



## Study of the Genetic Formation of New Formations during the Hardening of Pozzolanic Cement with a High Content of Ash and Slag Waste of Dry Selection

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**ABSTRACT:** The results of physical and chemical studies of the processes of hydration and structure formation during hardening of pozzolanic cements containing dry-selection ash and slag waste from the Angren TPP as an active mineral additive are presented. It has been established that, despite the replacement of up to 50% of the clinker part, the experimental cements acquire high hydraulic activity, which ensures their grade 400–500, which is facilitated by the presence of active silica, alumina and low-basic calcium silicates in the composition of the additive, which in the process of chemical interaction with hydration products clinker minerals are involved in the formation of a dense microstructure of the cement composite.

**KEYWORDS:** Active mineral additive, Hydration, Hardening, Microstructure, Lime absorption, Pozzolanic cement, Phase composition, Slagash from thermal power plants of dry selection, Student's criterion, Strength.

### INTRODUCTION

The world experience of some European countries shows that with a rational approach to the processing of ash and slag waste, TPP shows the possibility of their 70–80% utilization [1]. One of the ways to use ash and slag waste is to obtain new types of complex binders based on them, which have increased strength and low cost. Replacing part of the cement with an active mineral additive makes it possible to achieve significant savings in the binder. The intensive development of the construction industry around the world, including in the Republic of Uzbekistan, requires the use of high-quality building materials and products that ensure the reliability and durability of concrete. A change in the material composition of cement by the introduction of active mineral additives or filler additives is reflected in a change in the operational characteristics of concrete, which is achieved by partially replacing the highly basic Portland cement clinker in cement with additives that change the rate of hydration and the formation of hydrate neoplasms of the hardening binder system, enriching it with crystalline hydrates with different morphological characteristics and structure [2]. In the presence of carbonate-containing additives, the hydrated phases in the hardening cement stone are the remains of clinker minerals, portlandite, calcite, hydrosilicates and calcium hydroaluminates, ettringite, as well as calcium hydrocarboaluminate  $3\text{CaO}\times\text{Al}_2\text{O}_3\times3\text{CaCO}_3\times32\text{H}_2\text{O}$ , which is similar in structure to ettringite. At the same time, hydrosilicates crystallize better calcium – tobermorite and  $\text{C}_2\text{SH}_2$ , and the content of ettringite decreases [3–5]. The addition of high-silica additives and microsilica increases the degree of absorption of calcium hydroxide from the liquid phase and, by increasing the amount of hydrosilicates formed, causes corresponding changes in C–S–H at the macrolevel, which also leads to a change in the structural features of the cement stone [6–11].

Earlier, in the scientific laboratory and testing center “Strom” of the Institute of General Chemistry of the Academy of Sciences of the Republic of Uzbekistan, a technology was developed for producing pozzolanic cements of grades 400–500, containing in its composition the ash and slag waste of the Angren TPP of dry selection [12, 13]. In this regard, the role of this additive in achieving the same indicators of the hydraulic activity of cement stone is of some scientific interest, despite the fact that the proportion of highly active clinker in its composition is reduced by 25–50%.

The purpose of the research is to establish the relationship between the strength of pozzolanic cement with a high degree of filling and the phase composition and microstructure of the stone based on it.

**RESEARCH METHODS**

The rate of hydration of pozzolanic cement was estimated from the amount of water bound during a certain period of hydration by determining the loss on ignition of samples hardened within 1–28 days. The phase composition of the products of hydration of pozzolanic cement was determined by X–ray phase (on a Shimadzu XRO–6100 diffractometer), differential thermal (on a Netzsch thermoanalytical device Simultaneous Analyzer STA 409 PG) and IR spectroscopic (on the Fourier spectrometer “IRTracer – 100”) analysis methods. The route of evolution of neoplasms during hardening of a new type of pozzolanic cement was studied using a JSM–6490 LV scanning electron microscope with energy–dispersive microanalysis systems INCA Energy and Structural Analysis HKL – Basic.

