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The utilization efficiency of natural alumosilicates in composite binders

Kozhukhova Natalia Ivanovna[1a], Fomina Ekaterina Victorovna[2b], Zhernovsky Igor Vladimirovich[3c], Strokova Valeria Valerievna[4d], Chizhov Rostislav Valerievich[5e]

[1,2,3,4,5]Belgorod State Technological University named after V.G. Shoukhov, Russia, Belgorod, Kostukov St., 46
[a]kozhuhovanata@yandex.ru, [b]fomina.katerina@mail.ru, [c]zhernovsky.igor@mail.ru, [d]vvstrokova@gmail.com, [e]rastis-lav@yandex.ru

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Abstract. The opportunity of application of natural aluminosilicate – perlite – as reactive mineral admixture and as individual binding component when production of construction materials.

Introduction

For last decades a very intensive development of low-height construction determines a continuous expansion of the spectrum of construction materials and development of new materials. Cellular concrete based on different type of binders has a particular importance among them.

The most popular among them became cement-based cellular concrete. However, it should be noted, that a clinker production is of complex and energy demanding process, required considerable material and operating costs [1]. Besides, cement production is followed by CO_2 emission and dusting adversely affects ecological condition of environment. In this regard, there is a problem to search alternative methods of construction materials production, allowing to reduce or eliminate a concentration of high-cost and ecologically harmful cement binder.

Taking into account the specificity of the mentioned problem to produce high-effective construction materials, it is extremely actual for develop composite binders based on non-traditional mineral raw.

A significant interest attracts aluminosilicate materials of natural and industrial origin [1–6], which, because of their genetic peculiarities include a nanosized (ultra dispersed) phase. One of such alumosilicate materials can be presented by perlite, which is classified as a nanoheterogenic mineral substance of natural origin [7].

Because of random network, alumosilicates are not stable in presence of alkali solution that is the base of their pozzolanic properties. Hence the pozzolanic activity became a criterion to choose perlite in this research to develop high effective autoclave composite binders (based on lime) and alumosilicate binders (like alkali-activated binders – geopolymers). One of the factors of applicability for alumosilicate material in high-alkali binders is structural – phase transformations during hydration and curing processes with formation of Na and K zeolites as final products of reaction, which are analogues of rock-forming minerals of the Earth crust with longer durability [8].

Materials and methods

The investigations in this work were carried out with using perlite from Muhkor-Talinsk deposit, quartz sand (Nizhne-Olshansk deposit) was used as a reference material (table 1). Quick lime and caustic soda were used for production of binders.

In order to study raw materials as well as obtaining composites in this work was used following analytical equipment. XRD and XRF analyses to determine a mineral composition of quartz sand and perlite were run with spectrometer ARL9400 and diffractometer DRON (DRON–3.4) with using of Cu$A\beta$ radiation. The full-width at half-maximum (FWHM) of these patterns was 0,05°.

X-ray microstructural analysis was carried out with using of Rietveld method, where the calculations were made by FullProf software.

Table 1

Chemical composition of mineral components (by weight, %)

Mineral	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	H_2O	SO_3	LOI
Perlite	75,5	13,6	1,0	1,0	0,3	0,1	4,8	3,8	5,3	-	-
Quartz sand	92,4	2,36	0,77	1,88	0,2	-	-	-	-	0,05	1,95

Perlite, as well known, is a rock of volcanic origin, containing 98% of glass phase, which is X-ray amorphous component, confirmed by XRD analysis (Fig. 1, a). At the same time, the used quartz sand is a magmatogenene-effusive quartz, that is more common sedimentary rock with content of more than 80% of crystal substance of quartz mineral (Fig. 1).

High chemical activity of perlite occurs because of its typomorphism peculiarities. A formation of silica-bearing rocks with different genesis predetermines their activity. During the process of magmatogene-effusive formation of quartz mineral, big and regular crystals with low chemical activity are formed. At the same time, in the result of magmatogene-effusive genesis of glass phase of perlite, small enough crystallites are formed; moreover, in some cases, because of crystallization is not happened, an amorphous mineral is obtained.

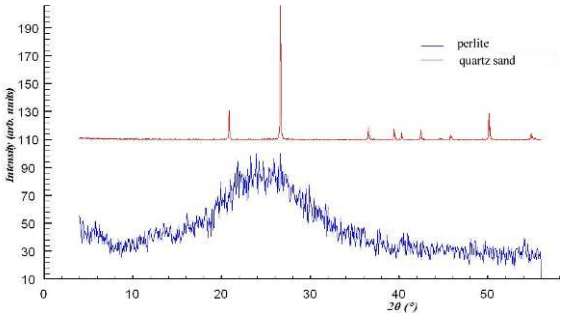

Fig. 1. X-ray diagram of studied component

Results and discussions

The factors of chemical activity for silica-bearing rocks can be estimated by the ratio of silica modifications, the crystallites of which are in the range of different size limits. In this study, the determination of quantity characteristics was performed with computer calculation of XRD data by FullProf software. Phase composition of studied perlite presented by high-temperature polymorphous modifications of quartz – crystobalite and tridymite with the size of crystallites of 1–1,6 nm (table 2), that means the studied perlite will react to binder components more intensively.

