

Comprehensive solution to environmental problems of ceramic production by recycling their waste in cement industry

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Abstract. The paper presents the results of studies to determine the suitability of the dump battle of fired ceramic products based on kaolin clays of the Angren deposit, the positive effect of the addition of fractionated ceramic battle on the formation of the structure and physico-mechanical properties of portland cement stone is established. For use as an additive in cement, the need for fractionation of ceramic production waste with separation of the burnt part of ceramic waste was noted; its chemical and mineralogical compositions and hydraulic activity were determined according to the Student's criterion, the value of which was $t=21.21$, which is higher than its regulated value of at least 15 according to GOST (State Standard) 31108-2020. Based on the obtained research results, ceramic waste is recommended as an active mineral additive in cement. The positive effect of the addition of fractionated ceramic waste on the process of origin and evolution of neoplasms in terms of acceleration of hydrolysis, hydration of clinker minerals, and cement hardening with the formation of a low-porous structure of cement stone, which, despite a decrease in the proportion of high-temperature Portland cement clinker up to 20%, is characterized by high hydraulic activity corresponding to the grade of cement PC400-D20.

1 Introduction

Cement is one of the most popular types of building materials. Therefore, its production is constantly growing worldwide, including in Uzbekistan, with the developing industrial pace of the construction industry [1, 2].

In recent years, the use of thermally activated clays as additives to Portland cement has become particularly relevant, which reduces the proportion of clinker in cement. It reduces its cost and environmental burden due to reduced carbon dioxide emissions [3-5]. However, the synthesis of metakaolin by thermal activation of kaolinite and polymineral clays requires the creation of a special line with the installation of roasting machines and

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auxiliary equipment, which will lead to an increase in its cost. In addition, it cannot be introduced into cement in large quantities; therefore, in recent years, composite additives have been obtained with its participation [6, 7].

This study aims to study the effect of burnt ceramic waste on the rate of hydration, structure formation, and strength set of cement stone. Portland cement (PC) clinker of JSC "Akhangarantsement" was used in the matrix, gypsum stone (GS) of the Karnab deposit was used to regulate the setting time of cements, and ceramic waste (CW) was used as an active mineral additive after fractionation of waste of JSC "Kulol" [Table 1].

2 Materials and methods

Standard methods for determining the chemical and mineralogical composition of Portland cement clinker, ceramic waste, and gypsum stone were used in the research. The phase composition of the studied components was determined on the XRO-6199 diffractometer (Shimadzu, Japan). The hydraulic activity of the ceramic waste was established according to the Student's criterion (t-criterion) following the methodology of GOST (Interstate Standard) 25094, the physico-mechanical parameters of cements with a modifier – according to the methodology of GOST 310.1-310.4. The results of physico-mechanical parameters of additional cements were evaluated in accordance with GOST 10178. The structure of composites based on modified cements was studied using a JSM-6490LV scanning electron microscope with INCA Energy Energy microanalysis and HKL-Basic structural analysis systems.

3 Results and Discussion

In the chemical composition of burnt ceramic waste, the content of SiO_2 and Al_2O_3 is very high (64.85% and 23.89%, respectively). The total content of iron, calcium, magnesium oxides, sulfuric acid anhydrite, and other impurity inclusions is 9.56%. (Table 1).

The diffractogram of ceramic waste detects intense reflections of quartz and dissimilar calcium aluminosilicates such as hercynite, mullite, and anorthite formed during the primary firing of ceramic masses on products.

Table 1. Chemical composition of the starting materials

Name	The content of the mass fraction of oxides, %							
	Incineration losses	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Pr.
Portland cement clinker of JSC "Akhangarantsement"	0.75	20.54	5.19	3.56	62.04	3.60	0.62	4.24
	Saturation coefficient (SC)-0.91; silicate module (n)-2.34; alumina module (p)-1.46. C_3S -56.52%; C_3A -7.74%; C_4AF -3.08%; C_2S -32.06%; CaO_{cb} -0.6%							
Gypsum stone	At 400°C 19.10	1.52	0.13	0.14	33.04	0.20	43.46	2.41
Ceramic waste	1.70	64.85	23.89	2.79	2.24	1.00	1.28	2.25

The value of the Student's criterion (t-criterion) of ceramic waste was $t = 21.21$, which is higher than its regulated value of at least 15 – according to GOST 31108-2020, which justifies the possibility of its use as an active mineral additive in the production of general construction portlandcement. Cements containing (5-20)% of ceramic waste in terms of physical and mechanical properties differ somewhat from the control additive-free cement

PC-D0 in that their water demand increases by (5-9)%, and the setting time is extended from 200 to 345 min. The additive introduced in an amount of (5-20)% accelerates the hardening of cements; that is, the compressive strength of cements with the addition of ceramic combat at the age of 7 days is (6-12)% higher than the strength of PC-D0 (table 2).