**OBJECT OF STUDY**

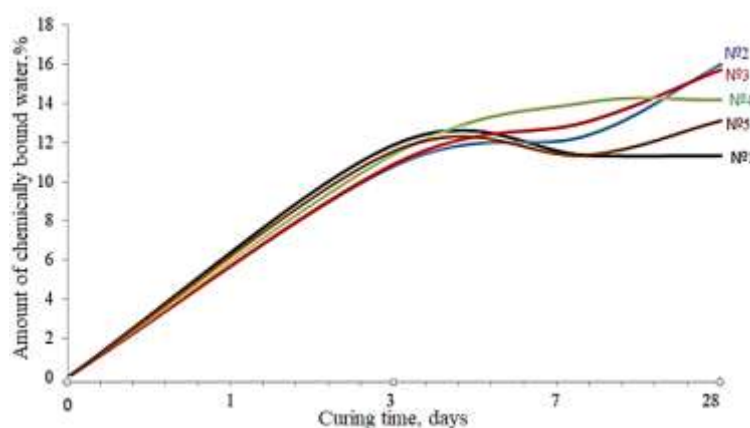
The composition of pozzolanic cement M500 containing 40% dry slagash waste was chosen as the object of study.

**RESULTS AND ITS DISCUSSION**

The results of determining the rate of hydration of pozzolanic cements containing 30–60% ASW of dry selection, estimated by the amount of chemically bound water, are shown in Table 1.

**Table 1.** Water binding rate by experimental PPC

No.	Cements	The amount of chemically bound water (%), through :			
		1 day	3days	7days	28days
1	PC–D0	7.77	11.89	11.35	11.32
2	PPC–D30	7.85	10.80	12.34	16.0
3	PPC–D40	8.43	10.91	13.04	15.73
4	PPC–D50	9.32	11.41	14.04	14.18
5	PPC–D60	9.21	11.57	11.35	13.12



**Figure 1.** Kinetics of water binding during hardening of experimental cements

The amount of chemically bound water during hardening of PPC–D0, which is 7.77% after 1 day of air–moist hardening, increases to 11.89% by the 3rd day, and in the future, its amount gradually decreases. The addition of 30% KZShO accelerates the binding of water into hydrate products, its amount by 1 day. slightly higher than for PC–D0 samples. In subsequent terms, up to 28 days, its amount gradually increases and exceeds the matrix index. An increase in the content of the additive leads to a slowdown in the process of water binding, however, its content is higher than in the samples from PC–D0 (Fig. 1).

To study the phase composition and microstructure, the composition of pozzolanic cement PPC–D40 with hydraulic activity after 28 days of normal hardening 50.42 MPa (PPC500–D40), obtained by modifying cement without additives grade PC400–D0,

which has a compressive strength of 42.60 MPa for the same period of hardening. The X-ray pattern of the PPC of the daily age of hardening reveals strong diffraction reflections of quartz ( $d/n = (0.424; 0.333; 0.245; 0.227; 0.181; 0.154 \text{ nm})$ ) and weaker reflections of clinker silicate minerals ( $C_3S$  and  $C_2S$ ) with  $d/n=(0.276; 0.218; 0.192) \text{ nm}$  (Fig.2a). Lines of multiphase hydrates  $C_3S - 5CaO \cdot 6SiO_2 \cdot 3H_2O$  and  $C-S-H$  (II), an analogue of tobermorite  $d/n=(0.490; 0.303; 0.279; 0.192 \text{ nm})$ , the main the lines of which are superimposed on the lines of  $Ca(OH)_2$  and calcium silicates of clinker. By 1 day, a sufficient amount of  $Ca(OH)_2$  is formed, part of which, due to its carbonization, turns into  $CaCO_3$  ( $d/n = 0.489; 0.333; 0.245$ ) nm. It should be noted that the lines of quartz and calcium hydrosilicates merge with the lines of calcium silicates, increasing their intensity. By the 3rd day, the intensity of the lines of calcium silicates significantly decreased, while  $Ca(OH)_2$  and  $CaCO_3$  increased, which indicates an acceleration of the hydrolysis of clinker minerals and hydration of PPC-D40 (Figure 2b).

