

# Study of Fly Ash Geopolymer Based Composites with Polyester Waste Addition

Konstantinos Sotiriadis, Olesia Mikhailova

**Abstract**—In the present work, fly ash geopolymer based composites including polyester (PES) waste were studied. Specimens of three compositions were prepared: (a) fly ash geopolymer with 5% PES waste; (b) fly ash geopolymer mortar with 5% PES waste; (c) fly ash geopolymer mortar with 6.25% PES waste. Compressive and bending strength measurements, water absorption test and determination of thermal conductivity coefficient were performed. The results showed that the addition of sand in a mixture of geopolymer with 5% PES content led to higher compressive strength, while it increased water absorption and reduced thermal conductivity coefficient. The increase of PES addition in geopolymer mortars resulted in a more dense structure, indicated by the increase of strength and thermal conductivity and the decrease of water absorption.

**Keywords**—Fly ash, geopolymers, polyester waste, composites.

## I. INTRODUCTION

THE industrial production of cement is an energy consuming process, which has also an important environmental impact due to large amounts of CO<sub>2</sub> generation. The reduction of CO<sub>2</sub> emissions is an issue of concern, in order to achieve sustainable development. The use of industrial by-products rich in aluminium and silicon oxide, such as fly ash, activated by suitable compounds, is a way to produce more environmental friendly binders [1].

Fly ash is a by-product obtained from coal or lignite combustion at electric power generation plants. It is made up of small glass spheres, consisting primarily of silicon, aluminium, iron, and calcium oxides. Its particle size ranges typically between 1 and 150 μm. Crystalline phases commonly identified in fly ashes are quartz, mullite and various iron rich phases such as hematite [2].

Fly ash can be used as raw material for the production of alkali-activated binders. In literature, these materials are often referred to as “geopolymers” [1]. However, other terms have also been used to describe these materials, such as “low-temperature aluminosilicate glass”, “alkali-activated cement”, “geocement”, “alkali-bonded ceramic”, “inorganic polymer concrete”, and “hydroceramic” [3]. The activators more often used to activate fly ash include alkali silicates, hydroxides, carbonates or mixtures of them. Other additions such as sodium aluminates or cement kiln dust can also be applied [1].

K. Sotiriadis is with the Brno University of Technology, Faculty of Civil Engineering, AdMaS-Advanced Materials, Structures and Technologies Centre, Veveří 331/95, 602 00 Brno, Czech Republic (phone: +420 541 148 214; e-mail: sotiriadis.k@fce.vutbr.cz).

O. Mikhailova is with the Brno University of Technology, Faculty of Civil Engineering, Institute of Chemistry, Žitkova 17, 602 00 Brno, Czech Republic (phone: +420 541 147 643; e-mail: mikhailova.o@fce.vutbr.cz).

If only alkali metal (Na or K) silicate or hydroxide is used for the fly ash-based geopolymerization, the early strength of the materials synthesized is low and their durability properties are not significantly improved [4].

Geopolymers comprise three classes of inorganic polymers that, depending on the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, are based on the following three different monomeric units: (–Si–O–Al–O–), polysialate (PS), SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=2; (–Si–O–Al–O–Si–O–), polysialatesiloxo (PSS), SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=4; (–Si–O–Al–O–Si–O–Si–O–), polysialatedisiloxo (PSDS), SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=6 [5]. According to [3], geopolymerization process follows the steps described in Fig. 1.

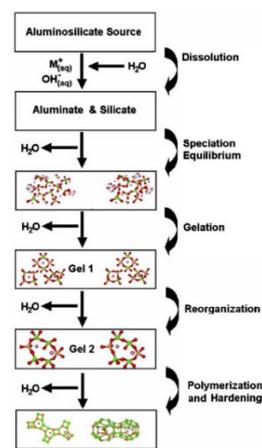


Fig. 1 Geopolymerization process sequence

In general, condensation at the temperature range of 20–90°C results in amorphous geopolymers formation, while crystalline ones are obtained in autoclave at 150–200°C [5]. The main reaction product of alkali activation of fly ash is an alkaline aluminosilicate gel. Its structure consists of tetrahedrally coordinated silicon and aluminum, forming a polymer chain in which the Al<sup>3+</sup> ions replace the Si<sup>4+</sup> ions. The resulting net anionic charge is compensated by the capture of monovalent alkaline cations [6].

