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The Effect of Silica Polymerization in Fly Ash on the Strength of Geopolymers

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ABSTRACT

The formation of the structure of geopolymer binders based on low-calcium fly ash is a multifactorial process that depends on the degree of solubility of aluminosilicate components in the solution of alkali activator. It is observed that the geopolymer binders based on fly ash with an identical chemical and mineral composition, the same grain size, and also activated by the same alkalis can result in a different strength.

This study is based on the assumption that there is dependence between the solubility of aluminosilicate components and the degree of polymerization of the silicates in glass phase. The degree of SiO_2-polymerization is an integral parameter that is equal to the Si molar ratio (f_{Si}) of the silicate component in the glass phase of fly ash. The degree of SiO_2-polymerization can be estimated from the molar composition of glass phase, which is determined from the chemical composition and quantitative X-ray diffraction analysis including identification of the amorphous phase composition.

The SiO_2 polymerization rates of investigated fly ash specimens are confirmed by the IR results, specifically, by comparison of absorption bands of silicate fragments with varying levels of connectivity (Q^{0-4}) in the range of wave numbers of 650–1350 cm^{-1}.

The comparative analysis of the correlation of 28-day strength of geopolymer binders based on fly ash from different sources and level of SiO_2-polymerization demonstrated an inverse relationship with f_{Si} molar ratio and compressive strength.

INTRODUCTION

Low-calcium fly ash (ASTM C618 class F) is a very fine aluminosilicate material formed by the combustion of a bituminous coal. Class F fly ash is an attractive source for geopolymer production [1–3]. Strength properties of geopolymers depend on many parameters: pH of alkali medium, alkali–aluminum ratio, particle size distribution, chemical and mineral composition of fly ash, content of vitreous phase of fly ash, the parameters of thermal curing, etc.

The differences in chemical composition of fly ash are related to mineralogical and geochemical features of enclosing secondary rocks, syngenetic to coal formations. Different concentrations of crystal- and vitreous- components in fly ash are due to the difference in thermal evolution of the materials, such as different fuel combustion temperatures and also cooling rates of dispersed aluminosilicate pyrogenic melt.

One of the basic characteristics of fly ash, reactivity (defined by solubility in alkali medium) is directly related to geopolymer structure [4–7]. The variation of fly ash based geopolymer binder properties is due to the variety of properties of aluminosilicate fly ash (especially, vitreous phase).

In this work, an attempt to demonstrate the correlation between the strength of fly ash based geopolymer and a degree of SiO_2-polymerization within the vitreous phase is undertaken. The degree of SiO_2-polymerization can be determined by the Si molar ratio [8, 9]:

$$f_{Si}=\frac{\nu_{SiO_2}}{\nu_{M_2O}+\nu_{MeO}+3\nu_{M_2O_3}+2\nu_{MeO_2}+5\nu_{M_2O_5}}, \quad (1)$$

where: ν is the molar concentration of oxides.

EXPERIMENTAL PROCEDURE AND RESULTS

The proposed geopolymer binder model is confirmed by using fly ash from five different sources: South African Republic (SA1, SA2), USA (WE1) and Russia (RU1, RU2). The chemical composition of fly ash is measured by X-ray fluorescence (XRF) analysis and using an ARL 9900 X-ray WorkStation (Thermo Scientific), Table 1.

Table 1. Fly Ash Chemical Composition

Oxide	**Chemical Composition, % by weight**				
	SA1	**SA2**	**WE1**	**RU1**	**RU2**
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

The XRD spectra of fly ash are obtained by using Cu $\lambda_{K\alpha1,2}$ and Co $\lambda_{K\alpha1,2}$ radiation, respectively. The quantitative full-profile XRD analysis for the fly ash is performed by using a Rietveld algorithm. To account for vitreous phase and to avoid the background effects, the Derivative Difference Minimization algorithm (DDM) software is used [10]. This algorithm is based on the minimization of local differentials of the difference curve for both experimental and calculated diffraction spectra (by reducing of the oscillation level of a difference curve). The DDM-diagram of fly ash WE1 is reported in Fig. 1. The distribution of mineral components for the studied fly ash specimens is listed in Table 2. The quantitative XRD analysis of fly ash is based on the structural data of: α-quartz (174-ICSD), mullite (66445-ICSD), magnetite (30860-ICSD), hematite (15840-ICSD) and anorthite (654-ICSD). To detect the content of amorphous phase, silica (29288-ICSD) and anatase (94566-ICSD) are added as an internal standard in 20% and 10% by weight of composite powder, respectively. In order to clarify the procedure validity for quantitative XRD analysis, the DDM-diagram for fly-ash WE1 is presented in Figure 1.

