



STRUCTURE FORMATION OF GEOPOLYMER PERLITE BINDER VS. TYPE OF ALKALI ACTIVATING AGENT

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ABSTRACT

Origins and genetic characteristics of raw materials as well as features of their preliminary preparation and production process are the basic factors when formation of structural and mineral features of geopolymer binders. In framework of this research, a wide range of experiments were carried out to study the influence of different factors on formation of phase composition and microstructure of perlite based geopolymer system. The character of degree of dispersion variation of perlite when its mechanoactivation taking into account a duration of grinding process as well as a type of grinding machine is determined. The application of alkalis and alkali salts is providing a high-basic medium in water solution as activating agent in geopolymer systems; is differently effects on perlite solution. The hardening mechanism as well as new formations when perlite geopolymer binder hardening is determined. The features of hardening process as well as structure formation of geopolymer system are recognized according to data of its phase-mineral composition and strength characteristics.

Keywords: aluminosilicates, perlite, geopolymer, alkali activation, phase formation.

INTRODUCTION

Studies of application of non-popular type of natural resources as reactive mineral raw materials when production of effective free-of-cement binders produced by low-temperature synthesis as well as construction composites, produced with environmentally friendly technologies are interest in some industrially developed countries including Russia. Primarily, it could be associated with annually increased shortage of wide range of high qualitative natural resources that limits of its availability and initiates a growth of its cost.

According to some earlier studies the low efficiency of application of valuable natural resources as inert and pozzolanic aggregates and fillers is observed at present time [1–4]. One of these materials is perlite that is widely applied when production of agricultural products such as expanded perlite. However, in recent studies of Russian scientists the opportunity of perlite application as reactive component with binding properties when production of nanostructured binder, obtained by longtime stage-to-stage wet grinding of aluminosilica-bearing component is confirmed [5, 6].

Also, the results of alkaline activation of perlite when geopolymer binders production are obtained [7, 8]. In the above two cases the results demonstrates quite high performance characteristics that is implication of viability of perlite using when production of construction materials of different purpose.

In this work the perlite from Mukhortalinsk deposit (the Buryat Republic, Russia) is used as raw component for geopolymer production.

Mukhortalinsk perlite-zeolite deposit is part of Mukhortalinsk volcano-tectonic basin of Ilkinsk tectonic depression dated by the Mesozoic Era. This deposit consists of volcanic and volcanic-sedimentary rocks of the Udi series (J2-3), placed on early-Paleozoic granitoids [9].

Perlite from Mukhortalinsk deposit is pyroclastic aluminosilicate rock with high content of cryptocrystalline silica. Brecciated perlite is productive strata of the deposit containing different-sized fragments of volcanic tridymite-crystalite-feldspar glasses with different shape [11].

Perlite is volcanic rock characterized by cryptocrystalline structure. It is formed when hydration of volcanic glass, that takes place when cooling of volcanic substance and further redistribution of containing water due to thermal and pressure gradient or in medium of hydrothermal solutions and surface water upon a long time after glass formation.

Perlite contains 1,5 % at least of associated water as well as different crystal inclusions in form of Einsprenglings and microlites (quartz, pheldspar, plagioclase, biotite, amphibole), spherulites, and secondary minerals (zeolite, montmorillonite). In some types of perlite the inclusions of obsidian and rhyolite present. Water, presented in volcanic glass is chemically bonded.

General physical, mechanical characteristics and chemical composition of perlite from different deposits are shown in Table-1.

In spite of high potentiality of perlite the earlier studies in field of geopolymer binders allow discussion of them as particular cases of alkaline activation of perlite due to a weak understanding of structure formation processes in geopolymer binder.

For more deep understanding of structuring processes in perlite geopolymer system the influence of character and duration of grinding process of perlite as well as type of alkali component on structure formation and phase-mineral composition of geopolymer binder was studied in this paper.

