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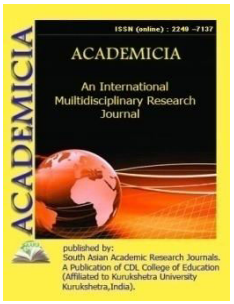


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# RESEARCH OF THE PROCESSES OF STRUCTURE FORMATION DURING HARDENING OF PORTLAND CEMENT WITH HIGH-SILICA ADDITIVES

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## ABSTRACT

*The paper presents the results of studies to determine the influence of local high-silica additives on hydration, structure formation and the formation of physico-mechanical properties of artificial conglomerate during hardening of Portland cement.*

**KEYWORDS:** *Portland Cement Clinker, Additive In Cement, Degree Of Hydration, Phase Composition, Structure, Cement Stone, Durability*

## INTRODUCTION

To better meet the needs of the building complex and fill the markets with high-quality building materials, the Concept of the Association "Uzpromstroymaterialy" provides for the rational, efficient use of the local raw material base of mineral resources, the development and implementation of new technologies that significantly reduce energy consumption in industrial production, and the implementation of economically sound policies 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 the use of local natural and technogenic raw materials. One of the energy-efficient areas of increasing the output of many types of cementitious materials, including cement, is the integrated use of active mineral additives of natural and man-made origin. In this regard, the search for simple in technological design and relatively cheap ways to increase the efficiency of composite binders and concrete based on them, each component of which plays a role in hydration and structure formation, is an urgent task [3]. Replacing a part of clinker in cement with a mineral additive contributes to a more rational consumption of natural resources, an increase in production volume, and also reduces production costs while maintaining high hydraulic activity of cement [4].

## FORMULATION OF THE PROBLEM

Factors determining the nature and speed of chemical reactions occurring in the system “ground clinker - active mineral additive gypsum - water", as well as the reasons for the greater or lesser reactivity of individual silica compounds in pozzolanic additives have not been studied sufficiently. Therefore, in each specific case, when a new type of active mineral additive, put forward as pozzolanic, is used, it is necessary to conduct a study to determine its suitability as an additive in cement and to study its effect on the physicomechanical properties of Portland cement. In this regard, the purpose of the research was to determine the hydraulic activity of local gangbang rocks, their influence on the strength indicators of Portland cement and the establishment of their applicability to “Kizilkumcement” JSC.

## OBJECTS OF RESEARCH

The objects of study were the flaky rocks of the “Chukursay” section of the “Ziaetdin-3” deposit in the Pakhtachi district of the Samarkand region and Portland cement with its additive. The Portland cement clinker of “Kizilkumcement” JSC and the gypsum stone of the Bukhara deposit were used as a matrix for producing additional Portland cement.

### Research Methodology

The chemical composition of the components is determined in accordance with GOST 5382-91 “Cements and materials of cement production. Chemical analysis methods. " The suitability of the flocking rock as an additive in cement is determined by its ability to absorb lime according to the Chapel method and by the value of the Student criterion in accordance with the method GOST 25094-94 “Active mineral additives for cements. Test Methods. " Physico-mechanical properties of Portland cement 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 cement with flocking rocks 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 HKL Basic polycrystalline samples.

## RESULTS AND DISCUSSION

In order to determine the possibility of using opoka-like rocks of the “Chukursay” section of the “Ziaetdin-3” deposit as an active mineral additive in cement, studies were conducted to determine their chemical and mineralogical composition, chemical and hydraulic activity. The

chemical composition of the flask rock of the "Chukursay" site and other components used as objects of study are shown in Table 1.

**TABLE 1 THE CHEMICAL COMPOSITIONS OF THE STARTING COMPONENTS**

| Name of material | The content of the mass fraction of oxides, % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | п.п.п | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $R_2O$ | Other |
| Portland cement clinker | 0,42 | 21,42 | 4,90 | 3,87 | 63,26 | 2,84 | 0,36 | - | 2,93 |
| Gypsum stone | at $400^0$C 19,57 | 1,59 | 0,49 | сл. | 31,45 | 0,49 | 44,00 | - | 2,41 |
| Flocking breed | 1,59 | 80,6 | 9,59 | 1,59 | 0,27 | 0.80 | 0,76 | 2,04 | 2,78 |

