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FEATURES OF PHASE TRANSFORMATIONS IN GEOPOLYMERS BASED ON BOTTOM-ASH MIXTURE CONTAINING NANO-SIZED COMPONENT

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Abstract.

At present stage of construction material science development is orientation on production technologies of free-of-cement construction composites like geopolymers. In this work the possibility of geopolymer binder production on the base of bottom-ash mixture from Apatite power plant is confirmed. The basic efficiency criteria of bottom-ash mixture usage as reactive component when production of alkali-activated binders are determined. They are following: CaO_{free} content is up to 5 %, concentration of vitreous phase is 60 % at least.

It is determined mechano activation process have positive effect on reactivity of bottom-ash mixture when the binder production with NaOH and Na_2SiO_3 agents as alkaline activators. It is found the most effective alkaline activator for bottom-ash mixture from Apatite power plant is NaOH providing the strength properties of geopolymer binder three times higher vs. Na_2SiO_3 based analogues. Data of XRD-analysis demonstrate intensification of solution process of aluminosilicate component in bottom-ash mixture after its mechanoactivation as well as crystallization of zeolite phase like cancrinite.

Keywords: Fly ash, alkali activation, mechanoactivation, phase formation, geopolymer, zeolite, free-of-cement binder

Introduction.

Taking into account the problem of shortage of mineral binders, especially, cement associated with ecological and economical factors when production process and exploitation the orientation on new energy effective production technologies of composite binders based on genetically different mineral resources becomes very actual [1-4]. Up-to-date scientific ways are focused on usage of energy potential of raw materials, more fully, including their genetic features [5-8]. The most prospective way is application of production technologies of low-cement and free-of-cement construction materials based on alternative raw material resources including industrial wastes [9–11]. Bottom-ash mixture from Apatite power plant (Murmansk region, Russia) is considered to be the most material-intensive mineral industrial wastes in the region/ At present time the waste volume is 7,5 million tons, placed in landfills of $4 \cdot 10^4$ m^2 within the city zone. Annual emissions as well as continuous storage of the wastes are 180–200 thousand tons. At the same time a zero-utilization of this bottom-ash mixture negatively effects on ecological situation of the city and health of townspeople. Therefore the basic goal of this region is effective utilization of bottom-ash mixture from Apatite power plant [12, 13].

Bottom-ash mixture can be used as raw material when production of geopolymer binder that is analogue of cement systems [14-16]. Geopolymer is non-hydrating binder characterized by polymerization-polycondensation hardening mechanism [17]. The main advantage of geopolymer binder vs. cement based analogous is high strength, corrosive resistance, durability, immobilization of toxic and radioactive wastes that provides a good prospective of its application. This work is devoted to study of synthesis of non-cement binders such as geopolymers based on industrial aluminosilicate raw materials – bottom-ash mixtures from Apatite power plant taking into account the different activation methods. It allows understanding the opportunities of production of energy-saving binders and construction composites more deeply.

Materials and Equipment

In this study the bottom-ash mixture from Apatite power plant is used as industrial aluminosilicate component when geopolymer binder production. Its chemical and mineral compositions as well as physical characteristics are presented in Tables 1–3.

Table 1: Chemical composition of bottom-ash mixture.

Aluminosilicate component	Oxides, (wt. %)													
	LOI.	SiO_2	Al_2O_3	Fe_2O_3	CaO	TiO_2	K_2O	Na_2O	MgO	SO_3	P_2O_5	MnO	V_2O_5	SrO	Σ
Bottom-ash mixture (Apatite power plant)	3.5	50.97	20.10	8.12	2.38	10.47	1.24	1.73	4.05	0.168	0.328	0.068	0.06	0.04	99.8

Results of chemical composition of studied bottom-ash mixture demonstrate, CaO content is 2.38 % that is in accordance with requirements (CaO≤10 %) for effective structure formation in geopolymer system. Also, according to Russian Standard 25818-91 «Thermal plant fly-ashes for concretes. Specifications» this waste is low calcium aluminosilicate.