**Table-1.** General physical, mechanical characteristics and chemical composition of perlite.

| Parameter | | | | Chemical composition, % | | | | | | | | |
|-----------------------------------|--------------------------------|----------------|------------------------------------|-------------------------|--------------------------------|---------|---------|-------------------|------------------|------------------|--------------------------------|------------------|
| Bulk density kg/m ³ | Heat conductivity, W (m·K). | Porosity, % | Real density, kg/m ³ | SiO ₂ | Al ₂ O ₃ | FeO | CaO | Na ₂ O | K ₂ O | H ₂ O | Fe ₂ O ₃ | TiO ₂ |
| 500-2500 | 0,96-1,08 | 1,8-70 | 2300-2390 | 68-76 | 11-14 | 0,4-1,5 | 0,5-1,5 | 2-4 | 1,5-4 | 1-9 | 0,2-1 | 0,1-0,5 |

Material and equipments

In the paper a perlite from Mukhortalinsk deposit (Russia) was used. Chemical composition is presented in Table-2.

As alkaline activators, providing strongly alkaline media (pH ≥ 13) in watersolution the followings components were used: sodium hydroxide NaOH (analytical reagent), potassium hydroxide KOH (analytical reagent), water glass Na₂SiO₃ and sodium carbonate Na₂CO₃ (analytical reagent).

To determine grinding features of perlite under different types of mechanical dispergation the followings three types of grinding machine were applied: ball mill, planetary mill and vibro-grinder.

Diffraction spectra of perlite are obtained with X-ray Workstation ARL 9900 with Co-anode. X-ray diagnostics of crystal phases (qualitative XRD-analysis) is realized with database PDF-2.

Table-2. Chemical composition of perlite from Mukhortalinsk deposit (% by wt).

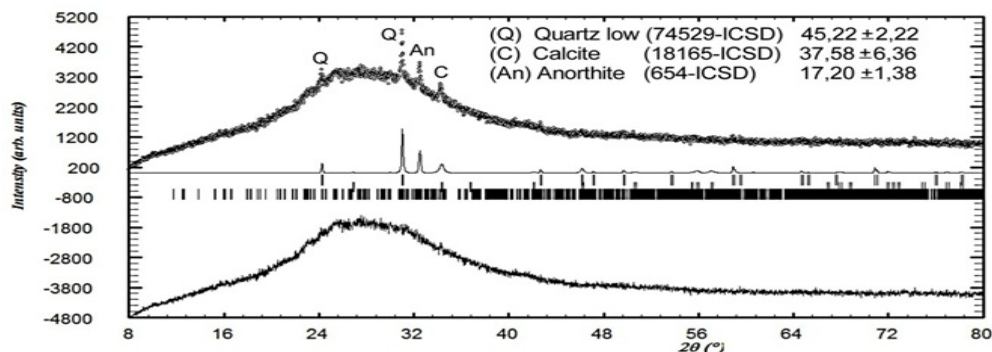
| SiO ₂ | Al ₂ O ₃ | MgO | Fe ₂ O ₃ | K ₂ O | CaO | Na ₂ O | TiO ₂ | Cr ₂ O ₃ | MnO | SiO ₂ /Al ₂ O ₃ |
|------------------|--------------------------------|------|--------------------------------|------------------|------|-------------------|------------------|--------------------------------|-----|--|
| 71,52 | 15,99 | 0,37 | 1,67 | 4,58 | 0,85 | 4,26 | 0,16 | 0,11 | 0,1 | 4,47 |

Quantitative XRD-analysis of crystal phases (by wt. %) is accomplished with Full Profile Quantitative XRD-analysis and calculated with DDM v.1.95e program based on Derivative Difference Minimization algorithm allowing refinement of approximate parameter of complex background of XRD-spectrum [10]. ICSD – Inorganic Crystal Structure Database is used as structural model of mineral components.

The microstructure analysis of perlite is carried out with SEM microscopy by using SM-300 Mira 3 FesSem microscope (Tescan, Czech Republic) under high-vacuum regime (InBeam) and with Schottky cathode. Polaron Equip. LTD-E5200 machine was used for the sample preparation with graphite as covering material.

Results of chemical analysis of perlite (Table 2) are in agreement with literature sources for aluminosilicate raw materials for geopolymer [12, 13], characterized by low content of CaO (< 10 %), as well as high content of K₂O и Na₂O (K₂O+Na₂O is more then 8 %). Also, SiO₂/Al₂O₃ ratio is equal 4.47, meeting requirement for aluminosilicate raw materials in geopolymer systems.