According to table 1, the chemical composition of the studied rock is represented by the predominant content of $SiO_2$ (80.6%) and $A1_2O_3$ (9.57%) with $Fe_2O_3$ impurities in the amount of 1.59%; CaO – 1.59%; MgO – 0.80%; $SO_3$-0.76, i.e. its composition in terms of oxide content is in the range ($SiO_2$ 59.3–80.8%, $A1_2O_3$ 7.2–16.5%), typical for clay flasks [5]. Therefore, according to the content of basic oxides, the rock of the "Chukursay" section of the Pakhtachi district of the Samarkand region is classified as a medium-clay flask with sufficient pozzolanic ability. The chemical activity of the gangue rock for lime absorption is 130 mg / g, and the hydraulic activity for compression according to the value of Student's t-test (t) is 13.88, which is more than its regulated value of 2.07 according to O'z DSt 901-98 "Additives for cements . Active mineral additives and additives are fillers. Technical conditions. " Based on the data obtained, it was concluded that the flaky rock of the Chukursay site meets the requirements of regulatory documents and can be used as an active mineral additive in cement.

To study the influence of the studied opokovate rocks on the physicomechanical properties of Portland cement, joint grinding (55-85) % of clinker, (10-40) % of the opokovoid rock in the presence of 5% gypsum stone was carried out. At the same time, it was found that when "flinker + gypsum" (10-20%) is introduced into the batch, the grinding process proceeds the same way as when grinding cement without additives: fineness of grinding, determined by the residue on sieve No. 008 of cements with and without flask amounted to 10-12%. The water-cement ratio of the normal density test (NDT) of experimental cements with the addition of flocking rock, depending on its content in cement, is (0.69-8.4) % higher than the water requirements of control cement ПЦ-Д0, which is associated with a higher content in them mass fraction of clay mineral oxides ($SiO_2$, $A1_2O_3$, $Fe_2O_3$) than in the ПЦ-Д0 cement. Depending on the content of the additive, the start of setting of the experimental cements is within 3 hours 20 minutes - 5 hours 45 minutes, end - 5 hours 10 minutes. - 6 hours and 45 minutes, and the larger the amount of entrained rock introduced, the later the onset and the end of the setting of the cement dough: experimental Portland cement containing (25-40) % of the additive have somewhat slower setting time compared to the control cement PC-Д0. This is explained by the fact that, with an increase in the content of the additive in cement, its clay part also increases, which quickly softens in water and envelops cement particles, slowing down the hydration and hydrolysis of clinker minerals, inhibiting the process of calcium ion release and transition into the liquid phase, which lengthens the setting time cement paste. Since, during the interaction of cements with

water, the reactions of hydration of aluminate and aluminoferrite structures occur precisely at the initial time and determine the onset of setting of cements, and the time of beginning of interaction with water of highly basic calcium silicates is the end of setting. Despite the slowed down process of hydration, the setting time of all experienced Portland cement meets the requirements of GOST 22266-94.

It is known that the operational properties of cements are determined by the structure formed in the cement stone, which is the result of physicochemical features of the processes of structure formation in the cement-water system [6]. The main factor is the implementation of directional structure formation during hardening of cements, control of the formation of the structure of cement stone at different stages of its hardening, which ensures high physic mechanical and high performance properties of cement stone and products with desired properties based on it.

It is possible to obtain effective materials and durable products by opening significant reserves in managing the operational properties of concrete and other cement-based materials by purposefully forming the structure and properties of cement stone during its hardening, including by introducing mineral and chemical additives. The identification of patterns that allow one to control the processes of structure formation and optimize the composition and properties of composites using natural and technogenic raw materials requires extensive research on selected objects [7]. 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 particularly sensitive to the conditions of hardening and formation of cement stone. Therefore, various additives are proposed to ensure the rapid formation of primary hydrated phases, the subsequent physicomechanical properties of cement stone and concrete depend on their composition. Consequently, one of the ways to increase the activity and strength of cement stone is the targeted formation of its properties by introducing additives that affect the hydration, structure formation and hardening of cement, which increase the early strength of the cement stone due to the rapid removal of $Ca^{2+}$ ions from the liquid phase with crystallization of hydrosulfoaluminates calcium, the crystals of which reinforce the cement stone, and its brand strength and durability - due to the hydrosilicate formed in the later periods calcium.

