Research Of the Influence of Opoka-Like Rocks on The Physical and Mechanical Properties of Portland Cement

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ABSTRACT

This article is devoted to the study of technological properties of opoka-like rocks of Uzbekistan and their influence on physical and mechanical indices of Portland cement of JSC "Kizilkumcement."

Keywords: Additive for cement, pozzolanic additives, opoka-like rock, clinker, physical-chemical properties, criterion incremental.

Introduction

The research and comparative analysis of the dynamics of the volume of construction and production of construction materials showed a significant lag in the production of the most demanded cement products on the market. For example, with the total growth of construction works by 116% in 2017-2018, the growth rate of cement production for 2017-2018 amounted to only 108.7%, which led to market imbalances, import increases and price increases. In order to better meet the needs of the construction complex and fill the markets with high-quality construction materials, the Concept of the Association "Uzpromstroymaterials" provides for rational, effective use of the local raw material base of mineral and raw materials resources, development and introduction of new technologies ensuring significant reduction of energy consumption in industrial production, implementation of economically sound import substitution policy. The concept also provides for the implementation of investment projects with the introduction of advanced innovative energy-efficient technologies, in particular, binding materials (high-grade and special types of cement, gypsum, lime) in all regions of the Republic. At the same time, as is known, the main consumers of TER, in particular gas, in the industry are cement and brick enterprises. Implementation of the Concept will allow to completely eliminate wet method lines by 2022 and bring the capacity of the dry method to 100% in the total capacity, which will be about 20 million tons. This measure will ensure relative gas savings in the amount of 35-40% per ton of cement from the current level of consumption [1].

One of the energy-efficient directions of increasing the volume of production of many types of binding materials is the complex use of

active mineral additives of natural and technogenic genesis. One of the ways to improve the quality of cement concrete with a high level of use of technogenic and natural raw materials is to switch to the production of new composite binders with the replacement of part of clinker with mineral additives, which significantly reduce the energy consumption of the production of construction materials of hydration hardening. In this regard, finding simple and relatively cheap ways to increase the efficiency of composite binders and concretes based on them, each component of which plays a role in hydration and structure formation processes, is a pressing task [2]. Replacement of part of clinker in cement with mineral additive contributes to more rational consumption of natural resources, as well as reduces production costs, while maintaining high hydraulic activity of cement [3]. Mineral additives differ from each other in structure, chemical-mineralogical composition and activity, i.e. ability in the presence of water to chemically react with calcium hydroxide at normal temperatures, forming compounds having binding properties. Generally, amorphous silica reacts much faster than crystalline silica, although it is very difficult to draw a clear line between hydraulic and non-hydraulic silica. Most pozzolanic materials contain a marked amount of impurities, and it is possible that other complex compounds containing alkali, iron and alumina are formed [4].

Putting up a problem.

Factors determining the nature and rate of chemical reactions occurring in the ground clinker-pozzolane additive-water system, as well as the reasons for the greater or lesser reactivity of individual silica compounds in pozzolane additives, are not yet known. Therefore, in each particular case where a new kind of additive, assumed to be pozzolanic, is used, it is necessary to carry out a study to determine the chemical activity and its effect on the physical and mechanical properties of Portland cement. In this regard, the purpose of the studies carried out below was to determine the hydraulic activity of local opoka - like rocks, their impact on the strength of Portland cement and to establish their applicability to Kizilkumcement JSC.

The scientific novelty of the research results lies in the scientific justification of the correspondence of the rocks of the Kizilkum region to the group of opes, their chemical activity and the possibility of use as additives for the production of pozzolanic Portland cements has been established, the relationship of the change in the physical and mechanical properties of cements from the type and amount of the introduced pozzolanic additive has been revealed.

The practical value of the research results lies in the fact that using local opococean rocks saves up to 20% of expensive high-temperature clinker, reduces cost, improves operational properties and expands the field of application of Portland cement.