The same patterns of strength gain of PC samples with the addition of ceramic waste were noted by 28 days of hardening: their hydraulic activity is within (41.9-42.8) MPa, which is higher than the strength of PC400-D0 cement (40.2 MPa) and which meets the requirements of GOST 10178-85 for PC400-D20 cement. The introduction of any type of active mineral additive or filler additive into the composition of the hardening system "ground clinker-gypsum-water" affects the speed of the hydration process and the formation of the artificial conglomerate structure during the hardening of portlandcement.

Table 2. Material compositions and physico-mechanical characteristics of PC with addition of ceramic waste

№	Conven-tional Designa-tion of cements	The material composition of cements, %			Fine-ness of grin-ding (residue on the sieve № 008),%
		Clinker	CW	GS	
1	PC-D0	95	-	5	10
2	PC-D 5	85	5	10	10
3	PC-D 10	80	5	15	10
4	PC-D 20	75	5	20	8

Continuation of table № 2.

№	Normal density	Setting time, <i>h</i> - min		Bending strength/compression, MPa	
		beginning	end	7d	28d
1	25.7	3-20	5-00	5.6/21.4	6.2/40.2
2	27.0	5-45	6-30	5.9/22.7	6.5/41.9
3	27.0	5-35	6-10	6.0/24.0	6.7/42.8
4	28.0	5-25	6-10	5.3/23.0	6.7/41.5

According to X-ray phase analysis, the hardening process of PC with ceramic waste is accompanied by the intensive formation of ettringite: by day 1, the diffractogram detects its lines at $d/n=(0.955; 0.730; 0.538, 0.424)$ nm, the intensity of which gradually increases to 21 days, and then stabilizes (Fig. 1).

This means that SO^{2-} ions, which pass into the liquid phase due to the hydrolysis of $CaCO_4$, are completely bound into calcium hydrosulfoaluminates. Hydrolysis and hydration of silicate minerals of clinker of composite Portland cement proceeds in parallel, as indicated by a gradual decrease in the intensity of the C_3S and C_2S lines ($d/n = 0.302; 0.277; 0.262; 0.192$ nm) with the age of hardening. This means that after the removal of Al^{3+} and SO^{2-} ions from the liquid phase, the hydrolysis of silicate minerals is accelerated with the release of $Ca(OH)_2$. Subsequently, Ca^{2+} ions are consumed for the formation of a hydrosilicate gel, and crystallization of calcium hydrosilicates, as a result of which the formed cement composite is gradually compacted and, despite a decrease in the proportion of the clinker part in composite binder up to 20%, acquires a strength exceeding the strength of matrix cement PC400-D0.