Proceeding from this, in order to elucidate the correlation dependence “composition - structure - property”, we studied the “evolutionary route” of hardening with the formation of the structure of cements with an opokovite rock. The results of studies on the genesis of the formation of the microstructure of cement stone are shown in Figures 5 and 6.

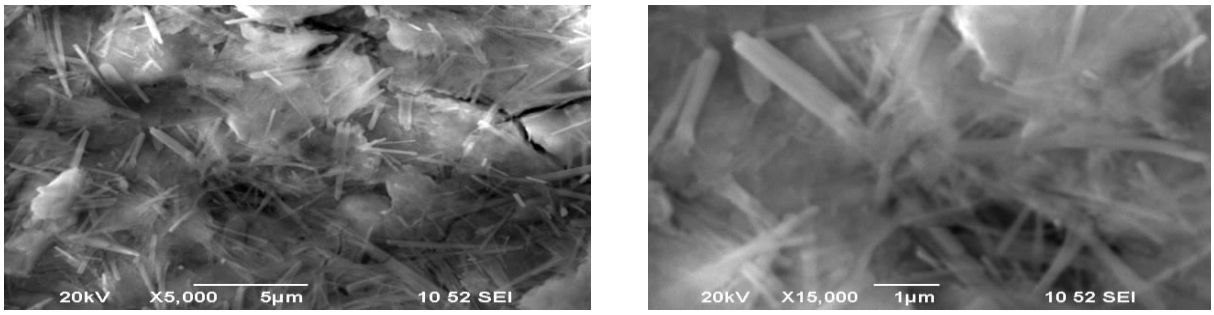


**Figure 5 - Electronic micrographs from the surface of a cleaved cement stone, hardened for 1 day.**

According to 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 randomly spaced 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 involved air pores of Portland cement with flaky rocks: the figure clearly shows that the surface of cement particles located in the pores and the side walls of the pores are covered with needle crystals (Figure 6).

