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Revisiting a Selection of Natural and Technogenic Raw Materials for Geopolymer Binders

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Abstract

The opportunity of production of nanostructured binders based on granite by mechanoactivation is studied. The effect of mechanoactivation period on pH value of system when production of granite nanostructured binder consisting in reducing of pH value after 20 % of mechanoactivation process is determined. Structure formation process during the granite activation is studied with IR-Fourier spectroscopy. Also the relationship between reactivity of geopolymer binders based on low-calcium fly ashes and vitreous phase consisting in is demonstrated.

Keywords: aluminosilicate raw materials, nanostructured binder, geopolymer, low-calcium fly ash

1. INTRODUCTION

Aluminosilicate alkali activated binders with polymer-type solidification are promising materials for the wide implementation of green building concept.

Alkali activation of aluminosilicate materials is a set of the chemical processes including: dissolution of a aluminosilicate component; movement and orientation of solution products; polyfunctional condensation and polymerisation of the generated elementary compositions.

Researches which are carried out in the sphere of alkali activation bindesr attract growing interest of academic community. This is due to that those materials have more advantageous parameters of an ecological compatibility and working life in comparison with conventional cement.

Theoretically, all materials containing silicon earth and alum earth can be activated by an alkaline component. In the researches [1–7] executed to the present time in this line, a number of natural and technogenic aluminosilicate raw materials

and their compositions has been investigated: a kaolinite clay; a metakaolin; a fly ash; a blast-furnace granulated slag; an ash and slag mix; an ash and metakaolin mix; a slag and metakaolin mix; a mix of slag and a red mud (obtained in bauxite processing); a mix of fly ash and unburned material materials such as a kaolin.

For today there are two models of a chemical reaction of the alkali activation [5] which mechanism depends on characteristics of used raw materials:

– Si+Ca: it occurs when interacting of the blast-furnace granulated slag in a alkalescence solution. Major reaction products are calcium silicate hydrates;
– Si+Al: the most common example is activation of a metakaolin by a solution of medium or strong alkali. Reaction products are compositions with polymeric structure and high strength characteristics.

16 types of natural components are studied as aluminosilicate components for which reactivity in high-alkali medium is characteristic; those components under certain conditions are capable to show binding properties and to form effective strong composites [7].

The materials which structure formation proceeds according the first model mechanism are abundant enough. It is possible to refer slag-lime and slag-cement binding materials to them. Solidification of such combinations is caused by a hydration of a slag glass under the influence of hydroxyl ions with generation of C-S-H (II) group low-base calcium silicate hydrates, and also hydrogarnets and sodium hydroalumosilicates (when using soda and a sodium water glass).

The systems which are solidifying according to the second mechanism are less abundant. It is possible to refer aluminosilicate binders with polymer-type solidification, or geopolymers to them. Key parameters essentially influencing reaction activity of raw materials were identified for aluminosilicate materials which can be used for production of geopolymers. First of all it is necessary to note such parameters as the content of reaction active silicon earth, the content of an amorphous phase, the content of calcium oxide, etc.

Recently, researches of geopolymer binders are carried out actively enough. There are some backgrounds for it. In spite of the fact that portland cement is a commonly used material in a building sector, is used from the middle of XIX century and has no analogues for today, it has some negative properties.

One of the basic preconditions to an increasing intensification of geopolymer researches is the problem of industrial waste utilization.

An actual problem of the building sector is involvement in production process of huge volumes of aluminosilicate wastes formed in mining and processing industry for production of binders and materials on their basis. Especially it relates to development of athermal technologies for creation of new types of silicate and aluminosilicate binders, that, according to authors, is one of the most promising directions of research studies in modern building material science [8].

Besides, in the majority of the developed countries of the world a power industry is based on use of organic solid fuel, first of all coal. Ongoing growth of consumption of solid fuels has led in the end of the last century to critical environment contamination by their combustion wastes: ashes and furnace clinkers.

One of the paths to utilize accumulated ash and slag wastes is use of fly ashes produced by thermal power plants in the capacity of a aluminosilicate component in production of alkali activated binders.