Considering that fly ash is classified as F (CaO<10%) or C (CaO>10%), depending on its calcium oxide content, different products are obtained after alkali activation. An alkali-activated binder with high calcium content usually forms a primary binder phase of C–(A)–S–H gel that is amorphous to partially crystalline, relatively highly cross-linked with a moderate degree of Al substitution and a low C/S ratio. Lower levels of calcium lead to a highly cross-linked aluminosilicate which is similar to zeolite frameworks but is generally lacking in long-range crystalline order. This type of gel is described as

N-A-S-H gel [7].

In the present study, fly ash geopolymer was used as a binder to produce composites, which included polyester (PES) waste in their structure. This waste, also known as polyester “synthetic wool” or “PES wadding”, is produced as by-product during the recycling process of PVC waterproofing sheets waste (useless edges of PVC sheets) [8]. After separation of PVC, the PES fibers waste obtained still contain small amount of PVC residual particles. The waste is disposed in landfills because currently it has no other application. The tests described in this study were an initial effort to elucidate whether PES waste could be used along with geopolymers.

## II. EXPERIMENTAL

### A. Materials

Fly ash, provided by the ČEZ thermal power generation station in Počerady (Czech Republic), was used as the basic material to prepare the geopolymeric binder matrix (Table I). Water-glass (silicate modulus  $M_s=3.0$ ; density  $\rho=1430\pm 10$  kg/m<sup>3</sup>), sodium hydroxide and water were also used. Their required quantities for the alkali activation of fly ash were calculated by setting as a prerequisite to achieve Na/Al and Si/Na<sub>2</sub>O ratio values of 1. The Si/Al ratio of the produced fly ash geopolymer was 2.073.

TABLE I  
CHEMICAL COMPOSITION OF FLY ASH (%)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>	LOI
54.6	29.5	5.46	1.81	0.96	1.34	0.25	0.08	1.07

Geopolymer composite specimens (prisms of 40×40×160 mm) were prepared using fly ash geopolymer and polyester (PES) synthetic wool, while normalized siliceous sand with a maximum size of 2 mm was also added in some of the mixtures. In Table II, each mixture's composition is presented. The quantities are given by weight of fly ash. The specimens were left in the moulds and subjected to thermal curing at 80°C for 24 h, and then remained at laboratory conditions for 14 days.

TABLE II  
MIXTURES COMPOSITION (%) BY WEIGHT OF FLY ASH

Code	Fly ash	PES	Sand	Water-glass	NaOH	H <sub>2</sub> O
FP5	1.0000	0.0500	-	0.2420	0.2310	0.3880
FPS5	1.0000	0.0500	0.5000	0.2420	0.2310	0.3880
FPS6	1.0000	0.0625	0.5000	0.2420	0.2310	0.3880

### B. Tests

Compressive and bending strength measurements were performed for all specimens. Three prisms were used for each measurement. The results presented in this paper are the average of the three values.

Water absorption test was performed on specimens which were prior dried at 75°C for 1 day. Before measurement, their side surfaces were covered with a waterproof adhesive tape, so as water could be absorbed only from their bottom surface which was immersed in water. The immersion depth was

approximately 5 mm. In Fig. 2, the schematic diagram of the test set-up used to measure water absorption is shown.

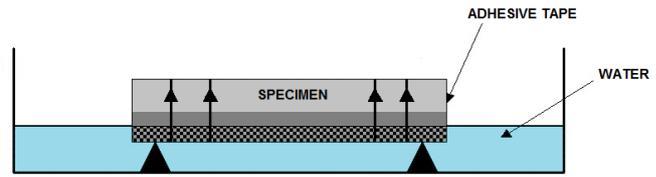


Fig. 2 Schematic diagram of the water absorption test set-up

The water absorption rate (sorptivity ( $S$ ), mm/min<sup>0.5</sup>) was determined, which is due to the capillary porosity of the materials tested. For this purpose, (1) was used:

$$i = S \cdot t^{0.5} \quad (1)$$

where:  $i$  is the total mass increase of each specimen per surface absorption unit (g/mm<sup>2</sup>);  $t$  is the time (min);  $S$  is the sorptivity (mm/min<sup>0.5</sup>).

