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On the Question of the Choice of Natural and Man-Made Materials for Geo-Polymer Binders

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Abstract: Aluminosilicate alkali activated binders of polymerization curing type are promising materials for the widespread introduction of green building ideology. Alkali activation of aluminosilicate materials is a combination of chemical processes including: dissolving of aluminosilicate component; movement and orientation of the dissolution products; polycondensation and polymerization of developed elementary formations.

Key words: Alkali, ideology, polymerization, dissolving, geo-polymer

INTRODUCTION

Research conducted in the field of binding alkaline activation is has growing interest in the scientific community. This is due to the fact that these materials have a more favorable environmental performance and durability compared to the conventional cement.

Theoretically, all material containing in its composition of silica and alumina may be activated with an alkaline agent. In studies (Davidovits and Sawyer, 1985; Davidovits, 1979, 1999; Barbosa *et al*., 2000; Palomo *et al*., 1999; Fernandez-Jimenez and Palomo, 2005; Xu and van Deventer, 2000) carried out to date in this area has studied a number of natural and man-made aluminosilicate materials and their compositions: kaolinite clay, metakaolin, fly ash, granulated blast-furnace slag, mixture of metakaolin and slag, mixture of ash and metakaolin, mixture of slag and metakaolin, a mixture of red mud and slag (obtained by bauxite treating) mixture of fly ash and unburned materials such as kaolin.

To date, there are two models of the chemical reaction of alkaline activation (Palomo *et al*., 1999) the mechanism of which depends on the characteristics of the raw materials used:

- -Si+Ca: emerges in the interaction of domain granulated slag in a solution of a weak alkali. The main products of the reaction are the calcium hydrosilicates
- -Si+Al: the most common example is the activation of metakaolin solution by medium or strong alkali. The reaction products are the formation of a polymerization structure and high strength characteristics

As an aluminosilicate component which is characterized by the reaction activity in highly alkaline medium was studied 16 types of natural ingredients which under certain conditions can have astringent properties and form effective strong composites (Xu and van Deventer, 2000).

MATERIALS AND METHODS

Materials the structure of which proceeds according to the first model are quite common. These include slag alkaline and slag-cement binding materials. Curing of such combinations is due to the hydration of the slag glass under the influence of the hydroxyl ions to form low-basic calcium hydrogarnets group C-S-H (II) as well as hydrogarnets and sodium hydroaluminosilicates (using soda ash and molten glass).

Systems curable by the second mechanism are less common. These include aluminosilicate binders of polymerization curing type-geo-polymers. Aluminosilicate materials which can be used to produce geo-polymers have key parameters significantly affecting the reaction activity of raw materials. It should first be noted that such parameters as the content of reactive silica, content of the amorphous phase, the content of calcium oxide, etc.

In recent years, the research on study of geo-polymer binders were quite active. For the above mentioned there are several conditions. Despite the fact that the Portland cement is widely used in construction the material used since the middle of the 19 century and today it has no analogues, it has some negative characteristics.

One of the main prerequisites for increasing intensification of research on geo-polymer topic is the problem of disposal of industrial waste.

Involvement of huge volumes of aluminosilicate mining and processing industry waste for the production of binders and related materials is represented an urgent

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task of the construction industry. In particular it concerns the development of athermal technologies to create new types of silicate and aluminosilicate binders that according to the researchers is one of the most promising areas of research of modern search of building materials (Fernandez-Jimenez and Palomo, 2003; Strokova and Zhernovsky, 2011).

Besides, in most developed countries the basis of energy is solid organic fuels, especially coal. The continuing growth in the consumption of solid fuel at the end of the last century led to the catastrophic pollution of waste from their combustion-ashes and fuel slag.

One way to dispose accumulated bottom ash is the use of fly ash of thermal electric power station as aluminosilicate component in the production of binding alkaline activation.

