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Application of Natural Aluminosilicates in Autoclave Cellular Concrete

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Abstract: In the article a part of the quartz component in autoclave cellular concretes has been replaced by aluminum silicate rock – perlite. In contrast to quartz sand the perlite rock consists of nano-sized glass phase, which determines its pozzolanic activity. With X-ray diffraction (XRD) analysis, infrared spectroscopy (IR spectroscopy), microscopy equipment mechanisms of interaction between components of the binder is established. Aluminosilicate rocks in the highly alkaline binders are actively involved in the structural and phase transformations during hydration and hardening of silicate binder producing a predominantly low-basic hydrated calcium silicates - 11Å-(Al)-tobermorite, hydrated calcium silicates with amorphous structure. The cation exchange capacity of the perlite is the main characteristic of zeolite synthesis of L-$K_{11.7}$ ($Al_{1.8}Si_{34.2}O_{72}$) type that is an analogue of rock-forming minerals of the lithosphere. The proposed mechanisms allow improving the physical and mechanical characteristics of autoclave cellular concretes resulting increasing in strength value by 35%, decreasing in density by 20% and prediction of their durability.

Key words: Aluminum silicates · Perlite · Zeolite · Hydrosilicates · Tobermorite · Cellular concrete · Autoclave

INTRODUCTION

The strength characteristics of autoclave cellular concretes, as well as some others performance properties are largely dependent on the phase composition and morphology of cementitious new growths formed under hydrothermal conditions. Therefore, the development of ways to control hydrosilicate phase formation when the production of autoclave materials is very important.

It is known that one of the widely used methods of modifying the composition of lime-silica-cement binders (LSCB) used in the production of autoclave cellular materials is the introduction of active aluminosilicate components [1-3].

In the composite binders natural and industrial aluminosilicate materials are widely used because of their pozzolanic properties, what allows activating the chemical reaction of components interaction and reducing quartz and cement content in the binder, as well as significantly alteration the phase composition of the final products [4-9].

Volcanic origin rock cause considerable interest when preparation of silicate materials because of their genetic characteristics containing a part of the active amorphous phase [10-12]. In this paper, the pozzolanic activity was the main criteria when selection of aluminum silicate rocks – perlite to create high-performance composite binders and based autoclave cellular products.

Main Part

Technique: The samples of cellular concretes was casted in moulds with dimensions of 100 × 100 × 100 mm. Autoclave treatment was carried out at 183°C by the following regime: the autoclave ventilatingfor 40 min, buildup of steam pressure up to 10 bar for 1h, exposure at working pressure for 5h, buildup of steam pressure for 2 h. XRF analysis of the samples was carried out with a DRON -4 with using of Cu- anode radiation (Ni- filter to attenuate [beta]- radiation components). Scanning interval was 0.05°, the measurement of the intensity in the scanning points was 1s.

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IR-spectroscopy of aluminosilicate raw materials and obtained cellular concrete was performed using a FTIR spectrometer VERTEX 70/70v.

The microstructure of the samples was studied with a high-resolution scanning electron microscope (SEM) "Hitachi S-800".

Compressive strength test for autoclave cellular concrete and density determination test were carried out according to Russian Standards 10180-90 and 12730.1-78 [13, 14].

MATERIALS AND METHODS

Quartz sand with content of clay, silt and dust particles – 6.5% was used. The average grain-size of thesand by the module size is 0.65. The sand was ground to a specific surface 250-300 m^2/kg Chemical composition of the sand is shown in Table 1. Lime with CaO + MgO content was 70% at least and MgO content was no more than 5%. Lime activity was 92%. The lime was milled to a specific surface of 400 m^2/kg at least. Portland cement CEM I 42.5 N of CJSC "Belgorod cement" (Russia).
Gas-forming agent -was aluminum paste GPB-1.

In this study perlite of Mukhor-Tala deposit (Russia) was used. The chemical composition of wthe perlite is shown in Table 1

Physico-Chemical Properties of the Aluminosilicate Rocks: Perlite is a volcanic rock containing 98% of vetrous phase and a significant amount of sodium and potassium oxides (Tables 1 and 2). According to the results of XRD analysis the rock is a X-ray amorphous component (Fig. 1).

