 0.189; 0.179; 0.153...)$ nm; CaSO₄·0.5H₂O (0.278; 0.232; 0.189; 0.179...) nm; calcium hydrosulfoaluminates (C₃A·CaSO₄·12H₂O and C₃A·CaSO₄·3.1H₂O) at $d/n = 0.3.03; 0.257; 0.242...$ nm; calcium hydrosilicates (C₂SH (A), C₂SH (C), C₂SH (B) at $d/n=(0.329; 0.260; 0.241; 0.276; 0.189; 0.180...)$ nm; hydrosilicates of the tobermorite group (C₄ S₅H, C₄S₃H, C₆ SH₃, CSH (B), CSH (A), C₃S₂H₃) with $d/n =$

(0.296; 0.278; 0.274; 0.214; 0.180; 0.174.160; 0.153; 0.148. . .) nm; non-hydrated dicalcium silicates (α -C2S, β -C2S) at $d/n = (0.278; 0.262; 0.215; 0.180; 0.175. . .)$ nm) and calcium hydroxide Ca(OH)₂ at $d/n = (0.262; 0.193; 0.179. . .)$ nm. Therefore, in the additive "Phosphozol" composition, there are gypsum minerals (dihydrate, hemihydrate calcium sulfates), and hydrate neoplasms of hydrosulfoaluminate and hydrosilicate structures. The chemical activity of the studied additive "Phosphozol" was 54.5 mg, corresponding to the minimum permissible activity characteristic of groups of artificial (technogenic) aluminosilicate hydraulic additives.

The Gliège-like rock mass is represented by pieces of various sizes, which are painted in various colors (Fig. 2).



a

Fig. 2. External view (a) of the Gliège-like rock mass of the Angren deposit

This suggests that during underground fires of coal seams alternating with kaolin clay seams, the latter undergo various temperature effects: the seams that are close to the sources of underground fires are characterized by a dark burgundy and brown color, and those that are closer to the earth's surface are yellowish-cream color. Its chemical composition includes mainly quartz SiO₂ with $d/n = (0.334; 0.246; 0.228; 0.224; 0.197; 0.181)$ nm, calcium carbonate CaCO₃ with $d/n = (0.304; 0.249; 0.290; 0.191; 0.187)$ nm) and gellenite2CaO .Al₂O₃.SiO₂ with $d/n = (0.378; 0.290; 0.278; 0.256; 0.246; 0.239; 0.236; 0.224; 0.212; 0.209; 0.197; 0.191; 0.187; 0.176)$ nm .1, Fig. 3).

The hydraulic activity of the Gliège-like rock mass, according to Student's criterion, was $t = 37.80 > 2.07$. This means that the Gliège-like rock mass has passed the test for strength activity and, according to clause 4.2 of O'z DSt 901-98, can be used as an active mineral additive for cements.

The chemical composition of basaltic andesite is characteristic of igneous rocks, which are dominated by the content of aluminosilicates and ferruginous compounds. Visually, the rock is represented by dense pieces of dark gray with low porosity; in some places, there are inclusions of tiny brown grains (Fig. 3).

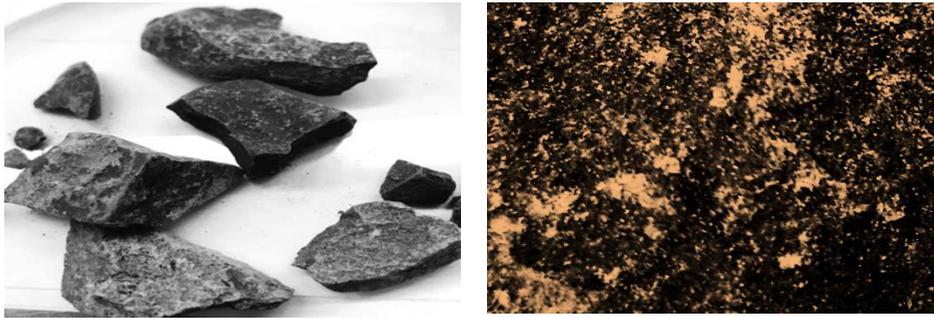


Fig. 3. Basaltic andesite of the Shavazsai deposit

By evaluating the differences in the average compressive strength of samples of a mixture of cement with sand and samples of a mixture with basalt andesite, it was found that the strength of the latter is lower than the average value of the strength of the control mixture and, therefore, basalt andesite is inert or has weak hydraulic activity. Therefore, after determining the chemical (pozzolanic) activity, it can be used as a filler additive or ingredient of a composite additive in the production of Portland cements. To obtain composite Portland cements, raw mixtures (charges) of various compositions were prepared, including Portland cement clinker, gypsum stone, and hybrid additives in the form of various compositions of gliege and basalt andesite with the participation of the Phosfozol additive. For comparative tests, Portland cement PC-D0 was used without additives. The material compositions of Portland cements with hybrid additives, and their accepted symbols are presented in Table. 2.