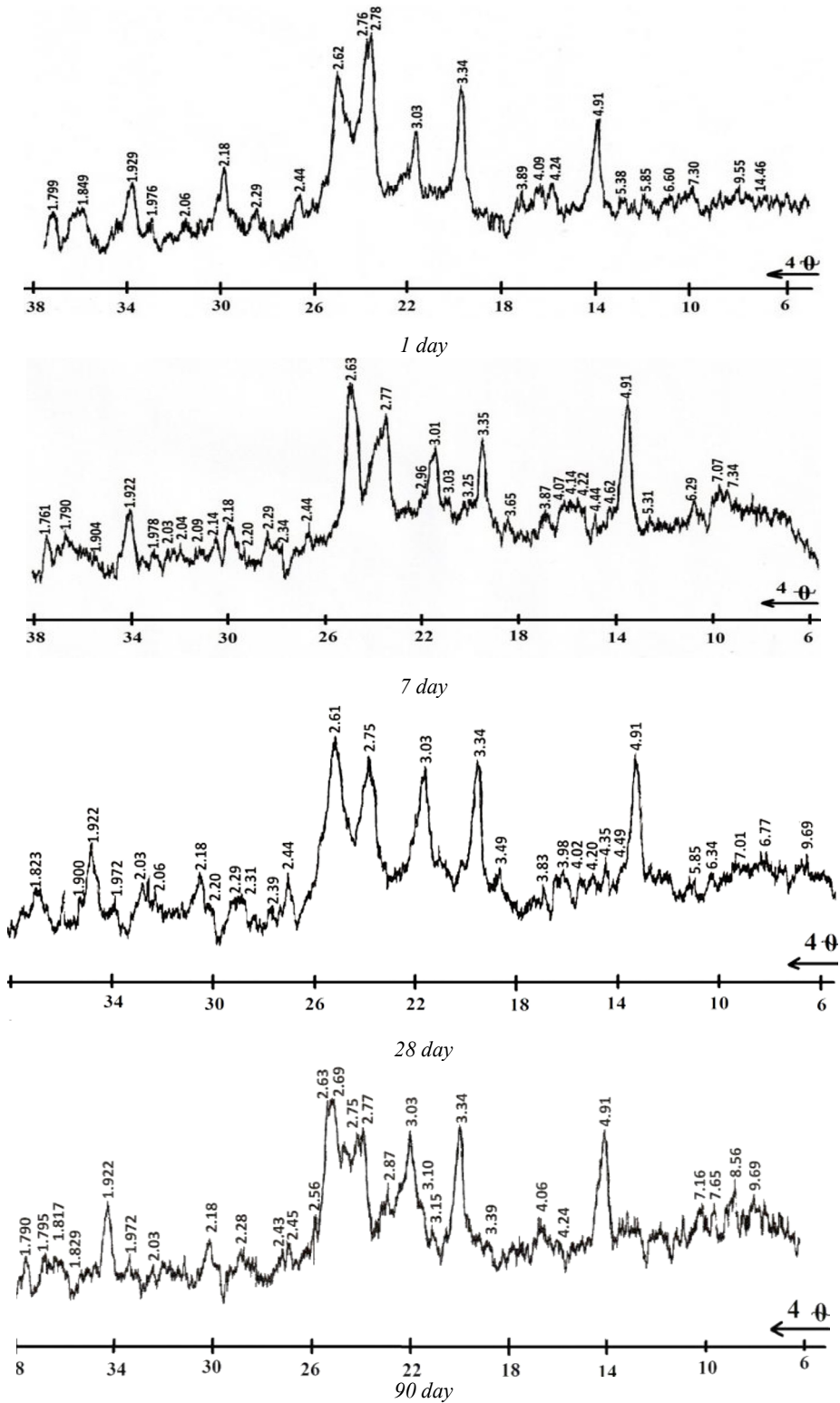


Fig. 1. Diffractograms of PC with addition of 20% ceramic waste

An electron microscope study revealed that ceramic waste serves as a "seed" for the rapid crystallization of hydrate products. After the experimental cement is sealed with water, rapid chemical interaction of the constituent components immediately begins. During 1 day of pre-storage in air-humid conditions, the entire surface of clinker particles in the pores was covered with growing needle-like crystals of ettringite, which were randomly located in different directions, began to fill the air pores, and the intergranular space of the solidifying cement paste (Fig. 2).

The accelerating effect of ceramic waste on the formation of the structure and strength of cement stone is provided by the pozzolanic effect of the additive, manifested in the intensive binding of lime with the formation of ettringite and hydrosilicates of the tobermorite group, micro-filling of the hydrate structure and increasing the structural density of the forming cement stone [8-10].