XRD-analysis of perlite from Mukhortalinsk deposit confirms the results of its mineralogical-petrological analysis [9] (Figure. 1). Wide profile of scattered reflection is associated with significant part of vitreous phase in perlite. On the base of earlier studies [14] it is assumed the vitreous phase to be consists of nano-sized crystals of cristobalite, tridimite and aluminosilicates.

**Figure 1.** Mineral composition of crystal phases of perlite.



Thus, parameters of chemical and mineral composition of perlite demonstrate a high potential efficiency of its application in geopolymer systems.

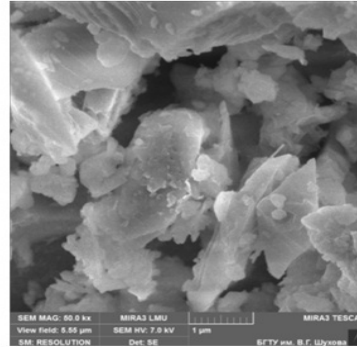
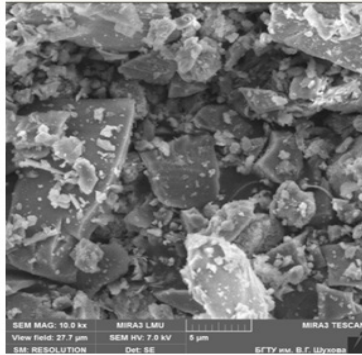


Figure-2. Microstructure of perlite (fraction 0,315–1,25 mm).

Microstructure of perlite particles with fraction of 0,315–1,25 mm is characterized by dominance of sharp vitreous grains without visible crystal formations in bulk of material (Figure-2), that the results of X-ray analysis confirm the data from Figure-1.

Experimental part

Study of kinetics and character of perlite grinding was accomplished with three types of dispergation:

- shock and crushing (ball mill);
- shock and scuffling vibro-grinder;

- scuffing only planetary mill.

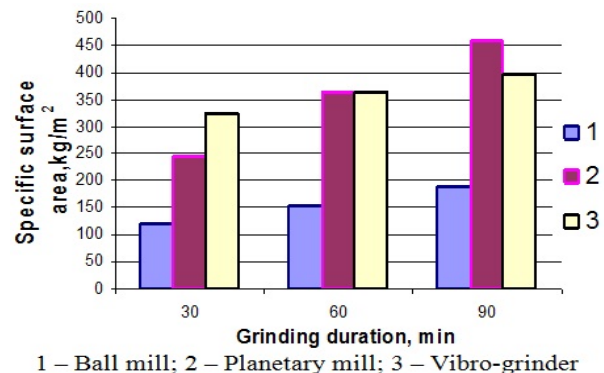
Character of perlite dispersity variation in time, dispergated by different types of grinding machine was studied by comparative analysis of grinding efficiency according to a specific surface area data after 30, 60 and 90 minutes of grinding. The results obtained in Table-3 and Figure-3.

Table-3. Dependence of perlite specific surface area on grinding parameters.

| Parameter | Ball mill | | | Planetary mill | | | Vibro-grinder | | |
|---|------------------------|-----|-----|----------------|-----|-----|---------------|-----|-----|
| | Grinding duration, min | | | | | | | | |
| | 30 | 60 | 90 | 30 | 60 | 90 | 30 | 60 | 90 |
| Specific surface area, m ² /kg | 120 | 155 | 190 | 245 | 362 | 457 | 325 | 364 | 397 |

According to presented data of perlite grinding (Table-4) under scuffing effect with vibro-grinder the grow of specific surface area is accomplished with dramatic improvement during the first 30 minutes with subsequent smooth slight grow up to 90 minutes (increasing of specific surface area in range of 30–90 min is 22 %) with maximal value after 90 minutes of grinding is equal 397 m²/kg (Figure-3).

Perlite dispergation under shock-crushing effect in ball mill is realized less intensively vs. grinding in vibro-grinder, providing minimal specific surface area of material (190 m²/kg) after 90 minute of grinding vs. data of two others grinding machines. In this case the more proportional increasing of perlite dispersity in time is observed (increasing of specific surface area in range of 30–90 min is 58 %).



1 – Ball mill; 2 – Planetary mill; 3 – Vibro-grinder

Figure-3. Effect of type and duration of dispergation on perlite grindability.