Research facilities and methodology. The objects of the study were opoka - like rocks of the section "Chukursai" of the field "Ziaetdin-3" of Pakhtachinsky district of Samarkand region. For studying of their influence on physicomechanical properties of the portlandtsement as a matrix portlandcement's clinker of JSC Kizilkumtsement and a plaster stone of the Bukhara field is used. Chemical analysis was performed in accordance with the requirements of GOST 5382-91 "Cement and cement production materials. Chemical Analysis Methods. Rock activity was judged by its reactivity to absorb lime determined by the Chapel method at the Institute of Ion-Plasma and Laser Technologies of AS RUz [5] and by the value of the Student criterion according to the method GOST 25094-94 "Active mineral additives for cements. Test Methods. The phase structure of the studied breed was determined by the HRO-6199 diffractometer (Shimadzu, Japan). The thermal analysis was carried out on a derivatograph of the Paulik-Paulik-Erdey system with a speed of hails/mines and a hinge plate - 0.1 g. At sensitivity of galvanometers T-900, ТГ-200, DTA -1/10, DTG -1/10. Recording was carried out under atmospheric conditions with regular removal of the gas medium by means of a water jet pump. The holder was a platinum crucible with a diameter of 7 mm without a lid. AL_2O_3 was used as a reference.

Results and their discussion.

Opokas, these are light dense thin-porous rocks consisting mainly of the smallest (less than 0.005 mm) silica particles. Average density is 1100-1600 kg/m3, porosity reaches 55% [4]. Clay minerals are a constant component of the opoka. Typical or "normal" opoka are opoka containing 54-80% opal silica, 10-40% clay minerals and up to 10% sandstone particles [5]. It is known that during the hardening of Portland cement, by hydrolysis and hydration of clinker minerals, $Ca(OH)_2$ is released, which is bound to water-insoluble hydrate compounds the faster the cement stone is compacted and strengthened. Molding in the structure contains the active silicon dioxide capable in normal conditions to interact chemically with lime with formation of slightly soluble calcium hydrosilicates in water: $Ca(OH)_2+SiO_2+yH_2O \rightarrow xCaO \cdot SiO_2 \cdot (x+y)\ H_2O$, so they are used as mineral additives to cement.

In order to determine the possibility of using the "Chukursai" section of the "Ziaetdin-3" deposit as a pozzolanic additive to cement, studies were carried out to determine their chemical and mineralogical composition, structural structure, chemical and hydraulic activity. Visual examination showed that the rock under study was a sufficiently hard milk-coloured material with a creamy tint. Small pieces of rock warm up between the fingers, feel fat and leave white spots. With water reacts quickly and immediately smears to form clay mass.

The chemical composition of the "Chukursai" section and other components used as subjects of the study are shown in Table 1.

Table 1. Chemical compositions of the starting components

Material Name	Content of mass fraction of oxides,%								
	loss on ignition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	others
PC clinker	0,42	21,42	4,90	3,87	63,26	2,84	0,36	-	2,93
Gypsum Stone	At 400^0C 19,57	1,59	0,49	сл.	31,45	0,49	44,00	-	2,41
Opoka - like rock	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 investigated rock is represented by an advantageous content of SiO2 (80.6%) and $A1_2O_3$ (9.57%) with Fe_2O_3 impurities in the amount of 1.59%; SAO-1.59%; MgO–0,80%; SO_3-0,76, i.e. its oxide content composition is within the reference data typical of the opoka shown in Table 1.

Comparison of the obtained data with chemical compositions of known supports of various deposits given in Table 3 showed that the content of the main oxides of the mountain rock of the "Chukurai" section of the Pakhtachinsky district of Samarkand region is classified as medium-clay opoka with sufficient pozzolanic capacity.