Experimental part

One of the basic criteria of reactivity of low calcium aluminosilicates is a high content of X-ray amorphous or vitreous phase as the most reactive one. In this case process of structure formation in alkali-activated system of geopolymer is the most probable.

Table 2: Mineral composition of bottom-ash mixture.

Aluminosilicate component	Minerals, %				
	Quartz	Mullite	Magnetite	Hematite	Vitreous phase
Bottom-ash mixture (Apatite power plant)	19,93	9,08	2,84	2,02	66,11

According to data of Mineral composition, shown in Table 2, vitreous phase content is more 66 %. It speaks for high potential of the studied bottom-ash mixture application as reactive component in geopolymer systems.

Also, physical, mechanical and morphological characteristics affected on technical efficiency of its application are significant.

Table 3: Physical, mechanical and morphological characteristics of bottom-ash mixture.

Aluminosilicate component	Parameter				
	Real density, kg/m^3	Specific surface area м^2/кг	Molar ratioSiO_2/Al_2O_3	CaO content, %	Natural radionuclides content, Bq /kg
Bottom-ash mixture (Apatite power plant)	2190	358	4,3	2,38	156,41 ± 41,90

Results of physical and mechanical characteristics (Table 3) demonstrate low density (219 g/cm^3) of studied bottom-ash mixture with high specific surface area (358m^2/kg). Perhaps it is connected with its morphological characteristics.

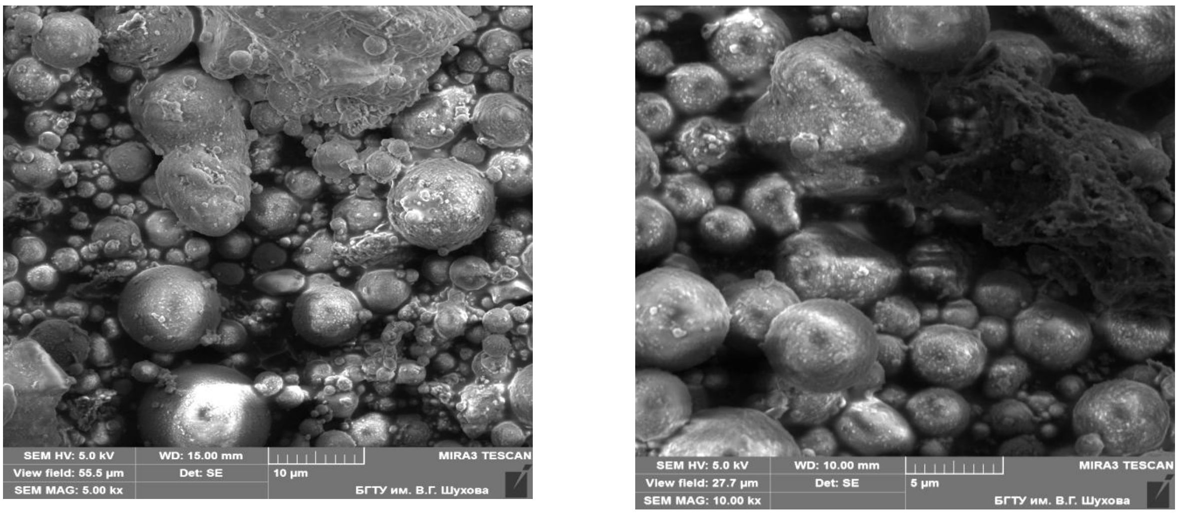

Figure 1. Microstructure of bottom-ash from Apatite power plant.

According to microstructure (Fig. 1), bottom-ash mixture from Apatite power plant is high-dispersed powder containing of spherical particles with smooth glassy surface. Molar ratio SiO_2/Al_2O_3 in the studied aluminosilicate component is in agreement with requirement of effective hardening process as well as formation of new phases in geopolymer system. Considering a technogenic genesis of the studied aluminosilicate its radioactivity should be taken into account according to standard requirements for construction composites.

Therefore, analysis of radioactivity of the bottom-ash mixture is realized by determination of natural radionuclides content with using of scintillation gamma-ray spectrometer «PROGRESS» according to Russian Standard 30108-94.