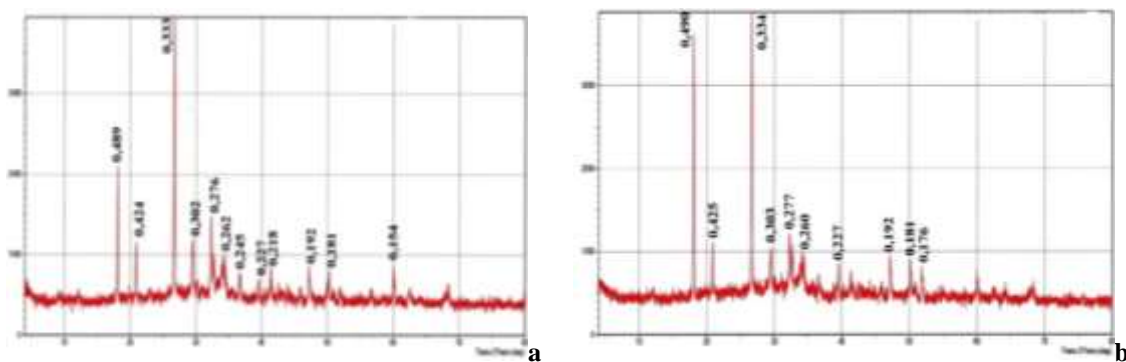


Figure 2. Diffractograms of PPC-D40, hardened 1 (a) and 3 (b) days

By 7 days, reflections of calcium silicates and  $Ca(OH)_2$  at  $d/n=0.490 \text{ nm}$  are greatly reduced due to its binding into hydrate products. At the same time, the content of  $CaCO_3$  prevails in the binder system, which makes a certain contribution to the compaction and strengthening of the cement composite. With further hardening up to 28 days, due to some acceleration of the hydration of PPC-D40, the composition of the hydrated phases changes towards an even greater decrease in the lines of clinker minerals and an increase in the lines of hydrosilicates,  $Ca(OH)_2$  and  $CaCO_3$  (Fig. 3a). By 90 days, the intensity of the line of initial minerals and  $Ca(OH)_2$  decreased significantly, while  $CaCO_3$  with  $d/n=0.333$  almost did not change (Fig. 3b).

