

Effect of phase and nano-sized heterogeneity of vitreous phase in low-calcium aluminosilicates on strength properties of geopolymer binders

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Abstract This paper concentrates in the development of prospective energy efficient and environmentally friendly construction materials through the use of binders based of natural and industrial aluminosilicates. The low-calcium (type F) fly ash is widely used as aluminosilicate component of geopolymers (GP) base on industrial by product materials. Perlite, is an effective material to produce GP binders. Typical characteristics of aluminosilicates are determined during the cooling from melt and presented by volume of vitreous phase. The aluminosilicate is the main component forming geopolymeric substance, therefore, the strength properties of geopolymer binders depend on the degree of solubility of aluminosilicate precursors in alkali media. According to IR-spectroscopy, the vitreous phase in this material is a nanostructured substance formed from silicate clusters with a different degree of polymerization. Empirical relation between the compressive strength of geopolymer and SiO₂ content in the vitreous phase can be established. Therefore, the complexity of phase and nano-sized heterogeneity of vitreous components of low-calcium aluminosilicates is a dominant factor governing the structure formation in geopolymer binders based on natural and industrial raw materials.

1. Introduction

In addition to hydropower and atomic natural gas and coal power plants remain the main facilities for energy production.

The coal is the main resource for electrical energy production and the consumption of this fuel in different countries is as follows: Australia – 77 %; China – 76 %; Czech Republic – 67 %; Greece – 69 %; Germany – 52 %; USA – 56 %. The leaders of coal fuel consumption are Poland (94 %), South Africa (93 %) and India (78 %) (Fig. 1).

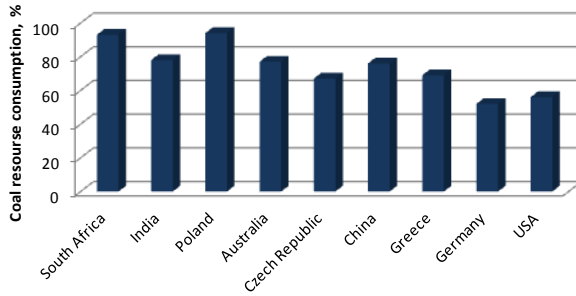


Fig. 1. Global consumption of coal resources

In Russia about 200 power plants work with coal and coal slates. Annually, 50 million tons of coal combustion products (CCP) formed in Russia and only 10 % of such volume is utilized. The most of the CCP stored in disposal areas. For example, annual world fly ash production in 2010 was about 800 million tons, which is 2.5 times less than annual global cement production. As of 2005, Russian power plants disposal areas contained about 1.3–1.5 billion tons of CCP. At the same time utilization of fly ash in industrialized countries varies dramatically: Finland, UK, Germany utilized more than 60 %; Japan, about 50 %; USA, 25 % [1].

Coal combustion product, low-calcium fly ash (class F) are fine-dispersed low-calcium aluminosilicate powders. F Fly ash is a traditional industrial raw material for geopolymer [2–4]. Performance characteristics of geopolymers depend on some factors such as oxide ratio in aluminosilicates, grain-size distribution, chemical and mineral composition, content of nanosized component (X-ray amorphous formations or vitreous phase) pH- value of reaction media, terms of thermal curing etc.

The basic characteristic of aluminosilicate as the main component in geopolymer affecting the structural formation and performance properties, is reactivity, i.e. its solubility in alkaline environment [5, 6]. The content of nanosized components, X-ray amorphous formations or vitreous phase, is the most active component in aluminosilicates. In this work the relationship between SiO_2 -polymerization of the vitreous phase in raw aluminosilicate and the reactivity of geopolymers was demonstrated. SiO_2 -polymerization of the vitreous phase is characterized by the polymerization of nano-sized $[\text{SiO}_4]^{4-}$ elements. According to previous research, this characteristic can be defined by Si/O ratio, determined as type of binding [SiO] in silicate clusters of vitreous phase where V is the molar concentration of oxides [7]:

$$f_{Si} = \frac{V_{SiO_2}}{V_{Me_2O} + V_{MeO} + 3V_{Me_2O_3} + 2V_{MeO_2} + 5V_{Me_2O_5}},$$

Comparative analysis on reactivity of nano-sized components of two different materials, perlite and fly-ash, which are low-calcium aluminosilicates were carried out.

2. Materials and Methods

For the experiment, eight types of low-calcium aluminosilicates of different geographies and genesis were used. Industrial specimens were represented by low-calcium fly ash materials from South Africa (2 sample), USA (2 sample) and Russia (3 sample). In addition, perlite specimen from Russia (1 sample) was used. Chemical composition was determined by XRF analysis using diffractometer ARL 9900 X-ray WorkStation (Thermo Scientific) (Table 1).