Theoretical and technological preconditions for production of binders on a basis of alkali activated aluminosilicate mineral and technogenic raw materials are created by works of scientific schools headed by V.D.Glukhovskiy and V.P.Krivenko (Ukraine), J. Davidovits (France), V.I.Kalashnikov (Russian Federation), etc.

The purpose of the present study is to consider possibility of application of natural aluminosilicate extrusive rocks (stone screening dust) and low-calcium fly ashes produced by thermal power plants (type F) to obtain geopolymeric binders on their basis.

Stone screening dust

[1]Development of modern building material science assumes wide application of geomimethic technologies [9]. Upon that using concepts of transformation of Earth crust aluminosilicate substance in hypergenesis processes for development of new building technologies became especially actual. First of all it is necessary to refer to such processes transformation of substance with structural change and chemical composition of rock-forming minerals in dispergation, in particular, mechanochemical leaching of aluminosilicates during their levigating in liquid medium [10].

So, according to V. I. Molchanov, "experimental data on levigating of aluminosilicates in various type solutions has shown that minerals lose at first their alkaline, and then alkaline-earth elements consistently turning into minerals of a micaceous series, in clayey minerals and, at last, in simple hydrated silicon, aluminium and iron oxides. Each stage of transformation is accompanied by corresponding increasing of a free energy (Gibbs potential). The final stage is marked by a peak value of the accumulated energy and the highest reactive capacity" [10]. On this base it is possible to formulate a working research hypothesis in the form of the assumption: in the case of mechanochemical activation of aluminosilicate raw materials in an aqueous medium formation of initial reaction components occurs for generation of geopolymer binders without external alkali activation.

2. MATERIALS AND METHODS

To check the suggestion made, a felsic rock in the form of stone screening dust of the Poltava deposit (the Gereevsky quarry, Ukraine) has been used in the capacity of a feed stock to receive a nanopatterned aluminosilicate binder.

Chemical composition of stone screening dust examples was determined by X-ray fluorescence analysis method (XRF) on ARL 9900 X-ray WorkStation (Thermo Scientific) (tab. 1). X-ray interference spectrums are obtained on diffractometer ARL X'tra with use of $\lambda Cu_{K\alpha}$- and $\lambda Co_{K\alpha}$- radiation.

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[1] Geomimethic (from Greek γ – "geo" and μίμησις – "mimic") technology is the approach to creation of artificial rock materials on a basis of mimic of natural mineral and petrogenesis processes.

Specific surface measurement was made by means of device SoftSorbi-II ver.1.0. intended for measurement of specific surface of disperse and cellular materials by comparison of volumes of the gas adsorbate sorbed by the investigated sample and a standard sample of a material with known specific surface. Nitrogen was used in the capacity of gas adsorbate.

Table 1
Chemical composition of the granite sample from the Poltava deposit (% wt)

Sample*	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	LOI	Total
0	69.2	15.7	3.35	3.14	0.89	0.09	2.06	4.29	0.75	99.7
1	70.6	15.7	3.33	2.6	0.49	0.03	2.01	4.06	0.7	99.2
2	66.8	16.2	4.69	3.05	1.24	0.11	2.21	3.75	1.14	99.9
3	67.4	15.6	4.82	3.13	1.33	0.1	2.25	4.01	0.62	99.2

* Sample 0 – unfractionated stone screening dust; sample 1 – fraction> 1.25 mm; sample 2 – fraction <0.315 mm and sample 3 – fraction 1.25 – 0.315 mm.

As it follows from data shown in tab. 1, various dimensional fractions of stone screening dust are characterized by small variations of chemical composition.

3. RESULTS AND DISCUSSIONS

Quantitative full-profile X-ray fluorescence analysis was made with use of DDM program (ver.1.95c) [12]. Data of ICSD[2]: α-quartz SiO_2 (74529-ICSD), an albite $(Na_{0.75}Ca_{0.25})$ $Al_{1.26}Si_{2.74}O_8$ (34916-ICSD), anorthite $CaAl_2Si_2O_8$ (654-ICSD), amphibole $Na_{0.9}K_{0.4}Ca_{1.6}Mg_{2.8}Fe_{1.4}Ti_{0.5}Al_{2.4}Si_6O_{23}$ (OH) (9661-ICSD) and biotite K $(Fe_{2.554}Al_{0.446})$ $((Al_{1.55}Si_{2.45})$ $O_{10})$ $(OH)_2$ (95359-ICSD) have been used in the capacity of structural models. To define concentration of an amorphous phase, anatase TiO_2 (94566-ICSD) in concentration of 20 wt. % is used in the capacity of the internal standard.