In order to identify the chemical-mineralogical composition of the analyzed opoka - like rock and to clarify its belonging to the class of opoka, X-ray phase analysis was carried out, and the obtained data were compared with diffractograms of opos of Volsky, Shevchenko and Stepan-Razinsky deposits. According to the data of Fig.1, the set of reflexes on diffract grams of supports of the specified deposits shows their polymineral composition [3]. The most intense and pronounced in all samples are quartz peaks, the main diagnostic lines of which are lines at d/n = (0.334; 0,424; 0,245; 0,228; 0,224; 0,212) nm.

Table 2. Classification of opium rocks, depending on the content of clay minerals and their average chemical composition

№	Breed Name	Maintenance of a clay component, %
1	Small-clay opoka	to 20
2	Medium-clay opoka	20-35
3	Clay opoka	35-50
4	Silicon clay	more 50

Breed	loss on ignition	Content of oxides, masses. %							
		SiO_2	Al_2O_3	Fe_2O_3 +FeO	CaO	MgO	$SO_{3gen.}$	K_2O	Na_2O
Clay molding	2,7-17,6	59,3-80,8	7,2-16,5	1,0-7,6	0,90-3,00	0,30-4,6	0,01-0,65	1,26-3,08	0,90-1,79

On the X-ray pattern of the "Chukursai" section of the "Ziaetdin-3" deposit, the most intense and pronounced are quartz peaks with the main diagnostic lines at d/n = 0, 334, 0.424, 0.224, 0.245, 0.228, 0.212 nm (Fig. 2Aidd). According to [5, 6], the presence of halo (smooth background increase) in the region of angles 20-250 indicates the presence of amorphous silica in a large amount, which is confirmed by our studies, and it is known that the higher the halo, the higher the degree of cleavage of opal silica. The presence of small reflexes at 10-18°, corresponding to peaks 0.501 and 0.998 nm, indicates the presence of hydrolumen in the test rock. Low intensity $KA1_3Si_3O_{10}$ $(OH)_2$ muscovite reflexes are also observed. The X-ray pattern of the sample shows a small peak at 35° characteristic of magnetite and at 36° for calcium carbonate. Mineralogical composition of rock is represented mainly by amorphous silica and clay substance with small impurities of wollastonite, albite, muscovite, magnetite. In general, data of X-ray phase analysis and their comparison with diffractograms of opos of Volsky, Shevchenko and Stepan-Razinsky deposits reveal close similarity of their mineralogical composition, which makes it possible to classify the investigated rock of the site "Chukursay" as opoka - like rock.