The low-calcium aluminosilicates were activated using the alkaline solution. The product used to prepare the alkaline solution was chemical grade NaOH. The XRD spectra were obtained with diffractometer ARL X'tra and ARL 9900 X-ray WorkStation by using Cu $\lambda_{K\alpha 1,2}$ and Co $\lambda_{K\alpha 1,2}$ radiation, respectively. The full-profile XRD quantitative analysis was performed by using a Rietveld algorithm. The Derivative Difference Minimization algorithm (DDM) software was used to account for vitreous phase and to avoid the background effects.

3. Results and Discussion

Table 1. Chemical composition of aluminosilicates

	Chemical composition, %														
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Cr ₂ O ₃	NiO	V ₂ O ₅	ZrO ₂	LOI
SA1	53.41	34.55	1.64	3.17	0.05	1.05	4.23	0.10	0.58	0.46	0.04	0.01	0.03	0.05	0.76
SA2	53.44	30.21	1.74	2.92	0.03	1.85	6.38	0.39	0.85	0.93	0.02	0.01	0.03	0.04	1.01
US1	46.89	22.92	1.07	19.23	0.04	0.80	3.76	0.64	1.68	0.33	0.03	0.01	0.00	0.07	1.3
US2	47.83	28.7	1.07	16.16	0.02	1.04	3.36	0.87	1.65	0.48	0.02	0.01	0.05	0.03	1.9
RU1	59.43	30.39	1.10	4.75	0.09	0.55	1.38	0.64	0.64	0.54	0.00	0.00	0.03	0.05	5.19
RU2	58.98	28.29	0.97	4.63	0.08	1.00	3.74	0.63	0.65	0.36	0.00	0.00	0.02	0.00	6.07
RU3	60.20	30.92	1.17	3.35	0.066	0.577	1.28	0.52	0.75	0.48	0.00	0.00	0.00	0.02	1.85
Perlite	71.52	15.99	0.16	1.67	0.10	0.00	0.85	4.26	4.58	0.00	0.11	0.04	0.00	0.00	7.3

Tables 2 and 3, report on the mineral composition of aluminosilicates. For perlite, based on the calculated model of mineral composition demonstrated that the content of X-ray-amorphous crystallites is up to 100 %, which is the highest content of nano-sized component among studied aluminosilicates.

Table 2. Mineral composition of low-calcium aluminosilicates

	Composition, %							
	SA1	SA2	US1	US2	RU1	RU2	RU3	Perlite
Quartz	4.7	4.9	6.4	8.3	9.3	10.7	6.3	-
Mullite	23.8	22.2	13.5	15	18.7	23.5	25.6	-
Magnetite			7.2		1.9	1.0	1.8	-
Hematite			4.5	11.8				-
Anorthite						4.3		-
Albite							3.9	
Amorphous	71.5	72.9	68.4	64.6	70.1	60.5	62.6	100

Table 3. The mineral composition of perlite

Phase content (wt, %)		Size of crystallite, nm	
tridymite	critoballite	tridymite	critoballite
3	97	1,6	1

3.1. Calculation of polymerization of SiO_2

To calculate the polymerization of SiO_2 in vitreous phase based on oxide concentrations (Table 1) to molar concentration all the crystal phases (Table 2) were deducted. The results are reported in Table 4.

Table 4. SiO_2 -polymerization of vitreous phase

Parameter	SA1	SA2	US1	US2	RU1	RU2	RU3
Si/O	0.255	0.278	0.323	0.274	0.321	0.332	0.395
SiO_2 -polymerization type	Q^{0-1}	Q^{0-1}	Q^{1-2}	Q^{0-1}	Q^{1-2}	Q^{1-2}	Q^{2-3}

According to previous research [7] and the crystal-chemical theory of [SiO]-component in silicates, range of $\text{Si/O}=0,25\dots0,286$ is a characteristic for Si-O-tetrahedra with polymerization degree of Q^{0-1} (SA1, SA2); at $\text{Si/O}=0,286\dots0,333$ the Q^{1-2} structural conformations are formed (US1, US2, RU1, RU2); $\text{Si/O}=0,333\dots0,4$ corresponds to Q^{2-3} (RU3) and $\text{Si/O}=0,4\dots0,5$ results in a formation of Q^{3-4} .