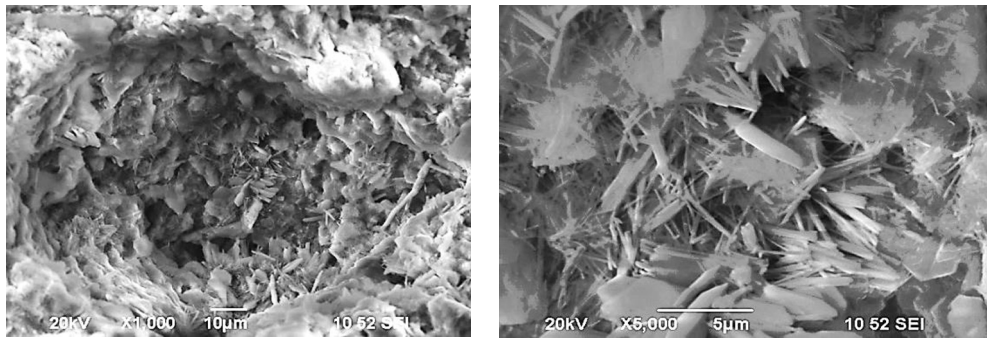
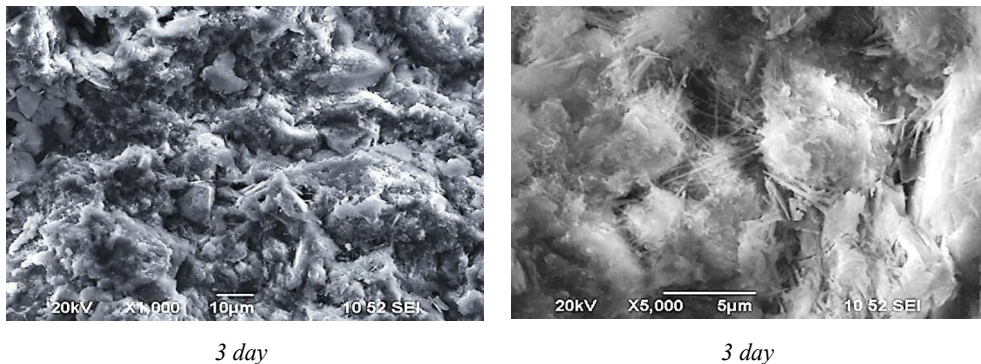


Fig. 2. Relief of surface of chip of hardened 1 day PC with addition of 20% ceramic waste

When introducing a thermally activated additive with high reactivity to the stage of particle nucleation, it can be noted that the process of supersaturation of the heterogeneous system "ground clinker – burnt ceramic waste – gypsum – water" is controlled by introducing nuclei (nuclei) from the outside to accelerate the formation of ettringite and calcium hydrosilicates. This determines the kinetics of the first stage in the evolutionary route of the hardening binding system.

By the 3rd day, the number of needle-like, fibrous, and prismatic crystals becomes larger, and the degree of pore filling is quite high (Fig. 3).



3 day

3 day

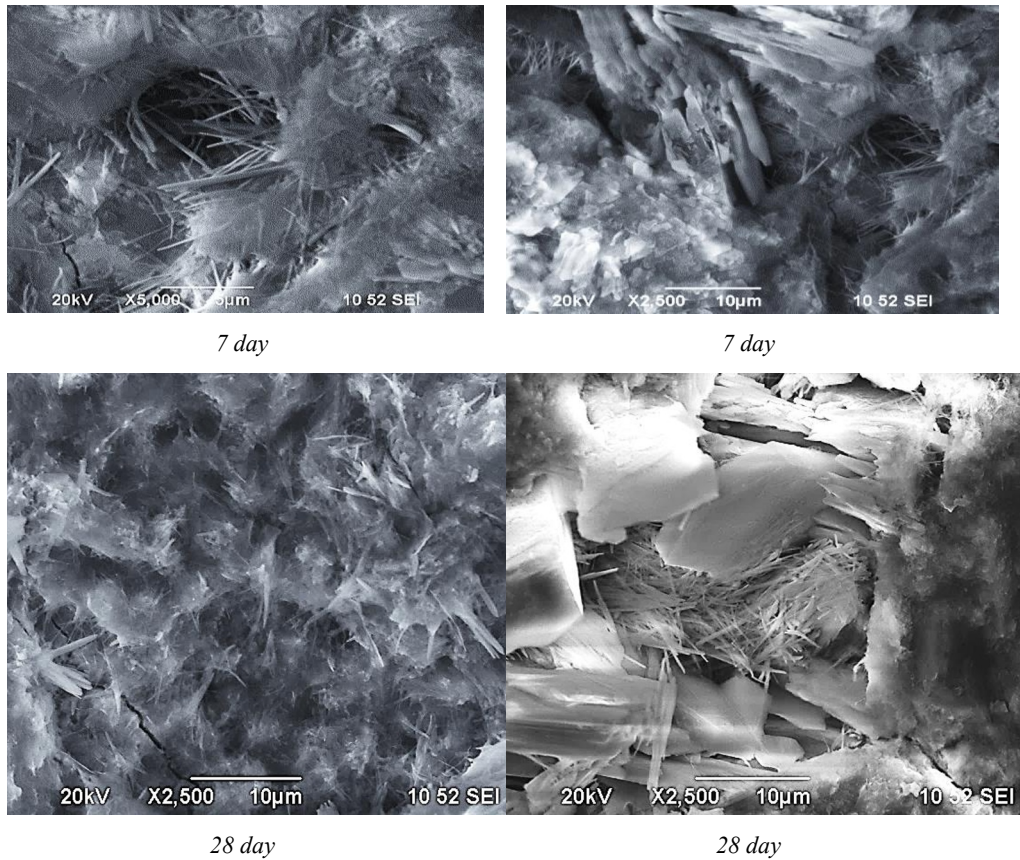


Fig. 3. Relief of surface of chips of PS samples hardened during (7-28) days with addition of 20% ceramic waste