The high activity of perlite connects with its typomorphic features. Perlite is a volcanic rock formed from siliceous lava, riched in alumina and alkali components (Table 2), including silica minerals (kristabolite, tridymite, quartz). In view of the rapid cooling of high temperature lava perlite crystallization degree is very low, so the dominant part rock is microcryptocrystalline and amorphous phases. Indicators of siliceous rocks reactivity can be determined by the ratio of silica modifications, where crystallites are in different size ranges. A high concentration of amorphous phase in perlite leads to a complicated background in Figure 1 that is approximated problematically during full-profile quantitative XRF analysis using classical Rietveld algorithm. To eliminate the need to consider the background component of X-ray diagram the program DDM was used to quantify full-profile XRD data as well as algorithm Derivative Difference Minimization was realized [15].

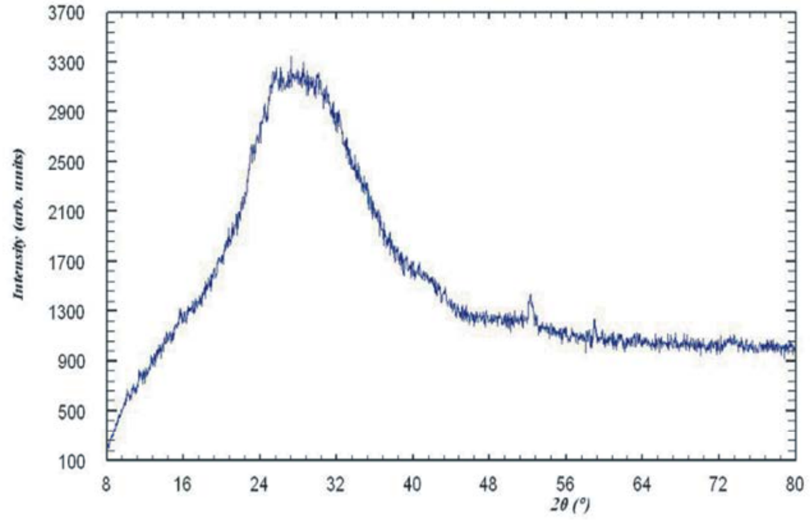

Fig. 1: X-ray diagram of aluminum silicate rocks – perlite

Table 1: Chemical composition of used minerals, wt.%

Mineral	SiO_2	Al_2O_3	Fe_2O_3	CàO	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

Table 2: Phase composition of the used rocks [16]

Name		Component content (wt.%)	Crystalline size, nm
Perlite	tridymite	3	1.6
	kristabolite	97	1
Quartz sand	[alfa]-quartz	84	67
	[beta]- quartz	16	20

Table 3: Composition of autoclaved cellular concrete

Composition	Perlite content exchanging quartz sand, wt.%	Components					
		Lime, wt.%	Cement, wt.%	Quartz sand, wt.%	Perlite, Macc.%	Al-paste, wt.%	Water-solid ratio, W/S
# 1 (reference)	-	19.99	19.99	59.86	-	0.16	0.5
# 2	5	19.99	19.99	56.87	1.99	0.16	0.5
# 3	10	19.99	19.99	53.87	5.99	0.16	0.5
# 4	15	19.99	19.99	50.88	8.98	0.16	0.5
# 5	20	19.99	19.99	47.89	11.97	0.16	0.5

Table 4: Physical and mechanical characteristics of the cellular concrete samples

Composition	Perlite content exchanging quartz sand, wt.%	Components					
		Lime, wt.%	Cement, wt.%	Quartz sand, wt.%	Perlite, MàCC.%	Al-paste, wt.%	Water-solid ratio, W/S
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# 4	15	19.99	19.99	50.88	8.98	0.16	0.5
# 5	20	19.99	19.99	47.89	11.97	0.16	0.5

The phase composition of the investigated perlite species consists of a high-temperature polymorphic modifications of quartz: cristobalite and tridymite with a crystallite size of 1–1.6 nm (Table 2), that determines its high activity in interaction with lime silicate mixtures at all stages of hardening.

Analysis of the Physical and Mechanical Properties of Cellular Concretes: The interaction degree of aluminosilicate component in silicate cellular systems was estimated by physical and mechanical characteristics of autoclave products.

Physical and mechanical properties of the samples are shown in Table 4.