3.2. FTIR of low-calcium aluminosilicates

The presence of certain SiO_2 polymorphs in aluminosilicates is characterized by the bond length in $[\text{Si-O-R}]_n$ clusters. The formation of discrete anionic units from the framework to isolated islands (like orthosilicate) was observed, depending on alkaline oxides in vitreous phase of aluminosilicate system. SiO_2 -polymerization can be recognized using FTIR-analysis. Based on existing research [8, 9], the vitreous phase in fly ash can be classified according to the degree of polymerization of Si-O- tetrahedra (n is the number of Si-O-Si bonds per a SiO_2 tetrahedra – Q^n). The vitreous phase of fly ash SA1 and SA2 corresponds to ortho- diorthosilicate glass with polymerization degree of Q^{0-1} . The amorphous phase polymerization in US1, US2, RU1 and RU2 consists of diortho-chain silicate glass Q^{1-2} ; ash RU3 is characterized by chain-band glass with Q^{2-3} . According to the FTIR-spectroscopy data, fly ash SA1 and SA2 have absorption bonds with wavenumber at $885\text{--}920\text{ cm}^{-1}$

associated with Si-O-Si bonds of ortho- and diorthogroups silicates Q^{0-1} ; US1, US2, RU1 and RU2 have the absorption bands at $980-1000\text{ cm}^{-1}$ typical for Si-O-Si bonds of diortho-chain silicate Q^{1-2} ; for RU3 reflections started to manifest at $1000-1050\text{ cm}^{-1}$, which are associated with Si-O-Si bonds characteristics for chain-band glass at Q^{2-3} .

To identify the influence of SiO_2 -polymerization of low-calcium aluminosilicates on strength properties of geopolymer binders, the compressive strength of eight series of geopolymer cube specimens with a size of 20 mm was tested. The composition of each binder was designed to provide a molar ratio of Na_2O to Al_2O_3 (Na/Al) of 0.75 for compositions #1–4, 6, 7; the ratio of 0.5 was used for composition #5; and 2 was utilized for composition #8 (Table 5).

There is no significant relationship between the strength of geopolymer binder and chemical and mineral compositions of aluminosilicates (Table 5). Lowest strength properties were typical to perlite-based binders.

Table 5. Composition and properties of geopolymer binders

№	Type of aluminosilicate	Content of components, %			$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio	Compression strength, MPa
		Aluminosilicate	NaOH-activator	Water		
1	RU1	63.3	13.7	12.4	0.75	45.2
2	RU2	66.5	10.1	17.2	0.75	34.1
3	RU3	65.7	11.5	22.8	0.75	19.7
4	US1	68.8	12.6	18.5	0.75	50.3
5	US2	71.3	8	20.7	0.5	46.4
6	SA1	73.8	8	28.7	0.75	50.1
7	SA2	72.7	10.5	23	0.75	80.1
8	Perlite	78.4	9.9	10.3	2	18.4

Figure 2 shows the relationship of 28-day compressive strength of geopolymer binders vs. SiO_2 polymerization degree.

The observed trend can be described with the equation $y = 45.863 + 27709 \cdot 10^6 \cdot \exp^{(x/-0.01244)}$, which has a correlation coefficient.

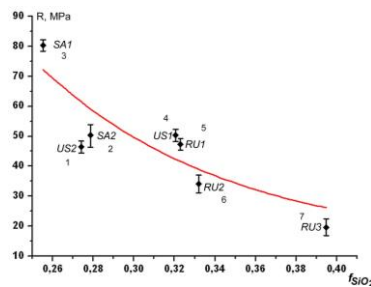


Fig. 2. The compressive strength (R) of geopolymer binder vs. polymerization degree of vitreous phase

This correlation can be used for a forecast of strength for geopolymers based on raw materials with minimal theoretical value (e.g., for orthosilicate $\text{SiO}_4^{-4}=0.25$) and maximal compressive strength for binders base on fly-ash. According to XRD-analysis of hardened geopolymers, the appearance of nano-sized formations like vitreous phase as well as zeolite phases (sodalite, cancrinite, zeolite of X-type) during the solid-phase evolution of amorphous aluminosilicate substance was observed (Table 6).

Table 6. Mineral composition of geopolymers

Type of nanosized component	Size, nm	Content of phase in geopolymer system, %							
		1	2	3	4	5	6	7	8
Sodalite	5	–	–	0.1	10.2	2.1	1.8	1.3	–
Cancrinite	–	–	1.6	–	–	–	–	0.3	–
Zeolite of X-Type	–	–	–	–	–	–	–	–	18
Vitreous phase	–	–	70.7	70.5	–	78.9	77.6	77.6	ND [*]

*– ND is not defined

Conclusion

The degree of cluster connectivity of SiO₂ is unimportant characteristic of low-calcium aluminosilicates affecting the structure formation as well as the strength properties of geopolymer binders.

Comparative analysis of geopolymers with two types of nano-sized components found in low-calcium aluminosilicates proves higher reactivity and strength of components with vitreous phase vs. nano-sized crystal phase.

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