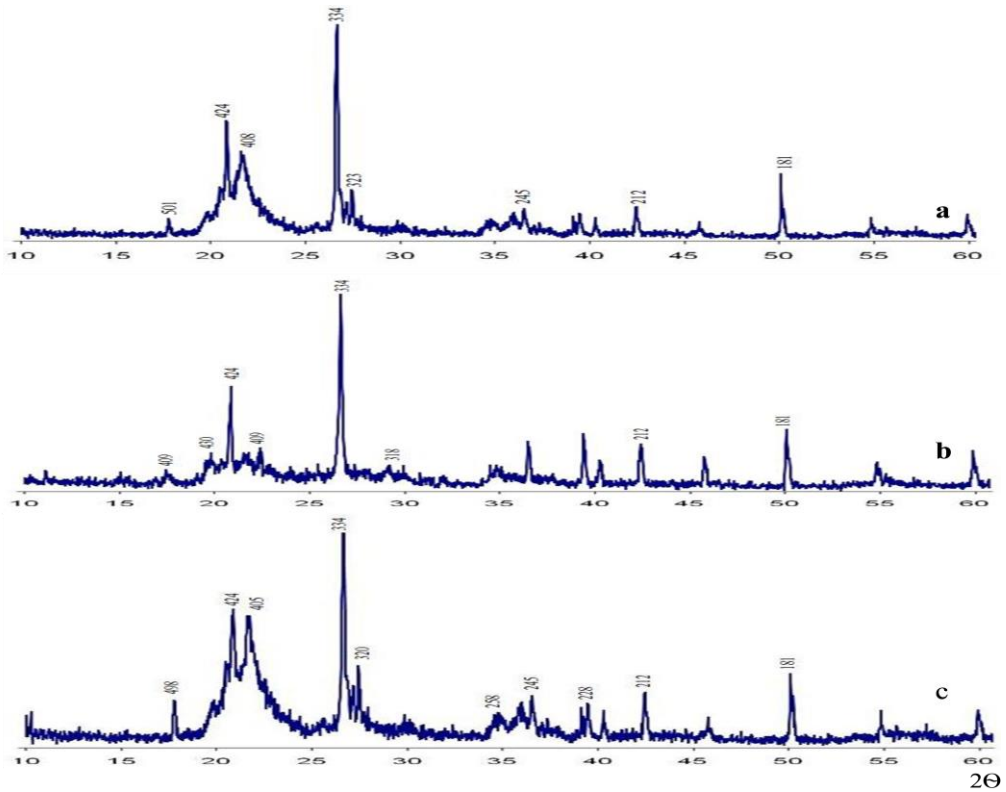


Figure 1. X-rays of opos of Volsky (a), Shevchenko (b) and Stepan-Razinsky (c) deposits of Ukraine