Table 2

Phase composition of the studied rocks

Material		Content of components (by wt, %)	Size of crystallites, nm
Perlite	tridymite	3	1,6
	crystobalite	97	1
Quartz sand	α-quartz	84	67
	β-quartz	16	20

Utilization efficiency estimation of alumoslicate rock of natural origin was done according to kinetic of mechano-active dispergation. The dispergation was made with using of lab planetary mill for 2, 4 and 6 hours. The resulting parameters were a specific surface and a size of the particles. A particle size distribution (PSD) analysis was run with laser granulometry.

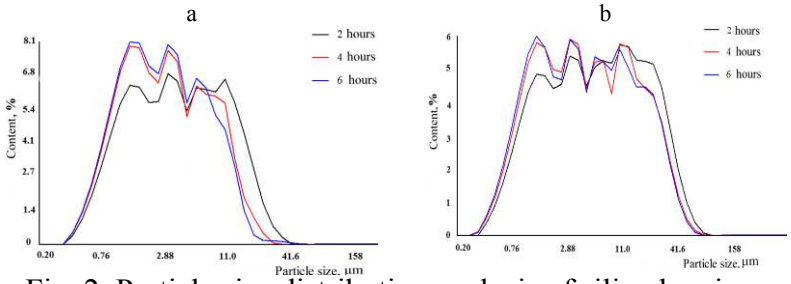

Fig. 2. Particle size distribution analysis of silica-bearing rocks:
a – sand quartz ; b – perlite

The difference of curves behavior of the particle distribution for studied specimens of quartz and perlite is in dimension heterogeneity. Granular composition of quartz specimen after 2 hours of milling is in the range of 0,40–40 μm, besides, with increasing of milling time till 6 hours, it can be noted two maximal picks with particle size of 0,9–3 μm. PSD curve for perlite specimen with increasing of milling time has a tendency to insignificant changing, the particle distribution is in a wide range of 0,25–100 μm, that confirm a regularity of material polydispersity.

It should be noted, that a favored factor of perlite is its high milling ability (table 3). That allows forecasting in increasing of production efficiency due to milling time of silica-bearing raw.

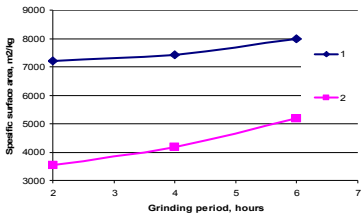

Fig. 3. Changing of specific surface during milling of silica-bearing rocks: 1 – perlite; 2 – quartz sand

In order to study the influence of autoclaving curing on the properties of composite binders, cubes of 2x2x2 cm with the composition presented in table 4 were casted. Based upon technological peculiarities of silicate material production, including replacement of quartz component by perlite in the content of the binder, a perlite after 2 hours of dispergation was applied. Strength test of studied specimens was run according to Russian Standard (GOST 8462-85).

Table 4

Mix design of silicate compound of composite binder

Mix number	Lime, %	Quartz sand, %	Perlite, %	Water, ml
1	50	50	–	15
2	50	45	5	15,2
3	50	40	10	15,4
4	50	35	15	15,6
5	50	30	20	15,8

Hydrothermal treatment of the specimens was carried out in a lab autoclave machine at pressure 8 atm in a following regime: increasing of steam pressure for 1,5 hours; exothermical curing for 5–6 hours; decreasing of steam pressure for 1,5 hours. On completion of the testing, the curve of dependence of strength on quantity of introduced perlite at replacement of quartz sand was plotted (Fig. 3).

On the diagrams with autoclaved specimens of the binder, its clearly observed a maximal increasing in strength up to 20% with introducing of 10% of perlite in the raw mixture. According to the results of a forward estimation for activity of silica in initial rocks, it can be stated, that the heaving of pozzolanic activity, perlite intensively reacts to lime at the first curing stages, that is very important, taking into account a decreasing in dissolving ability of $Ca(OH)_2$ with increasing of temperature. During the process of thermal treatment, amorphous phase of perlite transforms to dissolving modifications followed by activation processes of interaction of all the components of binders in liquid media. That energetically stimulates phase-forming mechanisms of cementitious material. According to XRD data (Fig. 4), introducing of nanocrystalled perlite in the mixture of autoclave silicates allows a formation of band low-basic calcium hydrosilicate – 11Å-tobermorite and reducing of concentration of high-basic orthosilicate phase α-C_2SH and formation of zeolite phase L – $K_{11.7}(Al_{1.8}Si_{34.2}O_{72})$ [9]. Wholly, that leads to formation of high strength properties of the material.