According to the data of Fig. 3, by the 28th day, the relief of the cement stone chipping surface is characterized by a denser packing of prismatic crystals of calcium hydrosilicates CSH (B) and lamellar crystals of tobermorite $5\text{CaO}\cdot 6\text{SiO}_2\cdot 5\text{H}_2\text{O}$, which form fibrous aggregates and separate blocks. Fibrous (filamentous) crystals are located between the blocks of these crystals, which, dissolving on their surface, penetrate the fine-grained mass and, as it were, "stitch" the grains of clinker minerals with each other.

It is known that, depending on the instability of supersaturation in the liquid phase, metastable calcium hydrosilicates recrystallize, which causes the occurrence of high stresses during the growth of crystal nuclei and leads to the appearance of defects in the crystal lattice and a decrease in the strength and density of cement stone [11,12]. Figure 4 shows that the intensive growth of hydrosilicate crystals and their aggregation inside the pores of cement stone leads to cracks and deformation.

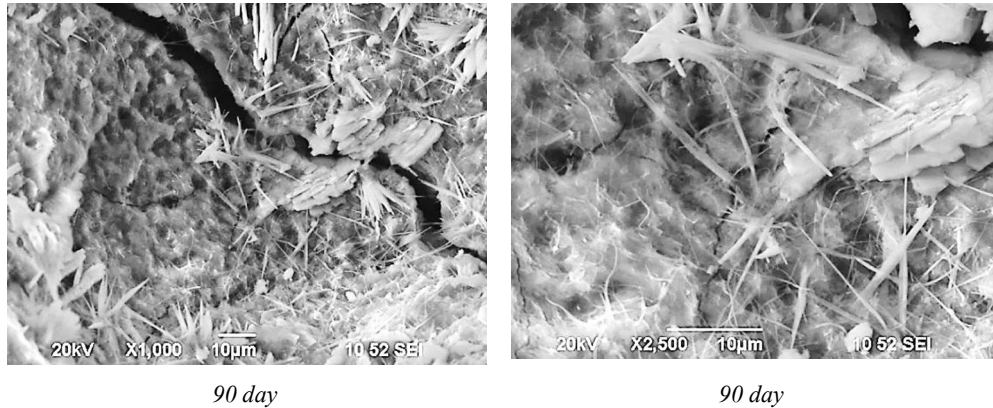


Fig. 4. Relief of surface of chips of PS samples hardened during 90 days, with addition of 20% ceramic waste.

However, along with the process of recrystallization of hydrosilicates, due to the continued hydration and supersaturation of the liquid phase with Ca^{2+} ions, the process of "self-healing" of the resulting cracks proceeds in parallel due to the formation of additional portions of calcium hydrosilicates and the intensification of polymerization processes that contribute to the homologation of the hydrate structure of the cement composite and a decrease in its total porosity, which is the main factor in maintaining the strength of cement with the addition of ceramic waste at the level of additive-free portlandcement [13-15].

Based on the results of research at JSC "Akhangarantsement", the production of portlandcement of the PC400-D20 brand, as well as PC400-CD30, has been established using a composite additive, in which one of the ingredients is waste from ceramic production.

4 Conclusions

With a rational approach to the disposal of waste from the production of ceramic products, they can become a valuable raw material for the cement industry. Adding up to 20% of fractionated burnt ceramic waste to cement accelerates the formation of calcium hydroaluminates and hydrosulfoaluminates in the early stages of its hardening. This contributes to the creation of a block-aggregate structure of low porosity, which provides an increase in the hydraulic activity of the PC, which, despite a decrease in the proportion of highly active clinker in cement, by day 28 is (41.5–42.8) MPa, which corresponds to the grade of PC 400-D20 cement. The developed technology provides up to 20% savings for expensive clinker, reducing the cost of cement, increasing its production volume, and improving the environmental situation in industrial areas.

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