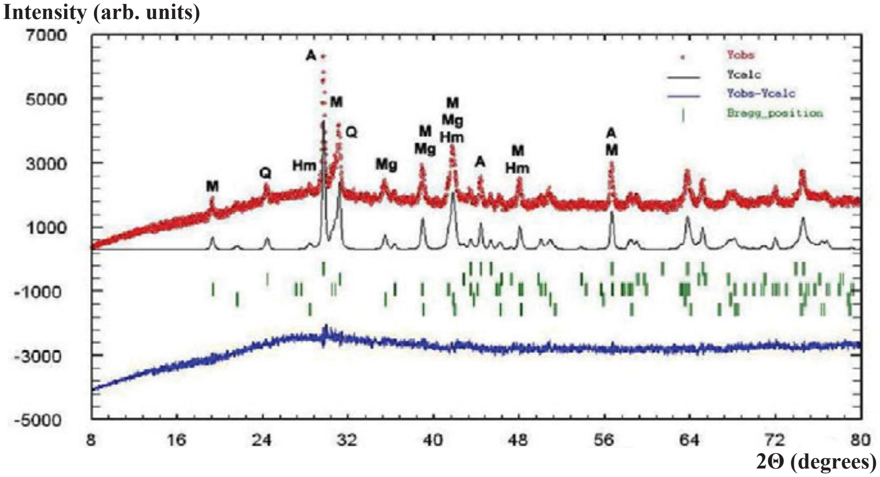


Figure 1: Calculated X-ray spectrum for fly ash WE1A – anatase (standard), M – mullite, Q – quartz, Mg – magnetite, Hm – hematite.

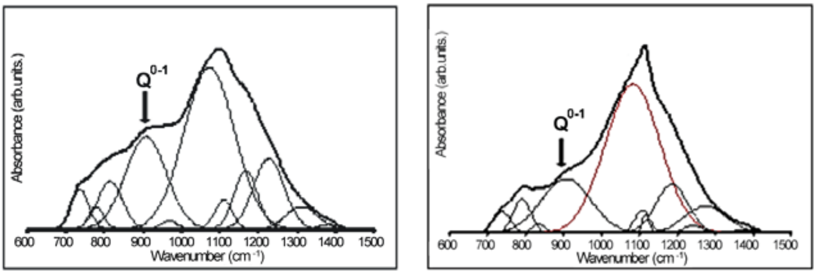
Table 2. Mineral composition of fly ash

Phase	**Mineral Composition, % by weight**				
	SA1	**SA2**	**WE1**	**RU1**	**RU2**
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
Amorphous	71.5	72.9	68.4	70.1	60.5

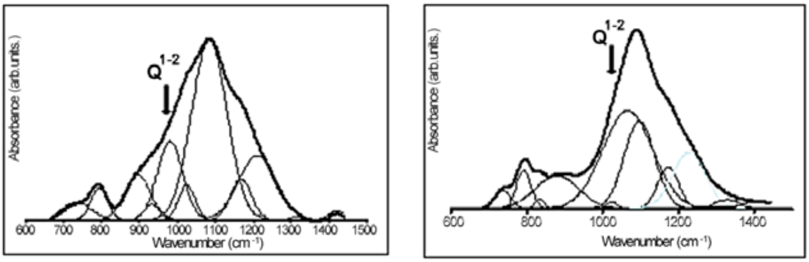
The degree of SiO_2-polymerization of vitreous phase of fly ash can be derived from the total oxide composition (Table 1) and transformed to molar concentration by subtracting the corresponding contribution of crystalline components from the totals (see Table 3). The reactivity of geopolymer binder can be classified using the strength test. Thus, the compressive strength of five geopolymer binder cube specimens with a size of 20 mm was investigated. The composition of each binder was designed to provide a molar ratio of Na_2O to Al_2O_3 (Na/Al) of 0.75. Prepared specimens were exposed to thermal curing at 80 ^{o}C for 24 hours. The specimens were de-molded and cured at 22±3 ^{o}C and relative humidity of 75 % and tested for the compressive strength at the age of 28 days.