The obtained results demonstrate the natural radionuclides content is less than 160 Bq /kg (Table 3), that is 2 times lower of a limit values (≤ 370 Bq/kg). So, according to radiation standard NRB-99/2009 the studied bottom-ash mixture refers to a first class of radiation hazards and can be applied in different types of construction.

On the base of experimental data the main criteria efficiency of the studied bottom-ash mixture application as reactive component when geopolymer binder production. They are followings: low CaO content (< 5 %), high concentration of vitreous phase (≥ 60 %) in aluminosilicate component.Results of chemical, mineral compositions as well as physical, mechanical and microsturctural characteristics, presented in Tables 1–3 and Figure 1 allow using the studied bottom-ash mixture as reactive aluminosilicate component when geopolymer production.

Alkali activation.For alkali activation the NaOH (AR grade, Russian Standard 2263-79), Na_2SiO_3 (Technical grade, Russian Standard 13078-81) are used as alkaline activators. Choice of these components is associated with providing of high pH-value in water medium for a long time.

2. Mechanoactivation.Mechanoactivation process is realized with vibration mill IV1 during 5 and 10 minutes. Grindability data of the studied bottom-ash mixture are presented in Figure 2.

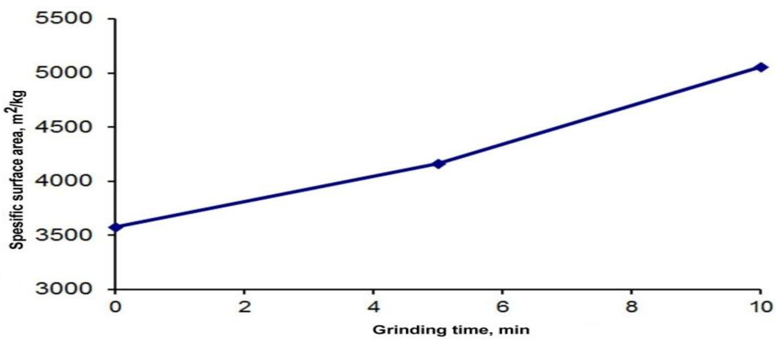

Figure 2. Kinetics of the bottom-ash grinding I time.

According to obtained results the studied bottom-ash mixture has a high degree of grindability. Average enhancement of specific surface area after 5-minute grinding is 17–20 %.

In the work an influence of different types of bottom-ash mixture activation on its structure formation in gepolymer binders as well as formation of physical and mechanical characteristics of geopolymer composites is also studied.

For this test a 6 compositions of geopolymer binders based on the bottom-ash mixture with flow of 2–4 cm is prepared (Table 4).

Table 4: Experimental compositions of geopolymer binders.

№	Aluminosilicate component	Alkaline activator	Duration of mechanoactivation, min.
1	bottom-ash mixture	NaOH	0
2	bottom-ash mixture	NaOH	5
3	bottom-ash mixture	NaOH	10
4	bottom-ash mixture	Na_2SiO_3	0
5	bottom-ash mixture	Na_2SiO_3	5
6	bottom-ash mixture	Na_2SiO_3	10

The samples of geopolymer binders were moulded in forms-cubes of 20×20×20 mm.

After that the experimental samples were cured at two different conditions:

1) Pre-curing at ambient conditions t=22±3 ^oC, relative humidity ≈ 60 %) for 30 min; curing in oven at 70 ^oC for 24 hours by following regime: heating up to 70 ^oCduring 90 min → isothermal period at 70 ^oC during 21 hours → cooling to 22±3^oC during 90 min

2) Curing at ambient conditions t=22±3 ^oC, relative humidity ≈ 60 % for 24 hours.

After a day of curing period two series of samples were tested for compressive strength (Table 5).

Table 5: Characteristics of geopolymer binders with different compositions after thermal treatment.