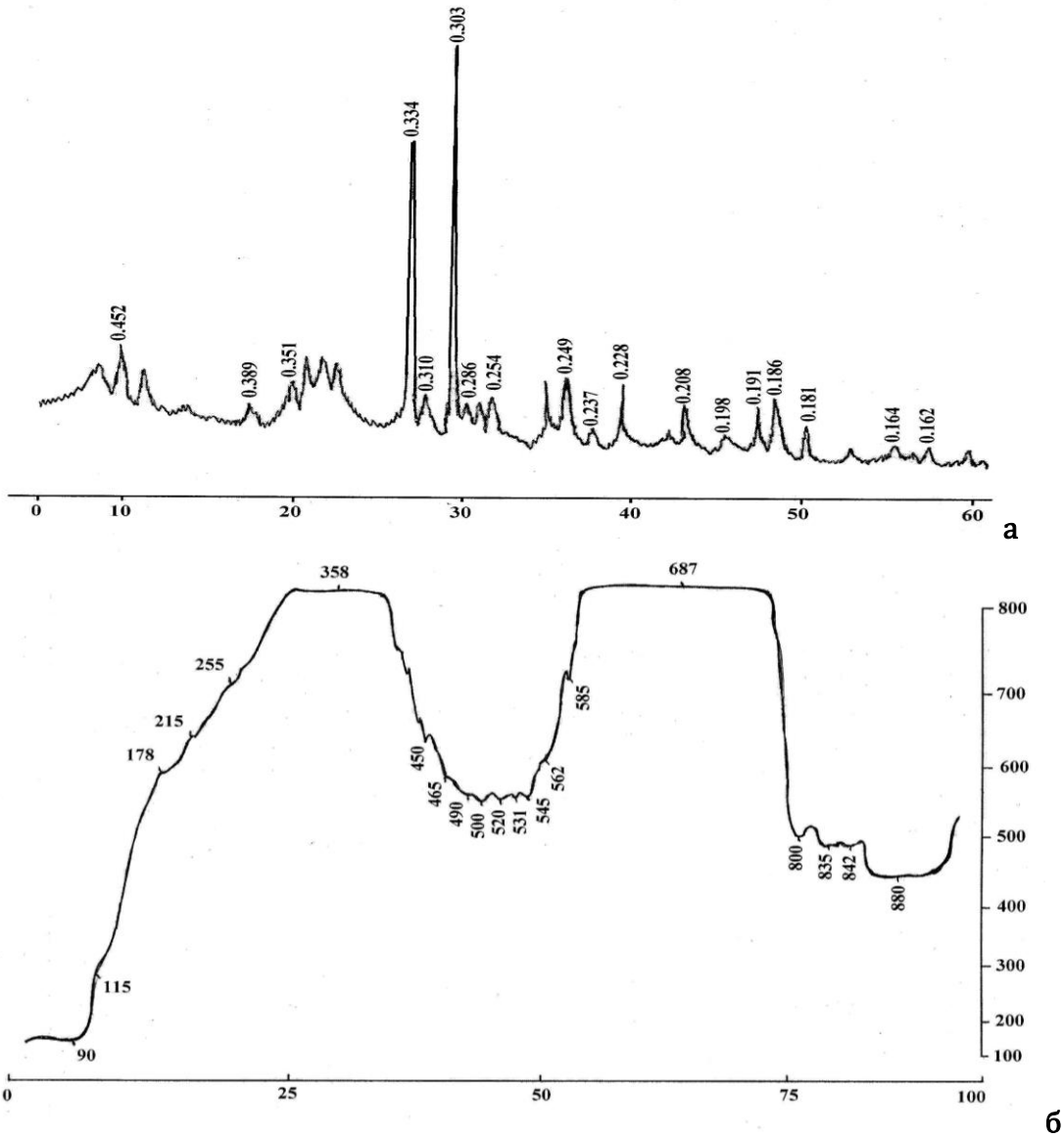


Figure 2. X-ray pattern (a) and thermal curves (b) of the "Chukursai" section of the "Ziaetdin-3" deposit

The thermal curves of the opoka - like rock (Figure 2b) show a small endothermic stop at 50-100 ° C with a maximum at 90 ° C, the appearance of which is related to the removal of hygroscopic moisture from the rock. Appearance of multiple endoeffects in the range of 170-260 ° C and 450-600 ° C dehydration of various modifications of aluminosilicate minerals in rock. The appearance of endothermic stops in the temperature range 800-850oC with maxima at 800, 835, 842 and 880oC is related to the complete removal of water from minerals and the beginning of destruction of their structure.

According to electron microscopy, the relief of the scum of the opoca like rocks is a rough surface with a microglobular structure consisting of particles of different sizes and various shapes, among which short prismatic crystals prevail and less often tablitic crystals, their gaps are filled with dense grain mass, and on their surface there are fleshy formations belonging to the hydrolumen

In order to determine the possibility of the analysed opoka - rock as an additive to cement, its chemical activity on lime absorption, which amounted to 130 mg/g, was determined. Due to that according to O 'z DSt 901-98 "Additives for cements. Active mineral additives and filler additives. Specifications, "materials can be used as additives for cements, if their efficiency is confirmed by the

results of tests of their hydraulic activity according to the Student 's criterion, the suitability of the opoka - like rock as an additive for hydraulic activity for compression was also determined. At the same time, the Student 's criterion value for the studied rock was $t = 13.88 > 2.07$. Consequently, the pock rock of the Chukursai site has passed the strength activity test, which means that it can be used as an active mineral additive in cement.

In order to study the effect of the analysed opoka - like rocks on the physical and mechanical properties of Portland cement, combined grinding of (55-85)% clinker, (10-40)% opocean rock in the presence of 5% gypsum stone was carried out. At the same time it has been found that when "clinker gypsum" (10-20%) is added to the mixture, the grinding process proceeds as well as when grinding non-packed cement: the fineness of grinding, determined by the residue on sieve No. 008 of cement with and without addition of opoka, amounted to 10-12%. The water-cement ratio of the normal-density dough (TNG) of the test cements with the addition of the opium-like rock, depending on its content in the cement, exceeds by (0.69-8.4)% the TNG of the control cement of the PC-D0, which is related to the higher content in them of the mass fraction of oxides of clay minerals (SiO_2, Al_2O_3, Fe_2O_3) than in the cement of the PC-D 0. Depending on the content of the additive, the start of setting of the test cements is within the range of 3h 20 min - 5h 45 min, the end - 5h 10 min - 6h 45 min, and the greater the amount of the introduced opoka - like rock, the later the start and end of setting of the cement paste comes: Experimental Portland cements containing (25-40)% additives have slightly delayed PC-D0 than the setting time of the control cement. This is because, as the content of the additive in the cement increases, the clay portion of the additive also increases, which rapidly drifts in the water and envelopes the cement particles, slowing the hydration and hydrolysis of the clinker minerals, inhibiting the extraction and transition of calcium ions to the liquid phase, which extends the setting period of the cement slurry. Since at interaction of cements with water hydration reactions of aluminate and alumoferritic structures take place in the initial time and start of cement setting is determined, and time of interaction with water of high-basic calcium silicates - end of setting. Despite the slow progress of the hydration process, the setting times of all the test Portland seeds comply with the requirements of GOST 22266-94.