The mineral composition of a granite according to quantitative X-ray fluorescence analysis results is presented by the composition (wt. %): a quartz – 35.9; an albite – 51.9; an anorthite – 3.9; an amphibole – 3.3 and a biotite – 3.9.

[2] ICSD — Inorganic Crystal Structure Database.

The binder was obtained using the method of a single-stage mechanochemical synthesis in an aqueous medium. Synthesis was made within 12 hours, in a 200-litre laboratory pebble mill (type RMSh-200) with a corundum lining.

Definition of strength characteristics: compression strength and a tension in bending, were made with use of hydraulic press PGM 100 with an average speed of a load rise when testing samples 10±5 kg/sm^2 per second.

According to test results, ultimate strength of the binder samples have made 10.8–11.2 MPa at compression and 6.5–7.0 MPa at bending down:.

The basic criterion of qualitative assessment of the obtained binder is increasing of content in the investigated system of the amorphized aluminosilicate component which by results of quantitative X-ray fluorescence analysis has made 25 wt. %.

Process of a felspars leaching from granite raw materials in a course of mechanochemical activation can be characterized by dependence of pH value on a time of mechanical activation (fig. 1).

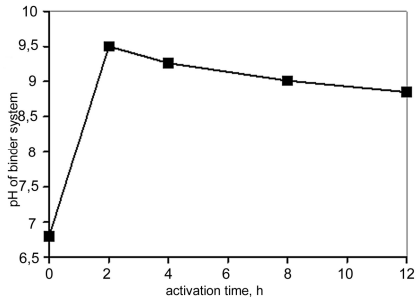

Fig. 1. Dependence of pH of the synthesized binder system on a mechanical activation time

pH value decrease at a stage after 20 % of an activation time can testify to the beginning of aluminosilicate colloidal binder component polymerization process.

In the process of mechanochemical synthesis growth of binder system temperature is observed that quite matches to the main schemes of production of nanopatterned silicate binders (fig. 2).

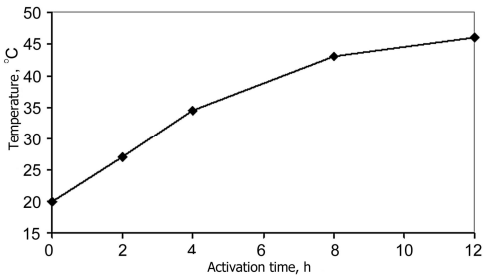

Fig. 2. Dependence of the synthesized binder system temperature on a mechanical activation time

As a rule, low-temperature polymerization in MeO - (Al-Si) O_2 system results in formation of zeolitic phases. It is necessary to note that their fixing is the positive evidence of geopolymeric processes. Unfortunately, it was not possible to detect them radiographically, probably because of nanosized crystallites. Therefore, it has been undertaken a trial to detect short-range order differences of aluminosilicate binder component in the course of activation by the infrared spectroscopy method.

Figure 3 represents the result of superposition of normalized infrared spectra absorption profiles for the binder at a time of activation 2, 4, 8 and 12 hours. It is possible to interpret the indicated increase in intensity of absorption bands related to bridge bonds Si–O–Si (Q^4) of a quartz with the account of spectra normalizing to the absorption band Si–O–Al (Q^4) of felspars as decrease of their concentration in a crystal phase, i.e. mechanochemical dissolution with formation of aluminosilicate colloidal gel.