Thermal conductivity coefficient was measured for each specimen composition using the hot wire method (ČSN EN ISO 8894-1). Thermal conductivity coefficient ( $\lambda$ , W·m<sup>-1</sup>·K<sup>-1</sup>) is determined according to (2):

$$\lambda = \frac{I^2 \cdot R_m}{4 \cdot \pi} \cdot \frac{\ln\left(\frac{\tau_2}{\tau_1}\right)}{\Delta t_2 - \Delta t_1} = \frac{I \cdot V_m}{4 \cdot \pi} \cdot \frac{\ln\left(\frac{\tau_2}{\tau_1}\right)}{\Delta t_2 - \Delta t_1} \quad (2)$$

where:  $I$  is heating electric current (A);  $V_m$  is voltage drop per unit length of the heating wire (V·m<sup>-1</sup>);  $R_m$  is electrical resistance per unit length of the heating wire ( $\Omega \cdot m^{-1}$ );  $\tau_1$ ,  $\tau_2$  are the times from the activation of the heating circuit (min);  $\Delta t_1$ ,  $\Delta t_2$  is the temperature raise of the heating wire after circuit activation in times  $\tau_1$ ,  $\tau_2$ , respectively (°C).

## III. RESULTS AND DISCUSSION

The results of each test are presented separately and their comparison has been done in such a way, so as to study the effect of PES content and the use or not of sand.

### A. Compressive and Bending Strength

Fig. 3 illustrates the compressive and bending strength values obtained for the specimens of each mixture composition. In general, compressive strength values are rather low, while those of bending strength are negligible. The comparison of FP5 and FPS5 compositions shows that the addition of sand in the mixture containing 5% PES increased compressive strength by 46%, while bending strength was 36% lower than that of FP5 specimens. The values obtained for the FPS5 and FPS6 specimens denote an increase of both compressive and bending strength by 76% and 74%, respectively, when PES content was increased in the mixture containing sand. The use of sand strengthened the specimens structure, while use of higher amount of PES contributed in significant increase of strength.

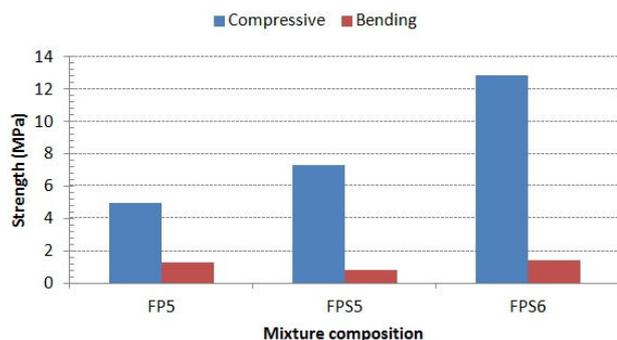


Fig. 3 Compressive and bending strength of the specimens of each mixture composition

### B. Water Absorption

The adaption of water absorption experimental data to (1) was very good, since  $R^2$  value was higher than 93% in all cases. The water absorption test revealed that the prepared materials had sorptivity values (Fig. 4) rather higher than those which are common for cement based mortars and concretes. For the latter ones the values, depending on composition, may range approximately between 0.1 and 0.4 mm/min<sup>0.5</sup>. The addition of sand in the mixture with 5% PES content increased sorptivity by 12%. However, the increase of PES content from 5% to 6.25% in the mixture containing sand reduced sorptivity value by 23%. The results indicate that the addition of sand probably led to a greater porosity of the final material, while the increase of PES content contributed towards the formation of a less porous structure.