Unlike quartz sand, whose solubility increases with temperature growth, the amorphous part in perlite actively participates in a chemical reaction in saturated lime mixtures at early stages of hydration with further growth of stable crystal of high strength phases under hydrothermal conditions enhancing strength values of autoclave products. This factor is important in view of reducing the solubility of $Ca(OH)_2$ at the growth of temperature when autoclaving. According to data of Table 4 the density of the product is reduced in comparison with the control composition. Probably, the formation of the crystalline framework at initial stages of hardening of cellular paste stabilizes a raw mixture at the time of gas extraction, excluding the paste shrinkage. According to the results the maximum activity is attributed to the sample with 15% quartz replacement on part perlite (Tables 3 and 4, the composition #4). Further increasing of aluminosilicate content up to 20% by reducing the quartz content causes decreasing in strength (Table 3 and 4, the composition #5), but in all these cases it is still higher than the reference composition.

The Study of the Phase Composition of Autoclaved Composite Binding: In order to study the phase composition was carried out XRD analysis and IR spectroscopy for hydrated formations in samples of autoclave cellular concrete. Identification of mineral components was based on database PDF-2 [17]. Comparison chart of X-ray diagrams for samples with different contents of perlite is shown in Figure 2.

To obtain the information about concentrations of crystalline phases The full-profile quantitative XRF analysis for autoclave binders samples using the program DDM v1.9 [15] in the version of Rietveld algorithm was carried out.

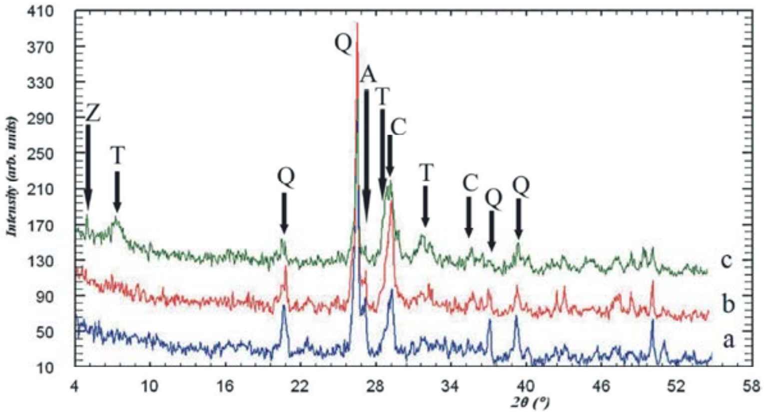

Fig. 2: X-ray diagrams for samples with different contents of perlite: a – composition # 1; b – composition # 3; c – structure # 4 (Table 3). Q – Quartz; C – $CaCO_3$, A – [alfa] C_2SH; T – 11Å-(Al)-tobermorite; Z – zeolite L-K11.7 (Al1.8Si34.2O72)

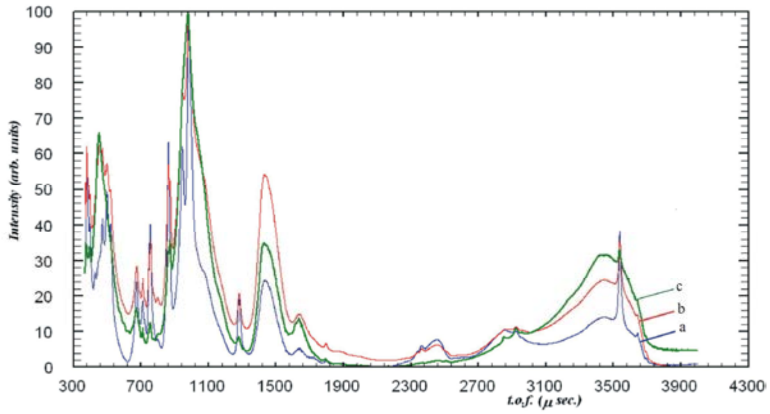

Fig. 3: IR-spectroscopy for specimens with different contents of perlite: a – composition # 1; b – composition # 3; c – structure # 4 (Table 3).

Table 5: Concentrations of crystalline phases

	Composition		
Mineral components	# 1	# 3	# 4
Quartz,%	43	40	21
Calcite,%	17	25	27
[alfa]-C_2SH,%	26	13	3
11Å-(Al)- tobermorite,%	14	22	47
Zeolite L,%	-	-	2

As structural models of mineral components were used followings: quartz (ICSD- 93974)*, calcite (80869-ICSD), [alfa] C_2SH (73404 -ICSD), 11Å-(Al)-tobermorite (93590-ICSD) and zeolite L (67031-ICSD). These concentrations of crystalline phases are shown in Table 5.