Theoretical and technological prerequisites for the creation of binders based on alkali activated aluminosilicate mineral and man-made materials are created by works of scientific schools of V.D. Glukhovski and V.P. Krivenko (Ukraine), J. Davidovich (France), V.I. Kalashnikov (Russian Federation) and others.

The aim of this research is to examine the possibility of using natural aluminosilicate igneous rocks (granites crushing screenings) and Ca-poorest fly ash from thermal electric power stations (type F) as a basis for geopolimeric binders.

Granite crushing screenings: The development of modern building materials science involves extensive use of geomimetic technologies (Geomimetic (Gr. Γ?-«Land" and μίμησις-«imitation") technology-an approach to the creation of artificial stone materials based on simulating the processes of natural mineral and petrogenesis) (Lesovik, 2012). In this case the use of knowledge to transform the aluminosilicate materials of the Earth's crust in the supergene processes for the creation of new technologies of building production gains importance. Primarily it should be taken with the substance conversion processes with changes in the structure and chemical composition of rock-forming minerals in the dispersion in particular the mechanochemical leaching of aluminosilicates at milling in a liquid medium (Molchanov *et al*., 1988).

Thus, according to V.I. Molchanov "experimental data on shredding of various types of aluminosilicates in different types of solutions showed that the minerals lost first alkaline and alkaline-earth elements are then successively transformed into a number of micaceous minerals, clay minerals and finally hydrated simple oxides of silicon, aluminum and iron. Each stage is accompanied by a corresponding increase in the conversion of the free energy (Gibbs potential). The final stage shows the maximum value of accumulated energy and the high reactivity" (Molchanov *et al*., 1988). On this basis we can formulate a working hypothesis of research in the form of assumptions: the mechanical activation of aluminosilicate materials in an aqueous medium leads to formation of the initial reaction components for the formation of geo-polymer binders without external alkaline activation.

To test the proposed position we used solid of acid composition in the form of granite screenings Poltava deposit (Gereevsky quarry, Ukraine) as a source raw material for production of nanostructured aluminosilicate binder.

The chemical composition of samples of granite screenings was determined by X-Ray Fluorescence analysis (XRF) at ARL 9900 X-ray WorkStation (Thermo Scientific) (Table 1). X-ray diffraction spectra were obtained on a diffractometer ARL X'tra using λCuKα and λCoKα-radiation.

Measurement of the specific surface area was held using SoftSorbi-II ver.1.0., designed to measure the specific surface area of dispersed and porous materials by comparing the volumes of gas-adsorbate sorbed by the test sample and a standard sample of material with a known specific surface area. Nitrogen adsorbate was used as gas-adsorbate.

As follows from Table 1 various size fractions of granite screenings are characterized by small variations in the chemical composition.

Quantitative classic full RFA was performed using DDM Program (Ver.1.95c) (Solovyov, 2004). ICSD (ICSD-Inorganic Crystal Structure Database) data were used as structure models-α-quartz SiO_2 (74.529-ICSD), albite (Na0.75Ca0.25) Al1.26Si2.74O8 (34916-ICSD), anorthite $CaAl_2Si_2O8$ (654-ICSD), hornblende Na0. 9K0.4 Ca1.6 Mg2.8 Fe1.4 Ti0.5 Al2.4 Si_6O_{23} (OH) (9661-ICSD) and biotite K (Fe2.554Al0.446) ((Al1.55Si_2.45) O10) (OH) 2 (95,359-ICSD) to determine the concentration of the amorphous phase as an internal standard we used anatase TiO_2 (94566-ICSD) at a concentration of 20 wt.%.