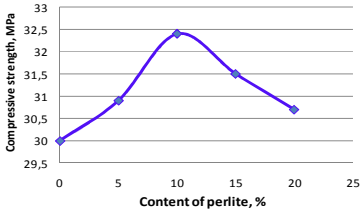

Fig. 4. Strength properties of autoclaved composite binder

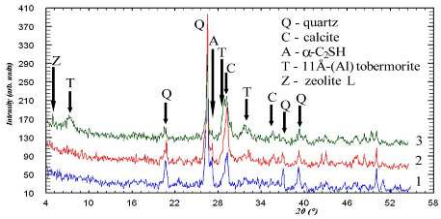

Fig. 5. X-ray spectra of gas concrete samples 1 – reference (composition 1), 2 – composition 3, 3 – composition 4 (Table 4)

In order to estimate a possibility of geopolymer binders production based on perlite, as well as influence of perlite dispersity on strength performance, specimens based on perlite and alkaline binder were casted in this work. Preliminary milling of perlite was done in a wider timeframe (Table 5). The specimens of the composite binder were subjected to thermal treatment for 12 hours at 80 °C.

Table 5

Compositions of geopolymer binders

Composition	Milling time, h	Dispersity, cm^2/g	Perlite, %	Water, %	NaOH, %
1	1	3620	75,3	21,55	3,1
2	1,5	4570	75,3	21,55	3,1
3	2	5670	75,3	21,55	3,1
4	2,5	5730	75,3	21,55	3,1
5	3	6220	75,3	21,55	3,1

In compliance with obtained results, the initial dispersity of perilte has a significant impact on strength characteristics of a resulting composite binder (Fig. 6).

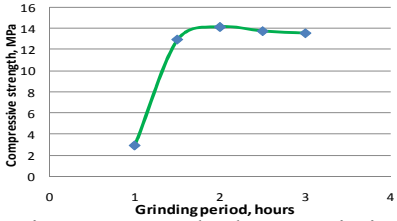

Fig. 6. Strength characteristics of geopolymer binder based on perlite

It can be noted a growth trend of strength properties with increasing of perlite milling time from 1 to 2 hour. The strength of the binder goes up to almost 4 times. Increasing in milling time till 2.5 hours leads to reducing of strength to 6%, however, the subsequent dispergation does not affect the strength performance.

For comparison and estimation of chemical reactivity of perlite under the conditions of alkaline activation , the specimens of quartz sand with a different extent of dispergation (2, 4 and 6 hours) were mixed with water-alkali solution of NaOH (Table 6).

The obtained specimens of alkali activated quartz sand were subjected to thermal treatment at 80 ^{o}C. Thermal treatment was performed for 36 hours till full cure of the system. In the process of thermal treatment was found, that during first 24 hours the system keeps moisture. However, during next 12 hours its cam be observed a dramatic drying and swelling of the system with formation of voids inside of the specimens. In this regard, evaluation of strength performance of the cured specimens turns to be impossible.

Table 6
Compositions of alkali activated quartz sand

Composition	Milling time, h	Dispersity, cm^2/g	Quartz sand, %	Water, %	NaOH, %
1	2	3540	70,8	12,5	16,6
2	4	4170	70,8	12,5	16,6
3	6	5200	70,8	12,5	16,6

X-ray diagram of alkali activated quartz sand showed a presence of sodium hydrocarbonates and crystallized quartz in the cured system. At the same time, the presence of crystallized new formations that is the products of the chemical reaction is not found (Fig. 7, a).

In the resulting X-ray diagram for the specimen of geopolymer binder with maximal strength value it can be seen, that the structuring band in the system is crystal zeolite-like new formations of analcime type $Na_2(AlSi_2O_6)\cdot 2H_2O$ (Fig. 7, b).

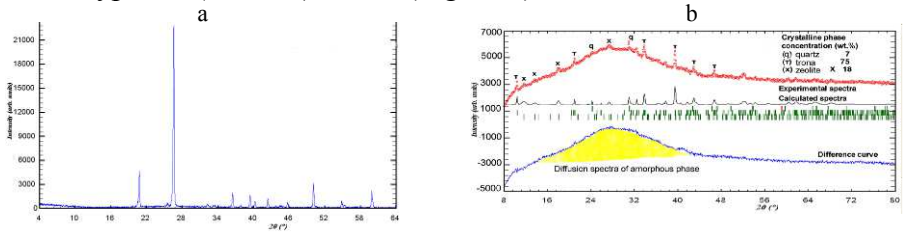

Fig. 7. X-ray diagram of: a – alkali activated quartz sand; b – geopolymer binder

Thus, it was found that the application of alumosilicate rock with high content of X-ray amorphous phase in the system of high alkaline binders affects the phase- and structure formation with improving of quality and efficiency of their production.

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