When grinding of perlite with planetary mill under scuffling effect the dramatic growth of specific surface area during all time of grinding process (increasing of specific surface area in range of 30–90 min is 86 %) (Figure-3). It manifests the highest grinding efficiency of planetary mill vs. others two grinding machine for perlite.

Mechanism of structure formation as well as phase composition depending on type of alkali agent was studied on the base of four experimental compositions of perlite geopolymer binder (Table-4) with four activators: NaOH, KOH, Na₂SiO₃, Na₂CO₃.

Earlier studies in this field [8] reported that such alkalis as NaOH, KOH as well as salts Na₂SiO₃ and Na₂CO₃ provide saturated water solutions with pH-parameters ≥ 13 , initiating intensive dissolution of amorphous phase of aluminosilicate component in perlite up to colloid substance with subsequent its monolitization to alkali-aluminosilicate system and formation of new structural forms.

Table-4. Composition of perlite geopolymer binder.

| № | Geopolymer binder composition, % | | |
|---|----------------------------------|---|-------|
| | Perlite | Alkali agent | Water |
| 1 | 77,6 | 5,3 (NaOH) | 17,1 |
| 2 | 68,4 | 7,7 (KOH) | 23,9 |
| 3 | 70,1 | 5,3 (Na ₂ SiO ₃) | 24,6 |
| 4 | 73,2 | 5,5 (Na ₂ CO ₃) | 21,2 |

To improve the activating effect of alkali component when dissolution of aluminosilicate component in perlite and further geopolymerization process the most effective method of its addition in the binder system is in form of saturated water solution. In this case, content of alkaline cations in geopolymer system should be minimally required to avoid its carbonatization and exudation in surface layers of the formed solid carbonate products. At the same time water content in the binder system must be minimal because it doesn't participate in structure formation processes and extra water prevent a reaction process. Thus, the most preferable components with good solubility in water medium in ambient conditions are presented in Table-4 and are able to form a saturated water solutions with pH-parameter ≥ 13 .

Determination of the most effective alkali agent the four compositions of perlite geopolymer binder with followings alkali components: NaOH, KOH, Na₂SiO₃, Na₂CO₃ are molded and thermally cured at 65 °C for 24 hours with following demolding of experimental samples and its hardening in ambient conditions up to 28 days. The samples are tested by compression after 3, 7, 14 and 28 days of hardening. The results obtained allow determination the application efficiency of studied alkali components in geopolymer system as well as a strength development of the experimental samples (Figure-4).

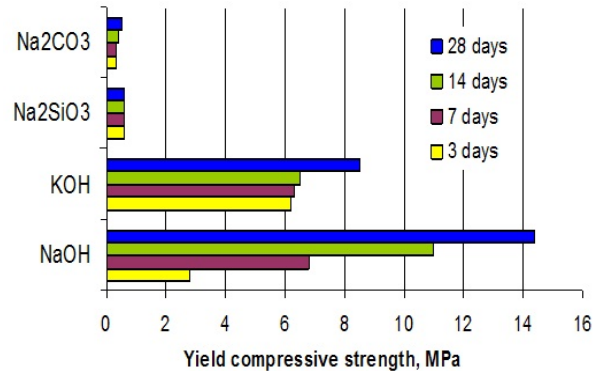


Figure-4. Strength development of geopolymer pastes in time.

Figure-4 demonstrates activating effect of alkali component in NaOH- and KOH-bearing geopolymer systems for a long time period. It confirms the initial compressive strength at the age of 3 days followed by increasing of 50 % at least at age of 28 days.

Geopolymer pastes, obtained with Na₂CO₃ and Na₂SiO₃ demonstrate compressive strength less than 1 MPa at age of 3 days holding this parameter constant up to 28 days.

So, the highest strength parameters are typical for geopolymer systems on the base of NaOH (14,3MPa); lower strength is referred to geopolymer systems on the base of KOH (8,6 MPa). Geopolymer binders with Na₂CO₃ and Na₂SiO₃ components demonstrate a minimal strength.

According these results we can conclude the most effective alkali activators for perlite in geopolymer systems are NaOH and KOH. It can be associated with good size compatability of atoms in alkali-aluminosilicate systems as well as favorable combination of priority and intensity of chemical reactions in geopolymerization process and activators Na₂CO₃ and Na₂SiO₃ have low activating effect in perlite geopolymer binders.