Table 1: Chemical composition of the sample granite from 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	99.47
1	70.6	15.7	3.33	2.60	0.49	0.03	2.01	4.06	0.70	99.52
2	66.8	16.2	4.69	3.05	1.24	0.11	2.21	3.75	1.14	99.19
3	67.4	15.6	4.82	3.13	1.33	0.10	2.25	4.01	0.62	99.26

*Sample 0: unfractionated granite screenings; sample 1: fraction>1.25 mm; sample 2: fraction<0.315 mm and sample 3: fraction 1.25-0.315 mm

The mineral composition of granite according to the results of quantitative XRF presented by composition (wt.%): Quartz-35.9; albite-51.9; anorthite-3.9; hornblende-biotite and 3.3-3.9.

The binder was obtained by one-stage mechano-chemical synthesis in aqueous medium. Synthesis was carried out for 12 h in 200 L laboratory ball mill (type: RLL-200) with alumina lining.

Determination of strength characteristics compressive strength and flexural strength were conducted on a hydraulic press PGM 100 with an average rate of increase of load during the test specimens: 10±5 kg/cm^2/sec.

According to test results the strength of the binder samples made-10.8-11.2 MPa compressive and flexural: 6.5-7.0 MPa.

The main key criterion qualitative evaluation of the resulting binder is the increase of amorphous aluminosilicate component content in the system which according to the results of quantitative XRF was 25 wt.%.

Leaching of the feldspar of granite raw material during the mechanical activation can be characterized by the pH dependence from the time of mechanical activation (Fig. 1).

The decrease of pH on stage after 20% of the activation time may indicate the beginning of the polymerization process of colloidal silica-alumina binder component.

In the course of mechanochemical synthesis we can mark of the rise in temperature of the binder which is consistent with the basic scheme for obtaining of nanostructured silicate binders (Fig. 2). Generally, low temperature polymerization in MeO-(Al-Si) O_2 system results in the formation of the zeolite phases. It should be noted that their fixation is direct evidence geo-polymerization processes. Unfortunately, the X-ray could not detect them. Probably due to the nano-size of the crystallites. Therefore, we made an attempt to find short-range differences of aluminosilicate binder components in the process of IR spectroscopy activation.

Figure 3 shows the result of the superposition of the normalized profiles of IR spectra absorption of binder at

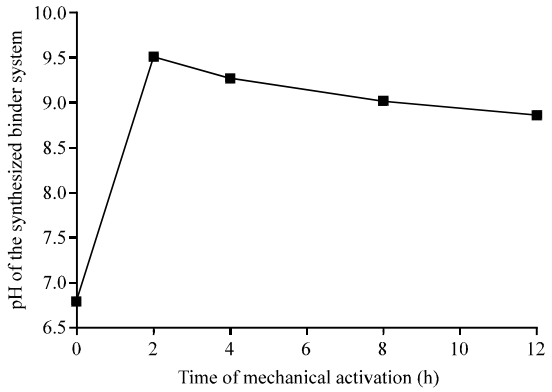

Fig. 1: Dependence of the pH of the synthesized binder system from time to time of mechanical activation

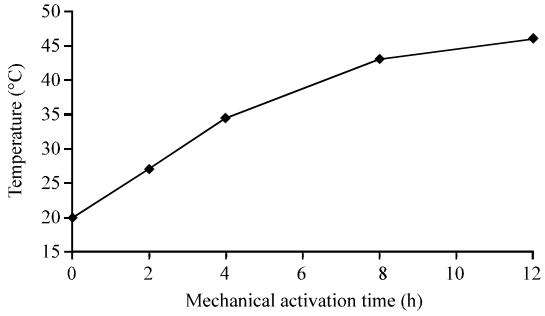

Fig. 2: Dependence of the temperature of the synthesized binder system from the time of mechanical activation