DISCUSSION

According to the obtained results, the relationship between the strength of geopolymer binder and chemical and mineral composition of fly ash is not observed. The degree of SiO_2-polymerization of the fly ash can be determined by the IR-spectroscopy as described by Figure 2.



(a) SA1 (b) SA2



(c) WE1 (d) RU1

Figure 2: The deconvolution profile of IR-spectra for investigated fly ash (the range of wave numbers 650-1350 cm^{-1}): Q^{0-1} – Si-O-Si bonds associated with silicate of ortho- and diortho- groups; Q^{1-2} – Si-O-Si bonds associated with diortho-chain silicates

According to the stereochemistry of silicates, all silicates divided to five main structural types in response to the association of SiO_4^{-4} structural unit: ortho- (diortho-), chain-, band, layered- and tecto-silicates [8, 9, 11]. The vitreous phase of fly ash can be classified according to the degree of polymerization of Si-O- tetrahedra (where *n* is the number of Si-O-Si bonds per a SiO_2 tetrahedron – Q^n) [8, 9, 11]. It can be observed that the vitreous phase of fly ash SA1 and SA2 corresponds to ortho- and diortho- silicate glass with polymerization degree of Q^{1-2}. The polymerization of amorphous phase in WE1 and RU1 is referred as diortho-chain silicate glass Q^{1-2} and RU2 ash is characterized by Q^{2-3} chain-band glass. The obtained data indicate the presence of silicate diorthogroups Q^1 in vitreous phase of fly ash, which can significantly affect the reactivity of geopolymer binder.

The degree of SiO_2-polymerization in vitreous phase can be considered as an integral parameter, which depends on the concentration of silicate clusters with different degree of SiO_2 connectivity. The degree of solubility of silicate glass in alkali solutions is known to be reduced with increase of the polymerization degree [9]. Figure 3 demonstrates the relationship of 28-day compressive strength (R) of geopolymer binders vs. the degree of SiO_2 polymerization in vitreous phase. With only five types of fly ash investigated, it is difficult to derive the comprehensive functional relationship between the compressive strength of fly ash based geopolymer binders and the degree of SiO_2 polymerization; however, there is a clear trend which predicts the improved geopolymer binder strength when fly ash with lower degree of SiO_2-polymerization is used.

Table 3. The strength of fly ash based geopolymer binders and corresponding degree of SiO_2-polymerization

Characteristics	**Type of Fly Ash**				
	SA1	**SA2**	**WE1**	**RU1**	**RU2**
Compressive strength (R), MPa	80.3	50.1	50.3	47.3	34.1
Degree of SiO_2-polymerization, f_{SiO2}	0.26	0.28	0.32	0.32	0.33

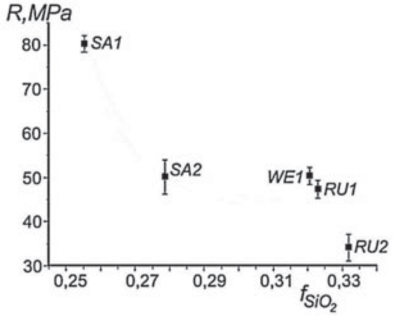


Figure 3: The compressive strength (R) of fly ash based geopolymer binder vs. polymerization degree of vitreous phase

CONCLUSIONS

The reported investigation estimated the degree of polymerization of the silicates in glass phase of fly ash component of geopolymer binders. The SiO_2 polymerization of investigated fly ash specimens are confirmed by the IR results, specifically, by comparison of absorption bands of silicate fragments with varying levels of connectivity (Q^{0-4}).

It is confirmed that the degree of SiO_2-cluster connectivity is a significant characteristics of vitreous component of fly ash affecting the strength of fly ash based geopolymer binders.

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