Table 2. Material Compositions of Charges for Obtaining PC with Hybrid Additives

№	Conventional designation of charges for the production of cements with additives	*Material composition of charge, %, by weight				
		Clinker	gypsum stone	Gliezh	Andezibazalt	Phosfozol
1	PC- AD 0	95	5	-	-	-
2	PC-G.Ph30	70	-	20	-	10
3	PC-G.Ph30	60	-	20	-	20
4	PC-G.Ph40	60	-	20	10	10
5	PC-An.Ph30	70	-	-	20	10
6	PC-An.Ph40	60	-	-	20	20
7	PC-Gl30	70	5	19	-	6
8	PC-Gl.An30	70	5	19	6	-

The fineness of grinding materials was assessed by the residue on a sieve with mesh No. 008 according to the method of GOST 310.2-76. The duration of grinding was 40 min. When grinding experimental mixtures, the fineness of the obtained cements almost did not differ from the dispersion of PC-D0.

In terms of strength indicators, Portland cements containing 30% of hybrid additives PC-Gl.F30 and PC-AF30 comply with the requirements of O'z DSt 2830: 2014 and, depending on the type of components used and their ratio in additive compositions, are characterized by grade 300, and experimental cements PC-GlFG30, PC-GlAG30 - grade 400 (Table 3).

Table 3. Strength characteristics of experimental Portland cements with hybrid additives

Conventional designation of cements	W/C solution 1:3	cone blur mm	Ultimate flexural and compressive strength, MPa				Cement grade according to RD
			7d		28d		
			R _{fl}	R _{comp}	R _{fl}	R _{comp}	
PC- Ad 0	0.40	112	6.20	26.8	8.00	45.8	400
PC-GI Ph30	0.40	114	5.06	26.0	6.56	37.2	300
PC- GI Ph 40	0.40	112	3.84	17.8	5.80	27.4	does not comply
PC-GIAnPh 40	0.40	110	3.95	23.0	6.03	26.8	does not comply
PC-AnPh30	0.40	110	5.00	21.4	6.45	35.7	300
PC-AnPh 40	0.40	110	4.68	17.4	6.27	29.4	does not comply
PC-GIPhG30	0.40	109	5.98	27.4	7.25	41.8	400
PC-GIAG30	0.40	110		26.8	7.14	40.4	400

In the manufacture of which hybrid additives were used in 40% (PC-GI F40, PC-GIA F40, PC-AF40), Portland cements do not meet the regulatory document's requirements in terms of compressive strength.

Based on the research results, the compositions of PC 400-KD30 composite Portland cements were optimized, in the manufacture of which hybrid additives of the following compositions were used as composite additives:

- "19% gliezh + 6% Phosphosol + 5 gypsum stone";
- "19% gliège + 6% basalt andesite + 5 gypsum stone".

Cements containing these compositions as additives meet the requirements of O'z DST 2830:2014 "Portland cement with composite additives. Specifications" and are characterized by a brand with the symbol PC 400-KD 30.

From pilot batches of PC 400-KD30 composite Portland cements with the indicated additives, concrete compositions were made and optimized, which withstood 25 cycles of alternate freezing and thawing and 25 cycles of drying and saturation with water determines their sufficient resistance to environmental influences. Following O'z Dt 2830: 2014, Portland cements with composite additives are classified as general construction cements and are used for concrete of prefabricated and monolithic structures and products of buildings and structures for various purposes.

Based on the results of research and pilot tests, changes have been made to the state standard, providing for the basic requirements and scope of Portland cements PC-KD30 with new types of hybrid additives, including Phosfozol mixed with gliez (up to 20%), gypsum stone (up to 5%), basalt andesite with a total content of additives of not more than 30%.

4 Conclusion

When replacing 30% of high-temperature clinker in Portland cement with hybrid additives from available and cheap ingredients, one of which is an increased content (up to 20%) of gliege-like rock mass and basalt andesite in the composition with "Phosfozol" - an additive of artificial and technogenic origin, the quality of Portland cement does not get worse.

The main effect of using the proposed hybrid additives in the manufacture of composite Portland cement, according to GOST 24640-91, is the saving (up to 30%) of clinker, which simultaneously reduces the cost and increases the volume of cement output.

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