№	Aluminosilicate component	Alkaline activator	Density, kg/m^3	Yield compressive strength, MPa
1	bottom-ash mixture	NaOH	1211	8,3
2	bottom-ash mixture	NaOH	1850	13,4
3	bottom-ash mixture	NaOH	1875	11,8
4	bottom-ash mixture	Na_2SiO_3	1133	0
5	bottom-ash mixture	Na_2SiO_3	1234	4,2
6	bottom-ash mixture	Na_2SiO_3	1290	4,3

According to the obtained compressive characteristics the machanoactivation positively effects on reactivity of the studied bottom-ash mixture under its alkaline activation by both activators: Na_2SiO_3 and NaOH.

At the same time mechanoactivation period longer then 5 min doesn’t effect on strength values of geopolymer binder based on Na_2SiO_3 component (compositions № 5 and 6) and leads to reduction of compressive strength up to 12 % in geopolymer binder based on NaOH (compositions № 2 and 3).

According to data from Table 5 the most effective alkaline activator for the studied bottom-ash mixture is NaOH providing the highest values of compressive strength in geopolymer binders (13,4 и 11,8 MPa for compositions №2 and 3, respectively) that more then 3 times higher vs. geopolymer binder based on Na_2SiO_3 (4,2 and 4,3 MPa for compositions 5 and 6, respectively). The optimal mechanoactivation period for the studied bottom-ash mixture is 5 min. providing a specific surface area value of 416 cm^2/g.

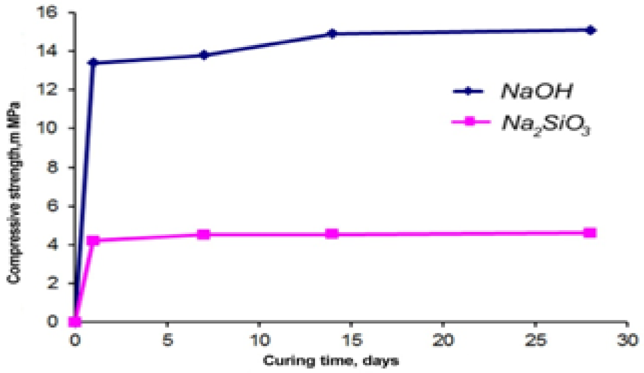

Figure 3. Strength development of geopolymer binders based on bottom-ash mixture from Apatity power station in time.

The series of experimental samples based on NaOH cured under condition № 1 after 24 hours of don't achieve the demoulding strength. The samples based on Na_2SiO_3 provide the strength values of 0,2 MPa at most (composition № 6). To study the features of strength development in geopolymer system based on the studied bottom-ash mixture in time the optimal binder compositions (№ 2 and 6) were tested on compressive strength after 7, 14 and 21 days of hardening (Fig. 3).