Visual analysis of experimental samples surface demonstrates the efflorescence of Na₂SiO₃, confirming a presence of non-reacted alkali agent due to low reactive effect in relation to perlite (Figure-5).



Figure-5. Blooms at surface of perlite geopolymer samples based on Na₂SiO₃.



To study the mechanism of structure formation when alkaline activation of perlite, the XRD-analysis of binding systems after 3 months of hardening is applied.

Figure-6 demonstrates XRD-spectra of perlite geopolymers with different alkaline activators.

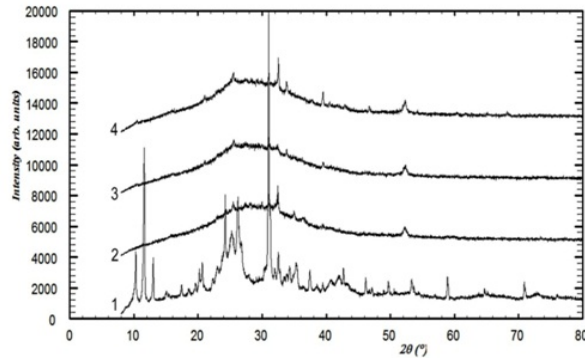


Figure 6. XRD-spectra of perlite geopolymers with different alkaline activators after 3 months of hardening
1 – NaOH, 2 – KOH, 3 – Na₂CO₃, 4 – Na₂SiO₃.

According XRD-analysis (Figure. 6) activation with NaOH leads to significant change of initial mineral composition of perlite. At the same time spectra of binding systems with KOH, Na₂CO₃ и Na₂SiO₃ are similar to spectrum of perlite (Figure-1).

X-ray diagnostics of NaOH-activated perlite (Figure. 6, Curve 1) realized with database PDF-2 demonstrates the absence of quartz low, muscovite, cristobalite and clinoptilolite. For better phase calculation the data of phengite (high-silica muscovite) is used. For description of wide diffraction profile in range of $2\theta=28^{\circ}\div 32^{\circ}$ (Figure- 6, Curve 1) that can be associated with CT-opal the data of tridymite is used.

In final calculation (Figure-7) the following reference phase from ICSD database are used: quartz low (74529-ICSD), cristobalite high (34924-ICSD), tridymite 2H high (200478-ICSD), phengite (34920-ICSD) и Na-clinoptilolite (97840-ICSD).

It is should be noted, a new formed phase in NaOH-activated perlite is Na-clinoptilolite (group of high-silica zeolite) (Na₈(Al₆Si₃₀O₇₂)(H₂O)_{9.04}).

Crystallization of zeolite phase confirms the geopolymerization process takes place. Crystal new formations in perlite geopolymer paste with Na₂CO₃ and Na₂SiO₃ are followings: quartz, cristobalite high, trona (Na(HCO₃)(H₂O)₂), as well as Fe-Ni- milling yield product. Information about of crystal phases in KOH-activated perlite will be presented in following works.