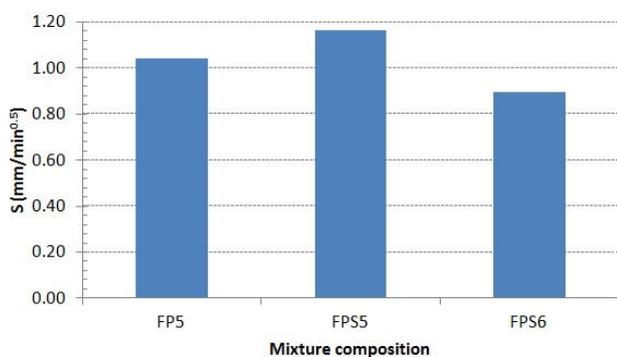


Fig. 4 Sorptivity  $S$  of the specimens of each mixture composition

It is also interesting to observe the evolution of mass increase, due to water absorption, for the specimens of each composition. As illustrated in Fig. 5, the water absorption of FP5 specimens was rather slow in contrast to what was recorded for FPS5 and FPS6 specimens. FPS5 specimens presented initially the most rapid absorption, however the rate was gradually reduced. In this case, the quantity of water absorbed was the highest, showing that FPS5 composition had the highest porosity. In the case of FPS6 specimens, although the rate of mass increase was rather steady and in general higher than that of FP5 and FPS5 specimens, the quantity of water absorbed was the less one until 45 minutes of the test process. This indicates not only lower porosity of FPS6 composition, but also a different pore structure, especially in

comparison to FPS5, which also contains sand. Additional detailed observations could provide more information about the obtained structures.

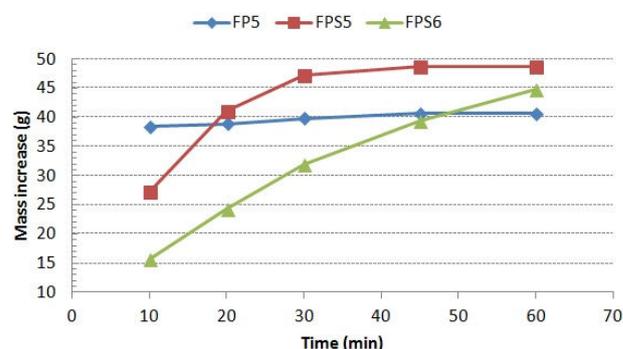


Fig. 5 Mass increase of the specimens during water absorption test

### C. Thermal Conductivity

The obtained thermal conductivity coefficient values were approx. between 0.24 and 0.35 W·m<sup>-1</sup>·K<sup>-1</sup>, being lower than those of hydrated cement pastes which are found in the literature [9]. However, they are higher than 0.1 W·m<sup>-1</sup>·K<sup>-1</sup>, which is a typical upper limit characteristic value for thermal insulating materials. Comparing the values for FP5 and FPS5 compositions (Fig. 6), a 23% reduction was observed when sand was added to the mixture of fly ash geopolymer and PES. The increase of PES content in the mixture of fly ash geopolymer, sand and PES (comparison of FPS5 and FPS6 compositions) had as a result a 45% increase of thermal conductivity coefficient.

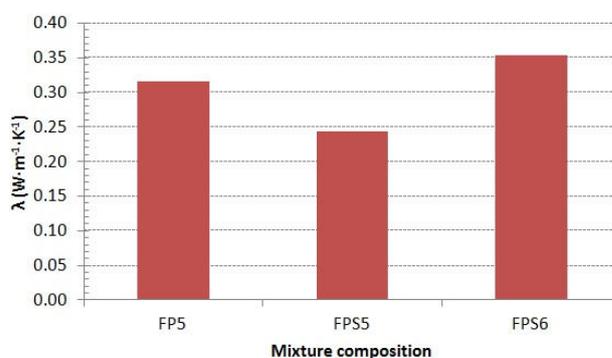


Fig. 6 Thermal conductivity coefficient  $\lambda$  of the specimens of each mixture composition

The obtained results revealed the effect of sand addition and PES content in the strength, water absorption and thermal conductivity of fly ash geopolymer mixed with PES waste. The specimens of FPS6 composition showed the highest compressive and bending strength values in comparison to the specimens of rest compositions. These results led to the assumption that a more dense structure was obtained when sand and 6.25% PES content were used for specimens preparation. The water absorption results confirmed this assumption, since the lowest sorptivity values determined for FPS6 composition indicate low porosity. The highest values of thermal conductivity coefficient may also be correlated to the

more limited quantity of air voids in the specimens of FPS6 composition. According to [10], there is evidence that increasing the apparent density leads to increase of thermal conductivity coefficient. This is due to the reduction of the overall porosity, which minimizes the voids where air could be trapped.