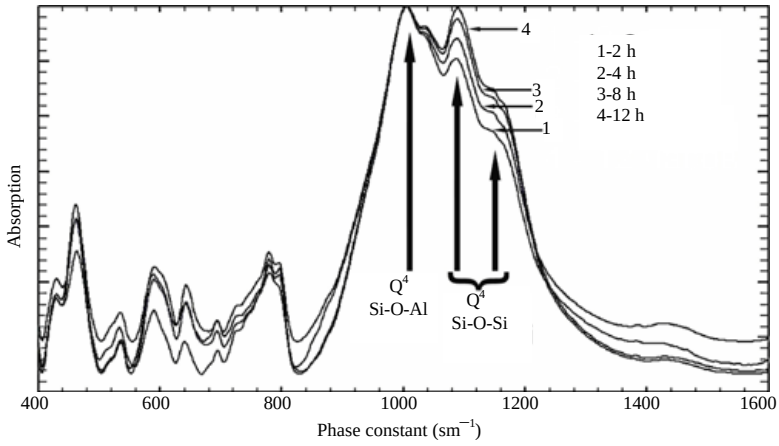

Fig. 3: Superposition of normalized IR absorption profiles of the binder with different time of mechanic activation

the time of activation 2, 4, 8 and 12 h. Noted increase in the intensity of bands absorption related to bridged Si-O-Si (Q4) of quartz with the normalization of the spectra to band absorption of Si-O-Al (Q4) of feldspar can be interpreted as a decrease in their concentration in the crystalline phase, i.e., mechanochemical dissolution with the formation of colloidal silica-alumina gel.

Formation of syngenetic with respect to the binder, nanosystems (aluminosilicate gel globules) leading to the formation of epigenetic nanosystems (nanoscale zeolitization) forming the mechanical properties in the synthesis of the binder allows to classify the resulting binder as nanostructured (Zhernovski *et al*., 2014).

RESULTS AND DISCUSSION

Low-calcium fly ash (type F): Formation of the strength properties of geo-polymer binders based on Ca-poorest fly ash is a multifactorial process and is directly dependent on the degree of solubility of silica-alumina components in the solution of alkali activator. In these conditions geo-polymer binders based on fly ash with the same chemical and mineral and granulometry composition and activators with the same molar concentrations of alkali have substantially differing activity (Glukhovsky *et al*., 1981; Duxson *et al*., 2005).

In this regard, it was suggested that there exists a dependence of the solubility of aluminosilicate components from the degree of connectedness (polymerization) of silicate structural motif of the glass phase. The degree of SiO_2-connectivity is an integral characteristic is equal to the ratio of Si/O in the silicate glass phase component of the fly ash. The calculation of the degree of SiO_2-connectivity is based on a molar composition of the glass phase that is determined from the data of chemical and quantitative full-profile X-ray analysis with the definition of amorphous phase concentration.

To test the hypothesized we used geo-polymer binders based on the five fly ashes from producers of different geographical origin: South Africa (2 samples), USA (1 sample) and Russia (2 samples). The chemical composition of fly ash determined by XRF analysis is presented in Table 2.

A typical of DDM diagram of fly ash from USA is shown in Fig. 4. The results of determination of the concentrations of mineral components of fly ashes are shown in Table 3.

Table 2: Chemical composition of the studied fly ash (wt.%)

	SAR			Russia	
Oxide	1	2	USA	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
Σ	99.37	98.84	97.46	99.59	99.35

For quantitative XRD of fly ash we used structural data-α-quartz (174-ICSD), mullite (66445-ICSD), magnetite (30860-ICSD), hematite (15840-ICSD) and anorthite (654-ICSD). As an internal standard to determine the concentration of the amorphous phase were used Si (29288-ICSD) and anatase (94566-ICSD) at a concentration of 20 and 10 wt.%, respectively