Additional cements at 28-day age of normal hardening have compression strength within the limits of (40.6-44.2) MPa, which characterizes them as cements of general construction grade 400 as per GOST 10178-85. At the same time, the activity of additional cements with 10% of opacea is 43.0 MPa, with 15% - 44.2 MPa, and with 20% - 40.6% MPa, which is higher than the strength of bottomless cement having a strength of 40.2 MPa (Table 5). It should be noted that the clinker must be of high quality and contain at least 55% of three-calcium C_3S silicate in order to obtain the cement with the support.

Table 3. Change of physical and mechanical properties of additional Portland cement depending on the content of opoka - like rocks

Cement symbol	Solution V/Ts 1:3	Cone fusion, mm	Bending and compression strength, MPa				Grade of cement as per LP
			7d		28d		
			Rиз	Rсж	Rиз	Rсж	
PC - D0	0,39	113	5,27	26,1	6,45	42,8	400
PCO - D 10	0,39	113	5,20	27,9	6,58	43,8	400
PCO - D 15	0,39	113	4,88	27,0	7,03	42,3	400
PCO - D 20	0,44	110	5,20	24,3	6,35	40,0	400

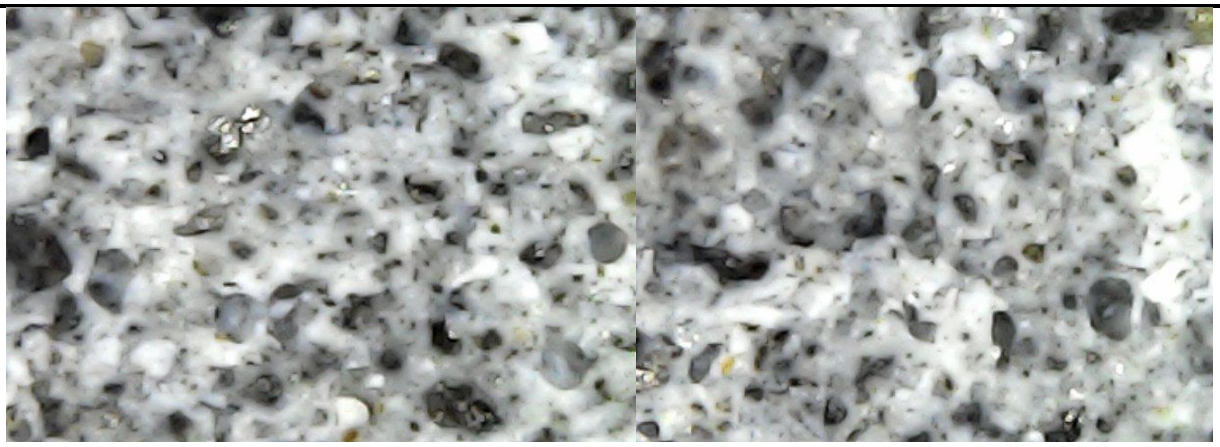
PPCO - D 25	0,50	110	5,82	21,6	4,15	26,0	not corres.
PPCO - D 30	0,52	110	2,81	18,1	3,97	24,9	not corres
PPCO - D 40	0,56	107	2,25	11,0	3,15	16,7	not corres