The results of quantitative XRD analysis suggest that the increasing in strength of LSCB with the addition of the small amounts of nanocrystalline perlite connects with increasing the amount of hydrated calcium silicates. From the results shown in Table 5 in the saturated lime mixtures extra alkali metal hydroxides are formed due to cation exchange reactions between aluminum silicate rock, which contains a significant amount of K_2O, Na_2O (Table 1). This promotes dissolution of quartz, its binding in hydrated calcium silicates with reducing of their basicity. At this moment free lime is carbonized. Formation of low-basic hydrated calcium silicates can be confirmed by an increasing in the intensity of the absorption bands in the region of $850–1100^{-1}$. Also the shape of the main bands of stretching and deformation vibrations ($430–460^{-1}$) of Si-O bonds in the tetrahedral SiO_4, diortogroups of tapes and layers is changed Broad absorption region in this range with optimal additive content of perlite in comparison with a narrow absorption band of the reference indicates increasing amounts of hydrated calcium silicates with high degree of

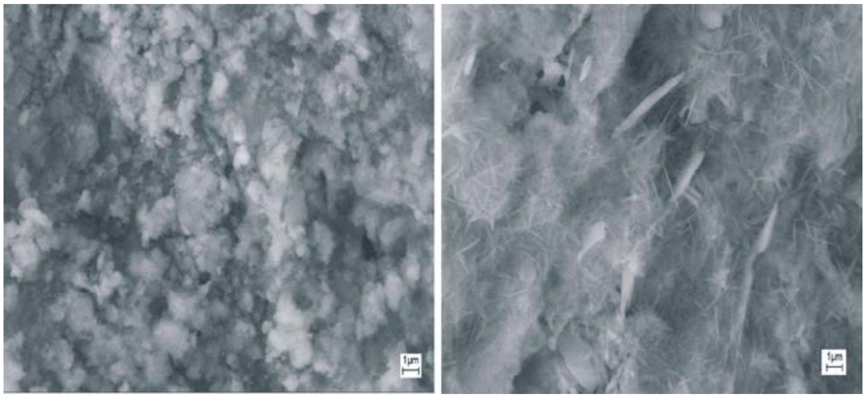

Fig. 4: SEM image of the interpore partition in autoclave cellular concretes: a – composition # 1; b – part # 4 (Table 3).

amorphization. Enhanced intensity of the vibrations in range of 3300–3800 cm^{-1} confirms the formation of hydrate phase of C- A -S- H or C -S- H type. As crystalline structures of these compounds were not detected with XRD analysis it should assume presence of this phase in the amorphous state. Hydrosilicate bond consists mainly of tape low-basic hydrated calcium silicates – 11Å-(Al)-tobermorite, the amount of which increases with a proportional increasing in strength. Aluminate phase presenting in perlite in cement, are involved in the formation of tobermorite formations. In this case, mixtures of saturated alkali ion Al^{3+} isomorphically substitute capable of Si^{4+} -ions in the crystal tobermorite lattice to form 11Å-(Al) tobermorite [18, 19]. Fluctuations in the frequency range of 400–540 cm^{-1} are associated with the delocalized valence and partially deformation vibrations of Si-O-Si (Al, Fe). The differences in the hydrogen bonding complex hydrated calcium silicates reflected valence vibrations of OH groups in the range of 3300–3800 cm^{-1} the band shifts to lower frequencies as well as reduction of vibrations in the 2300–2540 cm^{-1} show a decreasing in strength of hydrogen bonds. The absorption band at 1640 cm^{-1} (deformation vibrations of the H-O-H) show higher content of bounded water in the molecular complex of hydrated calcium silicates.

Formation of zeolite attributed to cation exchange of hydrated calcium silicates phase with alkali metals K_2O, Na_2O. Cations Na^{3+} and K^+-ions incorporated into the complex forming hydrosilicate analogue of the natural zeolite of L - $K_{11.7}$ ($Al_{1.8}Si_{34.2}O_{72}$) type, the absorption bands of 940–950 cm^{-1} shows rearrangements of Si-O-(K^+, Na^+).