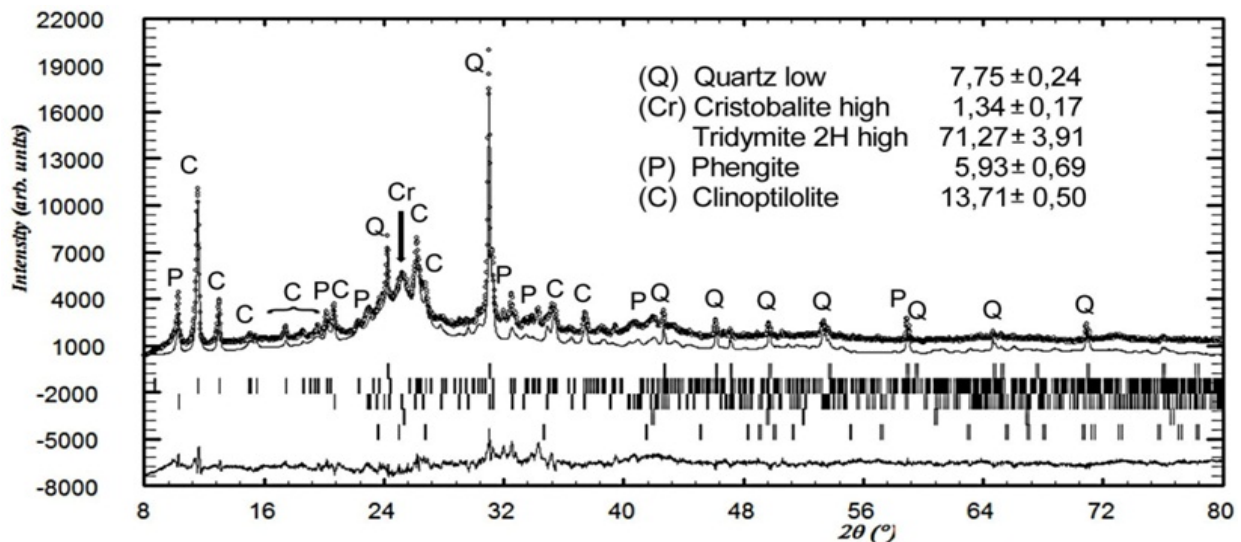
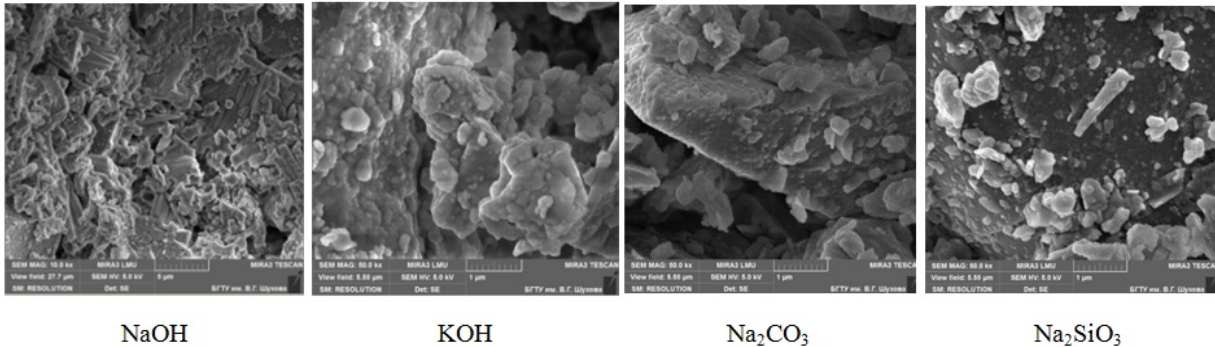


Figure-7. Results of Full Profile Quantitative XRD-analysis of NaOH-activated perlite after 3 months of hardening.

Microstructure of perlite geopolymer binder based on NaOH и KOH at age of 28 days presents compact monolithic structure without visible crystal formations (Figure-8).

Also in binding matrix the rounded particles of partially reacted perlite without visible contact zone «new formations – perlite grain», that manifests the following:

uncompleted solution process of aluminosilicate component in high alkaline medium followed by polymerization leading to formation of vitreous alkali-aluminosilicate substance; absence of contact zone indicates on high adhesion between new phases and non-reacted particles of aluminosilicate component providing high strength of geopolymer paste (Figure- 4).



NaOH

KOH

Na₂CO₃Na₂SiO₃**Figure-8.** Microstructure of geopolymer binder based on different alkali activators.

Opposite effect is observed in microphotographs of geopolymer pastes based on Na₂CO₃ and Na₂SiO₃, where in binder matrix a new formed amorphous phase is absent as well as there are a lot of isolated flake-like formations that can be associated with sodium hydro-carbonates and potassium hydro-carbonates as products of carbonatization of non-reacted alkali components. This confirms a quite slow chemical interaction alkali cations and aluminosilicate components.

CONCLUSIONS

Results of the perlite grindability obtained with planetary mill demonstrate the highest specific surface area vs. the same parameter of 140 % and 15 % obtained with ball mill and vibro-grinder, respectively.

It is determined the most effective alkaline activators for perlite are NaOH and KOH providing a formation of monolithic structure and high strength characteristics. High reactive capacity is associated with compatibility of atomic size in binding system as well as required sequence and intensity of geopolymerization process.

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