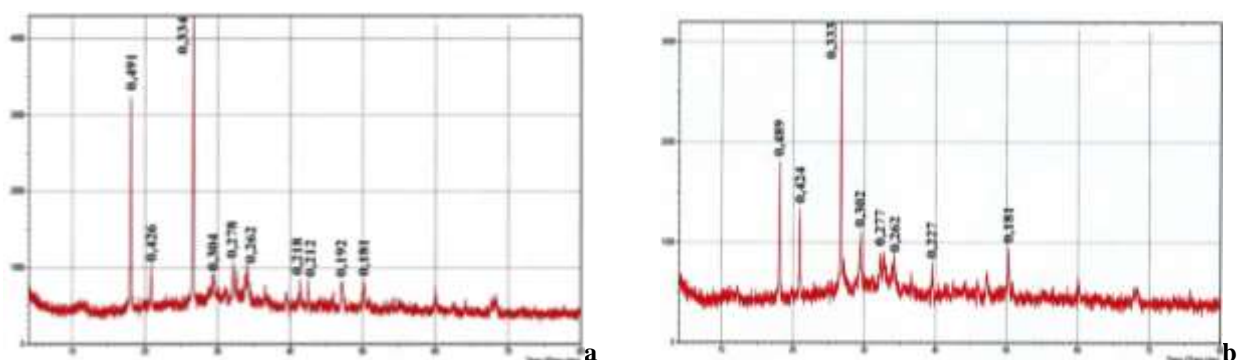


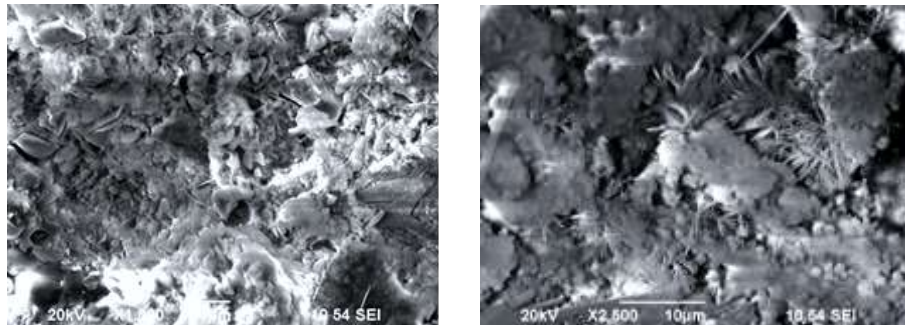
Figure 3. Diffractograms of PPC-D40, hardened 28 (a) and 90 (b) days

IR spectra of PPC-D40 after a day of hardening reveal absorption bands of different intensity in the range of wave numbers ( $400-1250 \text{ cm}^{-1}$ ) with maxima at ( $450; 452.92; 493.56; 550.50; 597.93; 630, 72; 873.75; 966.34; 1089.78 \text{ cm}^{-1}$ ). Absorption at wave numbers  $1200 - 1000 \text{ cm}^{-1}$  characterize the presence of  $Si - O - Si$  and  $O - Si - O$  bonds caused by deformation and valence vibrations of silicon-oxygen skeleton tetrahedra in silicate minerals. The appearance of absorption bands at  $630-873 \text{ cm}^{-1}$  is due to  $Si - O - Si$  vibrations of rings from  $SiO_2$ -tetrahedra. Deformation vibrations of  $AlO_4$ -tetrahedra in the IR absorption spectra are identified at  $550-450 \text{ cm}^{-1}$ . The presence of calcium carbonate in the test sample is evidenced by the appeared effect at  $873 \text{ cm}^{-1}$

and a fairly deep absorption band at  $1419\text{ cm}^{-1}$ , which confirms the data of X-ray phase analysis that part of the  $\text{Ca}(\text{OH})_2$  leached into the liquid phase carbonized to form  $\text{CaCO}_3$ .