Wave vibrations in range of 780–920 cm^{-1} correspond to isolated silicon-oxygen tetrahedra typical of nesosilicates and, therefore, can be attributed to the structural motif of highly basic hydrated calcium silicates [alfa]- C_2SH. As a result of XRD analysis the concentration of metastable phase [alfa]- C_2SH decreases as the perlite growing in the silica mixture, which is an additional source of $Ca(OH)_2$ and hydration products considerably increases the amount of calcium carbonate. The most intense absorption bands of CO_3^{2-}-ions (1580–1750, 840–857 cm^{-1}) are associated with the presence of C=O bond.

The differences in the phase composition of the samples are observed in the morphostructural features of hydrate formations. Figure 4 shows the interpore partition in the obtained cellular samples. The microstructure of the control sample represented microglobular aggregates of crystalline individuals with isometric shape that corresponds to the morphology of the orthosilicate [alfa]-C_2SH. While porous microstructure of the partition takes place. Adding of perlite leads to the formation of diverse columnar tobermorite aggregates, which are reinforced interporous partition. Zeolite-like growths are analogues of rock-forming minerals, rocks, whose presence in the silicate rock contributes to its further compaction and hardening. This effect allows reducing the shrinkage strain, then fix the precise contours, reducing the density of the product and create a solid structure porous stone.

This complex hydrosilicate bond was determined in structure of ancient concrete. Based on detailed analysis it is revealed that the exceptional durability and strength of the ancient concrete is predetermined by phase composition of hardening products, where, low-basic hydrated calcium silicates present [20]. The strength and durability is a major criterion when the application of zeolite based construction materials [21], so the hydrothermal synthesis of zeolites in the porous concrete allows predicting the durability of structural properties of the obtained silica stone.

CONCLUSION

The main goal when of high-strength cellular concretes is the synthesis low-basic hydrated calcium silicates present and hydrated tobermorite silicates. Generally, a the main factor for chemical reactions between the components is the ajoint fine grinding of quartz sand and lime with subsequent activation of the quartz component when hydrothermal synthesis. The used aluminum silicate rock – perlite, unlike quartz sand, is formed by the volcanic genesis and includes a high-temperature polymorphs of silica, which actively react with $Ca(OH)_2$ in the initial stage of hydration of the concrete paste before autoclaving process, creating the conditions for the synthesis of high-strength phases. Also in saturated lime mixtures by cation exchange reactions with aluminum silicate rock, which contains a significant amount of K_2O, Na_2O, extra alkali metal hydroxides form, which promote dissolution of quartz, its binding with calcium hydrosilicates decreasing their basicity. While free lime is carbonized and the concentration of the metastable phase [alfa]-C_2SH is significantly reduced, which makes a significant contribution to the development of strength. The apparent advantage of the research is modelling of synthesis of natural zeolite L-$K_{11.7}$ ($Al_{1.8}Si_{34.2}O_{72}$), which, according to the literature, makes a significant contribution to the ancient concrete structure, which has saved up to the present time. Crystal and chemical characteristics of perlite allow intensification the hydration reaction of binder in the early stages of hardening before autoclaving process with the possible formation of primary crystalline cellular concrete frame structure. This contributes to the stabilization of gas extraction raw mixture, reducing shrinkage deformation, fixing the optimum pore structure with decreasing of density and improving the strength of the product.

Due to full-profile quantitative XRD has been revealed the amorphous phase of perlite consists of a mineral silica cristobalite and tridymite with a crystallite size of 1–1,6 nm, which are actively involved in the synthesis of high-strength phases. According to the results of XRD analysis, IR spectroscopy and microscopy data has been established the cation-exchange reactions of aluminum silicate rocks in the highly alkaline mixtures help to increase the solubility of quartz and its binding to high-strength low-basic phase, forming an additional complex of hydrated phases of the amorphous structure. Aluminate phases introduced by perlite and presenting in the cement, involved in isomorphic substitution of Si^{4+}-ions in the crystal lattice to form of 11Å-(Al)-tobermorite. Cation exchange capacity of the perlite is the main characteristic of synthesis of L - K11.7 ($Al_{1.8}Si_{34.2}O_{72}$) phase (an analogue of the natural zeolite), the effect of which allows predicting the strength and durability of the products.

Obtained diverse columnar tobermorite aggregates microreinforce the structure, amorphous phase of dyscrystalline hydrated calcium silicate in combination with synthetic zeolite provide additional compaction of the crystal matrix of interporous partition in cellular concrete, which allows to fix the precise contours of pores, reducing the density of the product by 20% and increase the strength of the porous stone structure of 35%.

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