According to the requirements of GOST 22266-94, the content of additives in pozzolanic Portland cement (as a percentage of cement weight) should be 20 and not more than 40%. However, introduction of additive of the studied opoka – like rock breed in number of 25%, 30%, 40% led to sharp decrease in strength indicators of skilled portlandtsement of PPCO - D 25, PPCO - D 30, PPCO - D40 which values were respectively: 26.0 MRA, 24.9 MRA, 16.7 MRA that does not conform to requirements imposed to strength at compression the pozzolanic of the portlandtsement which are released in accordance with GOST 2266-94 (tab. 5). Strength indices of the experimental Portland cement PCO - D 10with the addition of 10% of the opoka - like rock at the age of 7 and 28 days of hardening slightly exceed those 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 10% are cements of general construction purpose. Therefore, a pilot Portland cement containing an additive of opoka - like rock in an amount of 10% and having a compressive strength of 42.9 MPa at the age of 28 days is characterized by a mark 400 with the symbol PC 400-D20.

According to the bending and compressive strength at the age of 28 days, the test cements containing 15 to 20% of the additive of the opium rock correspond to the brand "400" and, according to the requirements of GOST 2266-94, are classified as sulphate-resistant Portland cements with mineral additives with the symbol CCPC 400-D20.

According to picture 4, when hardening the cements PC 400-D0 and PC 400-D20 with 15% of the opoka - like rock within 28 days, almost the same structure is formed, which justifies the possibility of replacing up to 20% of the high-temperature clinker component in the cement with an affordable and cheap local additive – opoka -like rock without deterioration of the physical and mechanical properties of the bottomless portland cement. The use of this additive in cement is based on its high adsorption capacity to absorb lime released by the hardening of Portland cement. The rapid absorption of lime by an additive with a developed structure reduces the concentration of calcium ions in the liquid phase, as a result, the hydrolysis process of the minerals of Portland cement clinker is accelerated and the chemical reaction between them and the opium rock is intensified according to the principle of acid-basic interaction, which leads to an increase in the degree of compaction and strengthening of the formed cement composite.

In order to organize the production of Portland cements with opoka - like rocks of the Chukursay site for the purpose of their subsequent use for the production of dry construction mixtures of a wide range at Kizilkumcement JSC has been developed and registered with the Agency "Uzstandart" Ts № 00295455-48:2018 "Dry construction mixtures based on clinker-composite binder.



Picture: 4 Structure of stones on the basis of PC 400-D0 and PC 400-D20 with 15% opoca like rock (b), which have been solidified for 28 days in water

Conclusion

Reseachers of physical-chemical and technological properties of sedimentary rock of the "Chukursai" section of the Pakhtachinsky district of Samarkand region made it possible to assign it to a group of clay opoka, the use of which as an additive to cement is based on their high adsorption ability to absorb lime, which is released during hardening of Portland cement. Due to rapid absorption of lime by rock with advanced structure, the process of hydrolysis of Portland cement minerals and their chemical interaction with the additive on the principle of acid-basic interaction is accelerated, which leads to increased degree of compaction and structural strengthening of the formed cement composite. A sufficiently high chemical (130 mg/g CaO) and hydraulic activity of the opoka - like rock according to the value of the Student's criterion (t = 13.88) made it possible to recommend it for use as an active mineral additive in the production of general construction and pozzolanic Portland cement.

The hydraulic activity of Portland cements containing (10-20) % of the opoka - like rocks of the Chukursai site is provided by the brand PC 400-D20. For production of sulphate-resistant cements with opoka - like rock, clinker of normalized mineralogical composition with C3A content not more than 5% shall be used. On the basis of the developed Standard of organization Ts 00295455-48:2018 "Dry construction mixtures on clinker - composite binder," at present "Kizilkumcement" JSC produces dry construction mixtures in a wide range, containing opoka - like rocks of the "Chukursai" section of the "Ziaetdin-3" field.

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