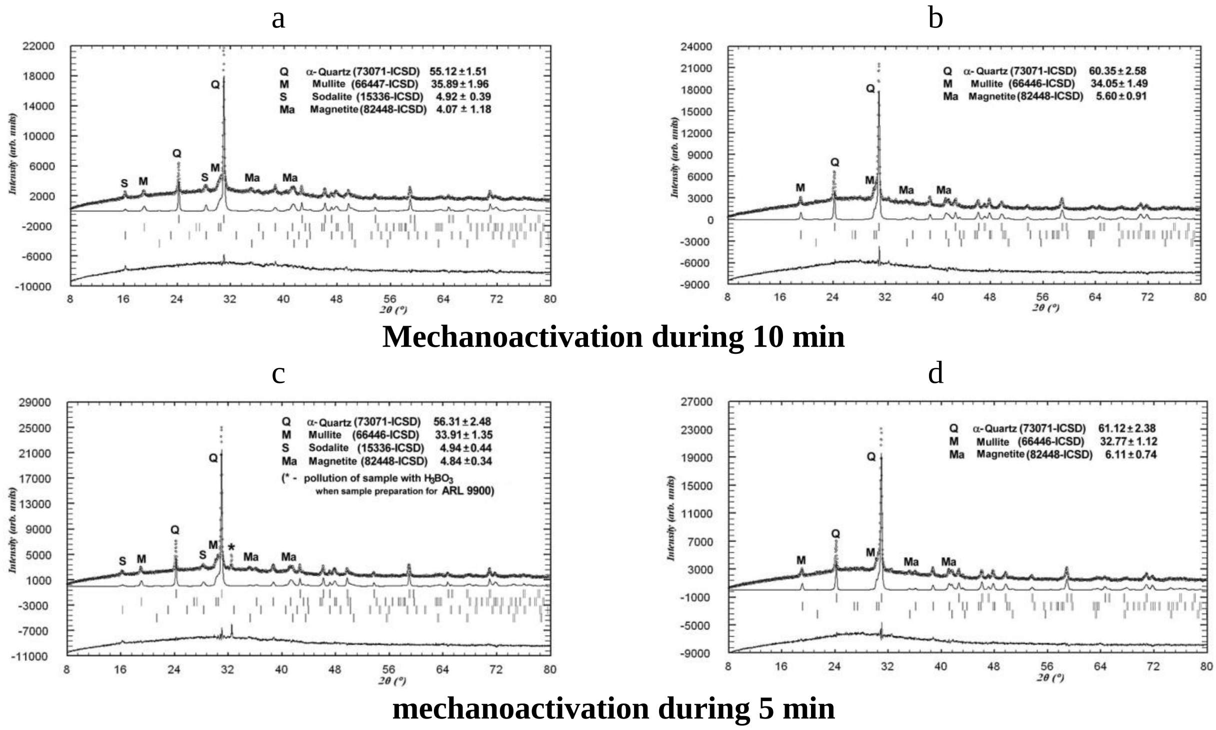

Fig. 4. XRD-diagrams of geopolymer binders based on bottom-ash mixture from Apatity power station with different time of mechanoactivation of bottom-ash mixture and with using a different alkaline activators: NaOH (a, c) и Na_2SiO_3(b, d).

According to data from Fig. 3 the 80 % of final strength of geopolymer binder is formed during a first 24 hours under thermal curing (curing conditions № 1). Further strength growth at ambient conditions during followings 27 days is accomplished not intensively. So, after 21 days of hardening the NaOH-based geopolymer binders provide a gain in compressive strength value of 12.6 %; Na_2SiO_3 -based geopolymer binders – 9.5 %.

Study of mechanism of structure formation and news phase formations in geopolymer binders with different types of the bottom-ash mixture activation was realized by XRD-analysis with Rietveld method [18]. The results are shown in Fig. 4.

XRD-analysis data demonstrate reducing a quartz content in mechanoactivated material vs. initial material (calculated as crystalline phases). It may be connected with a solution of aluminosilicate component of bottom-ash mixture up to gel-like state in alkaline media followed by its crystallization into zeolite like cancrinite (in NaOH-based geopolymer binder). In Na_2SiO_3-based geopolymer binder zeolite phases are not observed. However, solution intensity growth in both geopolymer systems after mechanoactivation takes place.

Conclusion

On the base of data obtained in this paper the opportunity of application of bottom-ash mixture from Apatity power station as reactive aluminosilicate component in geopolymer binders is confirmed. It is determined a positive effect of mechanoactivation on reactivity of the studied bottom-ash mixture under alkaline activation with NaOH and Na_2SiO_3 components when geopolymer synthesis. Experimentally determined the best activating affect of NaOH on the studied bottom-ash mixture, providing a strength characteristics of 3 times higher vs. Na_2SiO_3-based geopolymer binder. It is found the solution of aluminosilicate component of bottom-ash mixture in alkaline media followed by crystallization and formation of zeolite phases like cancrinite in NaOH-based geopolymer binder takes place.

Summary

Results of the obtained experimental and analytical data allow application of bottom-ash mixture from Apatity power station as reactive aluminosilicate component when geopolymer binder production. It also allows extension the area of effective utilization of aluminosilicate industrial wastes as well its application as principal raw material when construction materials production.