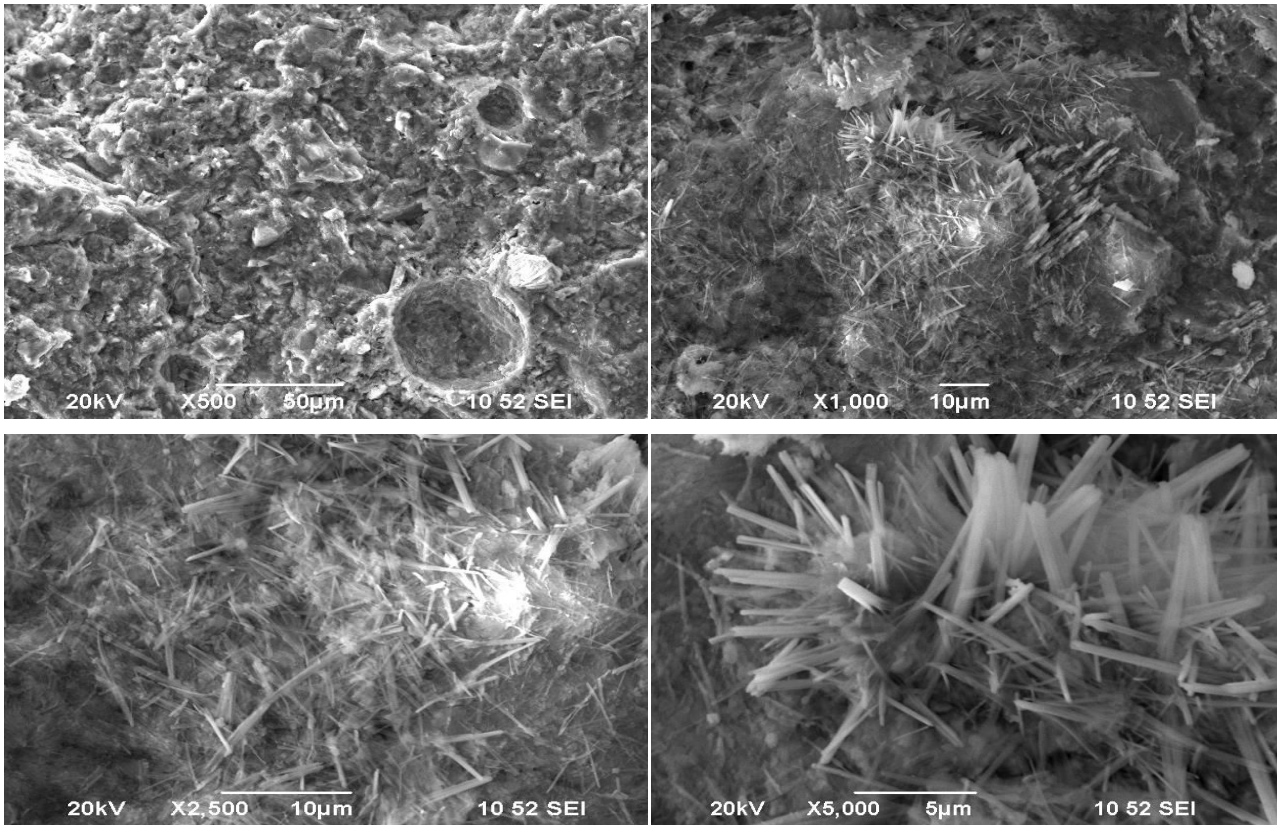


**Figure 6 - Crystals and druses of calcium hydrosulfoaluminates in the pores of a 3-day-old cement stone**

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 grow and grow in size, form crystal aggregates in the form of drusen, and they gradually fill the pores and microcracks of the cement stone. By the 7th day, the process of growth of crystals of neoplasms is accelerated both on the surface layers and in the pore spaces (Figure 7a). The number and size of plate crystals, related to hydrated products of calcium silicates, increase and, narrowing the pore space in the hydrating system "cement-water", contribute to the hardening of cement stone. By the 28-day hardening period, the cleaved surface of the cement stone is a rough plane with a low porosity created due to intergrowth of crystalline products, a sufficiently high degree of pore filling and monolithic filling (Figure 7b). In accordance with Figure 8, the surface of the cement-based stone chip with 15% of the opokovite rock, hardened 90 days in water, by this time crystalline products of various shapes and sizes coexist in the cement stone, which completely

fill the pores and voids of the cement stone with a block structure . On the cleaved surface, areas are noted where the pores are filled with densely packed lamellar and randomly arranged fibrous crystals, sometimes bundled with whiskers of calcium hydrosilicates.

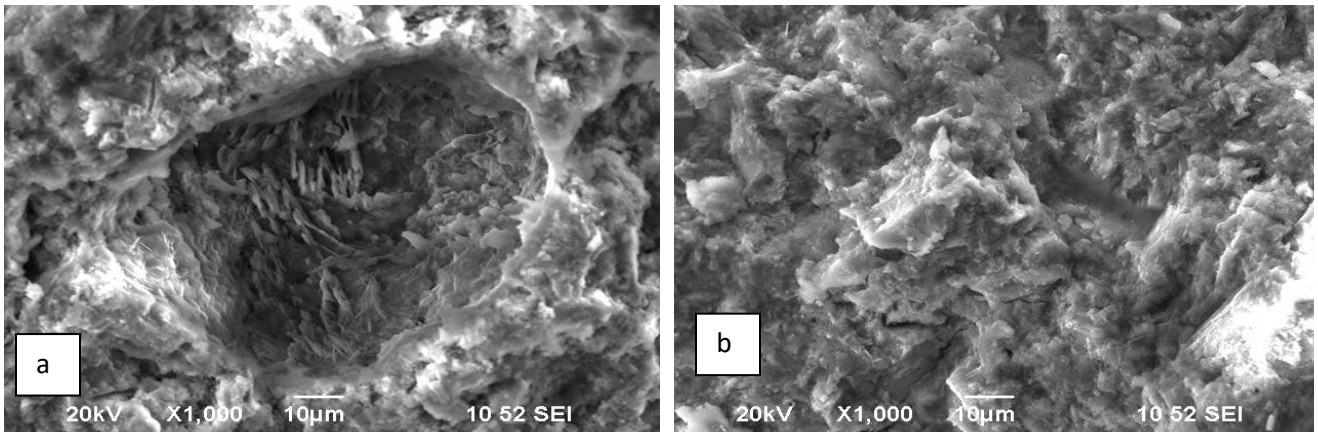


**Figure 7 - Cleaved surfaces of Portland cement with the addition of 15% of the high-silica additives solidified for 7 (a) and 28 (b) days in water**