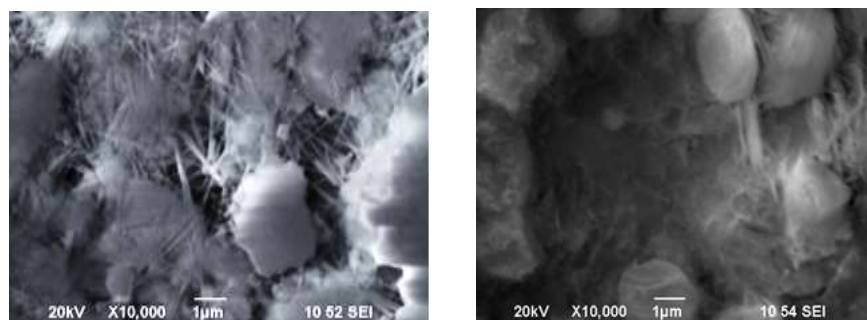
After 7 days of hardening, the pattern of the IR spectra somewhat changes towards a decrease in the depth of absorption of effects at all values of the wave numbers, which indicates a deepening of the process of hydrolysis and hydration of the PPC-40 components and recrystallization of hydrated products with the transition from one form to another. This is also indicated by the shift of the frequencies of the effects in the IR spectra in the range of wave numbers  $3700\text{--}1600\text{ cm}^{-1}$  towards their higher values, which is characterized by the structure of OH groups in different hydrated compounds. A 28-days hardened PPC stone exhibits an absorption band at the wavenumber at  $1471\text{ cm}^{-1}$ . The appearance of two more absorption bands with maxima at  $658$  and  $775\text{ cm}^{-1}$  was also noted, indicating the presence of coordinatively bound water, i.e. about the octahedral arrangement of water molecules around the aluminum atom and the existence of hydrogen bridge bonds with  $\text{SO}_3$  tetrahedral groups, probably in the structure of calcium hydrosulfoaluminates. With prolonged hardening of samples up to 3 months, the composition of neoplasms almost does not change, as indicated by the appearance of a wide absorption band at  $3700\text{--}3600\text{ cm}^{-1}$ , the depth of which is identical with the spectra of samples of 28-day hardening. At the same time, by this period, in the IR spectra, the absorption bands of the spectra with maxima at  $1417$  and  $1471\text{ cm}^{-1}$ , which are present in the IR spectra of samples of 28 day hardening age, merge into one absorption band with a maximum of  $1471\text{ cm}^{-1}$ , which indicates the stabilization of the composition and structure of hydrate products.

The relief of the surface of its fresh cleavage after 1 day of hardening is represented by a mixture of initial clinker grains, ash and slag and their hydration products – gels of submicrocrystals of silicates and calcium aluminates (Fig. 4). By the 3rd day, in addition to needle-like crystals, hydroaluminates also appear, having a cubic ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ ), hexagonal ( $3\text{--}4\text{ CaO}\cdot\text{Al}_2\text{O}_3\cdot 12\text{--}14\text{H}_2\text{O}$ ) and lamellar ( $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$ ) form. The presence of crystals that do not have a clear configuration, apparently related to hydrogarnets of variable composition, formed due to the introduction of silicon into the structure of calcium hydroaluminates, was also noted.



**Figure 4.** Relief of the surface of the chip PPC-D40 of the daily age of hardening

In the intergranular spaces and in the pores, the intensive growth of acicular crystals continues, which, orienting in different directions, create a network structure and, filling the free spaces, begin to compact and strengthen the hardening composite (Figure 5a).



**Figure 5.** PPC-D40 cleavage surface relief after 3 days of hardening



Crystalline formations growing from grains of cement particles, with their free growth, form fan-shaped aggregates, which will provide stronger resistance to external load and contribute to the formation of high strength of the cement composite. By the 28th day,  $C_2S$  undergoes intensive hydration, the surface of its rounded grains is covered with a film of calcium hydrosilicate gel, consisting of submicrocrystalline fibrous and prismatic formations that penetrate the main reaction mass and gluing the previously formed crystalline hydrates and non-hydrated clinker grains with each other, contribute to reduction of the pore size and monolithic structure of the artificial conglomerate based on PPC-D40 (Fig. 5b), which contributes to the achievement of high strength of the composite up to grade 500 and ensures its durability.

## CONCLUSION

Comprehensive studies of the processes of hydration and genetic formation of hydrate products formed during the hardening of highly filled pozzolanic cements revealed the features of the interaction of clinker minerals and ash and slag additives of dry selection with the establishment of a correlation relationship “composition–structure–property”. Due to the slow leaching of  $Ca^{2+}$  ions into the liquid phase and its gradual removal from the liquid phase, the process of hydration of highly filled PPC proceeds stepwise with the gradual crystallization of hydrate neoplasms, randomly growing and filling the macropores of crystals, which, by reducing their size, compact the forming composite, which, despite a decrease in the proportion of highly active clinker up to 40%, 28-day hardening acquires hydraulic activity, one grade higher than the strength index of the control cement PC400-D0.

## GRATITUDE

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