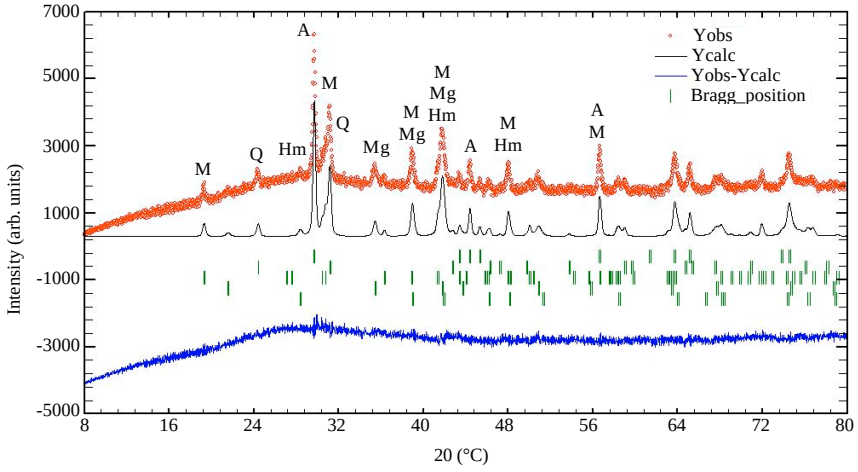

Fig. 4: The result of the calculation of radiographs of fly ash from USA. Denoted reflections: A: Anatase (standard), M: Mullite, Q: Quartz Mg-magnetite, Hm: Hematite

Table 3: The mineral composition of the studied fly ashes (wt.%)

	SAR			Russia	
Phase	1	2	USA	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
Hematite	-	-	4.5	-	-
Anorthite	-	-	-	-	4.3
X-ray amorphous phase	71.5	72.9	68.4	70.1	60.5

Table 4: The compressive strength of developed compositions of geo-polymer binders

Components content (%)			
NaOH	ЗУ	B/T	$R_{cж}$ (MPa)
Binder on the basis of fly ash form Troitsk RPS (fly ash Russia-1)			
10.00	90.00	40.0	23.40
15.67	84.33	40.0	45.21
Binder on the basis of Novotroitsk CHP station (fly ash Russia-2)			
8.200	91.70	47.2	18.02
13.65	86.34	35.0	34.13

As most demonstrated reactivity of geo-polymer binder, we should note the appearance of strength characteristics of the cement stone formed during polymerization as a consequence of binder curing. The magnitude of the compressive strength was chosen as the parameter defining the activity of geo-polymer. For the experiment we formed 5 series of sample- cubes 2×2×2 cm on the basis of study of five kinds of fly ash. Formed sample cubes were exposed to heat treatment for 24 h at a temperature of 80°C, followed by demoulding and keeping at temperature 22±3°C, relative humidity of 8-12% within 28 days.

The choice of factors and optimization parameters was carried out on the basis of literature sources (Rangan, 2008; Harjito and Rangan, 2005). Varying the ratio of Na/Al and temperature parameter was performed to identify the optimal ratio ensuring maximum compressive strength of hardened geo-polymer binder. Strength properties of developed geo-polymer binders compositions at Example 2 of fly ashes of domestic production are shown in Table 4.

According to the results shown in Table 4, it can be concluded that the shear strength of compositions of geo-polymer binders depending on the kind of fly ash and alkali content of the activator varies in a wide range and corresponds to marks on the compressive strength of concrete according to GOST 26633-91 "Heavy-weight and fine concretes. Specifications "in the range of M150-M400.

CONCLUSION

As can be seen from the data there is no obvious connection between the activity of geo-polymer binders and the chemical and mineral composition of fly ashes used.

A feature of the phase composition of fly ash is the essential content of the aluminosilicate glass phase which is the main source of aluminosilicate material in the process of geo-polymerization curing (Table 1). To characterize the structural state of X-ray amorphous glass phase we studied a SiO_2-connectivity parameter which is calculated on the basis of the chemical composition of the glass phase recalculated according to the Eq. 1 (Appen, 1974; Glukhovsky *et al*., 1981).

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

The degree of SiO2-connectivity of the structure forming elements in glass phase should be understood as an indicator of polymerization in into various nanosized clusters of structure forming elements-silicon-oxygen tetrahedral radicals.

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