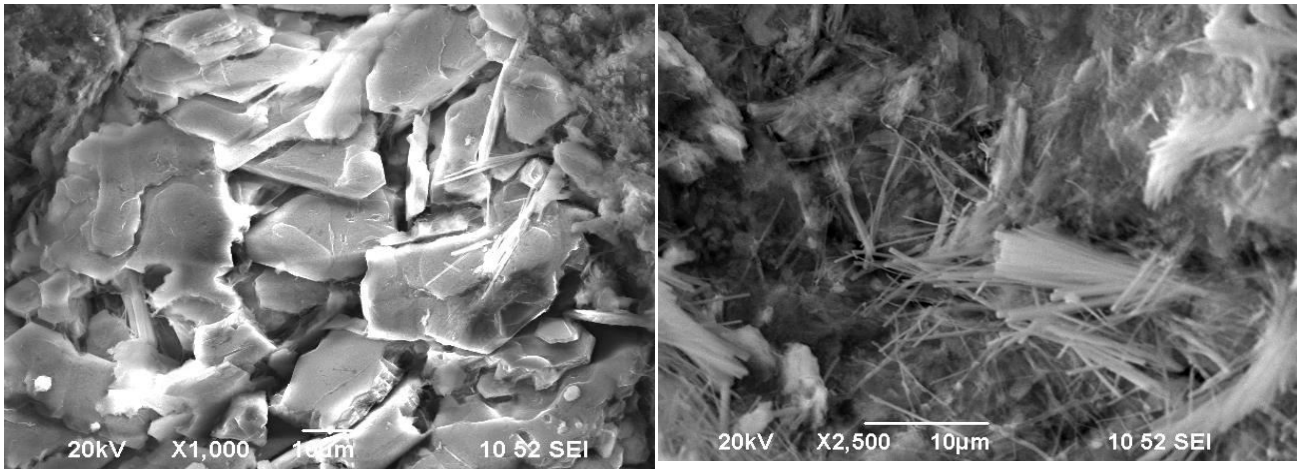


**Figure 8 - Electronic micrographs of stone based on Portland cement with the addition of high-silica additives after 3 months of hardening in water**

Thus, the positive influence of local ganglings on the hydration and structure formation during hardening of Portland cement, which is manifested in the intensification of the hydrolysis of clinker minerals, the accelerated binding of Ca (OH) 2, the accelerated crystallization of neoplasm products filling the pores and microcracks of cement stone, and thereby , contributing to the formation of artificial conglomerate, the strength indicators of which are at the level of non-additive Portland cement.

To organize the production of Portland cement with flocking rocks of the “Chukursay” site with a view to their subsequent use for the production of a wide range of dry building mixes,

"Kizilkumcement" JSC developed and registered with "Uzstandart" Agency TS No. 00295455-48: 2018 "Dry building mixes based on clinker" - composite binder. Technical conditions.

## CONCLUSION

The favorable chemical and mineralogical composition of the gangue rocks contributes to the creation of optimal conditions for the physicochemical transformation in the system "ground clinker - two-water gypsum - gangue rock - water", which is manifested in the intensification of the hydrolysis of clinker minerals and the intensive crystallization of neoplasms filling pores and microcracks of cement stone , and thereby ensures the synthesis of the optimal structure of artificial conglomerate.

Unlike traditional non-additive Portland cement, in Portland cement containing 15% of the opokovite rock, the process of hydrolysis of tricalcium silicate begins at an earlier hardening time. As a result of reducing the size of macropores and total porosity by filling them with crystals and crystal aggregates of needle crystals of ettringite, fibrous and lamellar crystals of calcium hydrosilicates, a cement stone is formed, the strength of which is at the level of non-additive Portland cement.

Based on the research results, the Organization Standard Ts 00295455-48: 2018 "Dry construction mixes on a clinker - composite binder" was developed for "Kizilkumcement" JSC, where dry construction mixes containing flocking rocks of the "Chukursay" section are currently produced in a wide range "Ziaetdin-3" deposits.

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