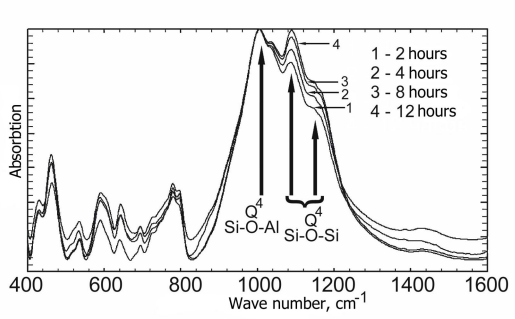

Fig. 3. Superposition of normalized infrared absorption profiles for the binder with a various mechanical activation time

Formation of syngenetic in relation to binder nanoscale systems (globules of aluminosilicate gel) in the course of binder synthesis resulting in formation of epigenetic nanoscale systems (nano-scale zeolitization) forming a mechanical properties allows the obtained binder to classify as nanopatterned [13].

Low-calcium fly ash (type F)

Formation of a mechanical properties of geopolymer binders on a basis of low-calc fly ashes is multifactor process and is in direct relation on extent of solubility of aluminosilicate components in a solution of the alkaline activator. Upon that, geopolymer binders on the basis of fly ashes with equal chemical, mineral and grain-size composition and activators with an equal molar concentration of alkali have essentially differed activity [8, 14].

In this respect the assumption on dependence of solubility of aluminosilicate components on extent of connectivity (polymerization) of silicate structural glass phase motif has been come out. The SiO2-connectivity extent is the integrated characteristic and is equal to relation Si/O in a silicate component of fly ash glass phase. Calculation of SiO2-connectivity extent was carried out on the basis of glass

phase molar composition defined from chemical and quantitative full-profile X-ray analysis data with definition of concentration of an amorphous phase.

To check the assumption made geopolymer binders on the basis of five fly ashes from manufacturers of various geographycal locations: Republic of South Africa (2 samples), USA (1 sample) and Russia (2 samples) were used.

Chemical composition of fly ashes defined by the X-ray fluorescence analysis method is presented in table 2.

Table 2
Chemical composition of the investigated fly ashes (wt. %)

Oxide	RSA		USA	Russia	
	1	2		1	2
SiO_2	53.41	53.44	46.89	59.43	58.98
Al_2O_3	34.55	30.21	22.92	30.39	28.29
TiO_2	1.64	1.74	1.07	1.10	0.97
Fe_2O_3	3.17	2.92	19.23	4.75	4.63
MnO	0.05	0.03	0.04	0.09	0.08
MgO	1.05	1.85	0.80	0.55	1.00
CaO	4.23	6.38	3.76	1.38	3.74
Na_2O	0.10	0.39	0.64	0.64	0.63
K_2O	0.58	0.85	1.68	0.64	0.65
P_2O_5	0.46	0.93	0.33	0.54	0.36
Cr_2O_3	0.04	0.02	0.03	0.00	0.00
NiO	0.01	0.01	0.01	0.00	0.00
V_2O_5	0.03	0.03	0.00	0.03	0.02
ZrO_2	0.05	0.04	0.07	0.05	0.00
$\sum$	99.37	98.84	97.46	99.59	99.35

For quantitative XRD analysis of fly ashes structural data (α-quartz (174-ICSD), mullite (66445-ICSD), magnetite (30860-ICSD), haematite (15840-ICSD) and an anorthite (654-ICSD)) have been used. Si (29288-ICSD) and an anatase (94566-ICSD) in concentration of 20 and 10 wt. % accordingly were used in the capacity of the internal standard for definition of an amorphous phase concentration.

The typical DDM-chart of USA fly ash is shown in figure 4.

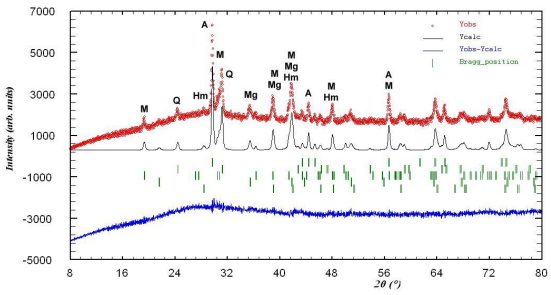

Fig. 4. Result of the USA fly ash roentgenogram calculation.

Data representations are marked out: A - an anatase (standard), M - mullit, Q - quartz, Mg - magnetite, Hm - hematite

Results of definition of fly ash mineral component concentration are shown in table 3.