References

1. Lesovik V.S., 2009. Enhancement of efficiency of construction materials production taking into account genesis of applied rocks: Scientific publication. Moscow: ACB,pp:526

2. Lesovik, R.V., Ageeva, M.S., M.Shakarna, 2013. Efficient binding using composite tuffs of the middle east. WorldAppliedSciencesJournal, Vol. 24, 10: 1286–1290.
3. Alfimova N.I., Lesovik V.S., Savin A.V., E.E. Shadsky, 2014. Prospective of composite binder application when reinforced concrete materials production.Bulletin of Belgorod State Technological University named after V.G. Shoukhov,5 (88): 95–99.
4. Fomina E.V., Kozhukhova M.I., N.I.Kozhukhova, 2013.Assessment of efficiency of aluminosilicate rocks application as component of composite binders. Bulletin of Belgorod State Technological University named after V.G. Shoukhov, 5: 31–35.
5. Lesovik V.S., 2012. Reducing of energy consumption of construction materials production by using the energy of geological and industrial processes.18. Ibaus. InternationaleBaustofftagung.Weimar.
6. Lesovik V.S.,2014. Geonika (geomimmetics). Implementation examples in construction material science: monography. Belgorod: BSTU,pp: 196.
7. Lebedev M.S., Zhernovsky I.V., Strokova V.V., Fomina E.V., N.I.Kozhukhova, 2014. Application of IR-spectroscopy for study of aluminosilicate raw materials. Applied Mechanics and Materials, Vol. 496–500: 96–101.
8. Fomina E.V., Kozhukhova N.I., Palshina Y.V., Strokova V.V., A.E. Fomin,2014. Influence of mechanoactivation on dimension parameters of aluminosilicate rocks. Construction materials, 10: 28–33.
9. Lesovik V.S., Ageeva M.S., A.V. Ivanov,2011. Granulated slag in composite binders production. Bulletin of Belgorod State Technological University named after V.G. Shoukhov, 3: 29−32.
10. Lesovik, R.V., Nosova, A.N., Savin, A.V., E.V.Fomina, 2014. Assessment of the Suitability of the Opal-Cristoballite Rocks of Korkinsk Deposit in the Construction Industry. World Applied Sciences Journal, Vol. 29, 12: 1600–1604.
11. Tolstoi A.D., Lesovik V.S., I.A. Kovaleva,2014. High-StrenghtDecorative Complexes with Organo-Mineral Additives. Research Journal of Pharmaceutical, Biological and Chemical Sciences. September-October RJPBCS, 5(5): 1607.
12. Boroukhin D.S.,2010. Problems of sustainable development of enterprises of electrical energy industry in Murmansk region in term of global financial crisis.Bulletin of MSTU,Vol. 13, 1: 165–170.

13. Pak A.A., R.N. Sukhorukova, 2012. Polystyrene gas concrete: technology and properties of composite materials. Apatity. Kola Scientific center of RAS,pp: 101.

14. Kozhukhova, N. I., Fomina, E. V., Zhernovsky, I. V., Strokova, V. V., R. V. Chizhov, 2014. The utilization efficiency of natural alumosilicates in composite binders. Applied Mechanics and Materials, Vols. 670–671: 182–186

15. Kozhukhova, N.I., Zhernovsky, I.V., Strokova, V.V., 2015. Evaluation OfGeopolymer Binders Biopositivity Based On Low-Calcium Fly Ash. International Journal of Applied Engineering Research, Vol. 10, 15: 35527–35529

16. Kozhuhova, N.I.,Zhernovskiy, I.V., Osadchaya, M.S., Strokova, V.V., Tchizhov, R.V., 2014. On the Question of the Choice of Natural and Man-Made Materials for Geo-Polymer Binders. Research Journal of Applied Science, Vol. 9(12): 1034–1039.

17. Oh, J.E., Moon J., Mancio, M., 2011. Bulk modulus of basic sodalite, $Na_8[AlSiO_4]_6(OH)_2 \cdot 2H_2O$, a possible zeolitic precursor in coal-fly-ash-based geopolymers. Cement and Concrete Research, 41: 107–112.

18. Solovyov, L.A., 2005. Includes Rietveld and Derivative Difference Minimization (DDM) methods. J. Appl. Cryst., 37: 743–749.