Table 3
Mineral composition of the investigated fly ashes (wt. %)

Phase	RSA		USA	Russia	
	1	2		1	2
Quartz	4.7	4.9	6.4	9.3	10.7
Mullite	23.8	22.2	13.5	18.7	23.5
Magnetite			7.2	1.9	1.0
Haematite			4.5		
Anorthite					4.3
X-ray amorphous phase	71.5	72.9	68.4	70.1	60.5

Development of the strength characteristics of a cement stone formed in the course of polymerization as a consequence of binder solidification process should be noted in the capacity of the most evident demonstration of the geopolymer binder reaction activity. Value of compression strength has been chosen as the key parameter of geopolymer activity. 5 series of cubic samples with a size of 2×2×2 cm on the basis of investigated five types of fly ashes were molded in order to perform experiment. The molded cubic samples have been subjected to a thermal treatment within 24 hours at temperature of 80 °C with the subsequent demolding and curing at temperature of 22±3 °C, relative humidity of 8-12 % within 28 days.

Selection of optimization factors and parameters was carried out proceeding from the literature [15, 16]. The variation of Na/Al relationship and the temperature parameter was carried out for the purpose to determine their optimum relationship providing maximum compressive strength of the solidified geopolymer binder.

Mechanical properties of the developed compositions of geopolymer binders on the example of 2 domestic production ashes are presented in table 4.

Table 4
Compression strength of developed compositions of the geopolymer binder

Content of components, %			R_{cs}, MPa
NaOH	Fly ash	B/T	
Binder on the basis of fly ashes from the Troitskaya State District Power Station (Russia-1 ash)			
10	90	40	23.4
15.67	84.33	40	45.21
Binder on the basis of fly ashes from the Novotroitskaya Thermal Power Plant (Russia-2 ash)			
8.2	91.7	47.2	18.02
13.65	86.34	35	34.13

By the results presented in table 4 it is possible to draw the conclusion that compression strength parameters of geopolymer binder compositions depending on a type of used fly ash and the content of the alkaline activator vary in a wide range and match to brands defined by concrete compression strength according to GOST 26633-91 "Heavy and fine-grained concretes. Technical specifications" over the range of M150–M400.

As follows from the obtained data, obvious relation between activity of geopolymer binders with chemical and mineral composition of the used fly ashes is not registered.

Feature of phase composition of fly ashes is the essential content of aluminosilicate glass phase which is the basic source of an aluminosilicate material in process of geopolymer solidification (tab. 1). SiO_2-connectivity parameter which is calculated on the basis of the converted glass phase chemical composition by formula (1) [17, 18] has been entered into consideration to characterize a structural condition of a X-ray amorphous glass phase:

$$f_{Si} = \frac{\nu_{SiO_2}}{\nu_{Me_2O} + \nu_{MeO} + 3\nu_{Me_2O_3} + 2\nu_{MeO_2} + 5\nu_{Me_2O_5}} \quad (1)$$

The extent of SiO_2-connectivity of structure forming elements in a glass phase should be read as a polymerization index in various nano-sized clusters of structure forming elements, or silica-oxygen tetrahedral radicals. Check of dependence of geopolymer binder (GPB) compression strength for various fly ashes from phase heterogeneity parameter (glass phase concentration) and parameter of phase-dimensional heterogeneity (SiO_2 polymerization extent) is presented on fig. 5.

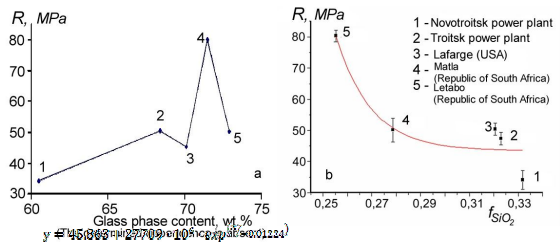

Fig. 5. GPB compression strength for various fly ashes as a function of phase (a) and phase -dimensional heterogeneity (b).

The SiO2-connectivity extent of the glass phase is an integral parameter which could be assumed as additively dependent on concentration of silicate clusters with various connectivity. Upon that the SiO2-connectivity extent is the important characteristic of a fly ash glass phase and has stable negative correlation with activity of geopolymer binders on their basis.

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