The strength values of FPS5 and FP5 specimens cannot be correlated with water absorption and thermal conductivity results so clearly as in the case of FPS6 specimens. Water absorption of FPS5 specimens was higher and thermal conductivity coefficient was lower than those of FP5 specimens. These findings denote a probable higher porosity of FPS5 specimens structure compared to that of FP5 ones. However, the specimens of FPS5 composition had higher compressive strength values than those of FP5 one (bending strength of FPS5 was lower than FP5, but the difference was minor).

The findings showed that the developed materials can be used in cases that certain application requirements are fulfilled by their characteristics. It should be noted that the study described in this paper was preliminary, in order to have an overview of using a combination of such materials. Further testing, using different binder compositions, is considered to provide more information about the use of PES waste along with alkali-activated inorganic materials.

#### IV. CONCLUSIONS

The following conclusions can be drawn from the present study. Fly ash geopolymer mortars containing PES waste presented higher compressive strength than specimens prepared only with fly ash geopolymer and the same PES waste content. Sand addition resulted in increased water absorption, but reduced thermal conductivity coefficient. The increase of PES waste content in fly ash geopolymer mortars contributed to a significant strength increase and to a more dense structure, since water absorption was decreased, while thermal conductivity coefficient was increased.

#### ACKNOWLEDGMENT

The preparation of this paper was supported by the project CZ.1.07/2.3.00/30.0005 – Support for the creation of excellent interdisciplinary research teams at Brno University of Technology.

#### REFERENCES

- [1] F. Winnefeld, A. Leemann, M. Lucuk, P. Svoboda, and M. Neuroth, "Assessment of phase formation in alkali activated low and high calcium fly ashes in building materials," *Constr. Build. Mater.*, vol. 24, pp. 1086–1093, 2010.
- [2] W. D. A. Rickard, R. Williams, J. Temuujin, and A. van Riessen, "Assessing the suitability of three Australian fly ashes as an aluminosilicate source for geopolymers in high temperature applications," *Mater. Sci. Eng. A*, vol. 528, pp. 3390–3397, 2011.
- [3] P. Duxson, A. Fernández-Jiménez, J. L. Provis, G. C. Lucey, A. Palomo, and J. S. J. van Deventer, "Geopolymer technology: the current state of the art," *J. Mater. Sci.*, vol. 42, pp. 2917–2933, 2007.
- [4] H. Mingyu, Zh. Xiaomin, and L. Fumei, "Alkali-activated fly ash-based geopolymers with zeolite or bentonite as additives," *Cem. Concr. Compos.*, vol. 31, pp. 762–768, 2009.
- [5] S. Andini, R. Cioffi, F. Colangelo, T. Grieco, F. Montagnaro, and L. Santoro, "Coal fly ash as raw material for the manufacture of geopolymer-based products," *Waste Manage.*, vol. 28, pp. 416–423, 2008.
- [6] M. Criado, A. Palomo, and A. Fernández-Jiménez, "Alkali activation of fly ashes. Part I: Effect of curing conditions on the carbonation of the reaction products," *Fuel*, vol. 84, pp. 2048–2054, 2005.
- [7] M. C. G. Juenger, F. Winnefeld, J. L. Provis, and J. H. Ideker, "Advances in alternative cementitious binders," *Cem. Concr. Res.*, vol. 41, pp. 1232–1243, 2011.
- [8] I. Špaček, and J. Kotovicová, "Recyclation of plastic wastes from production of PVC roofing sheets," *MendelNet '09 Agro Conf.*, Mendel University in Brno, Czech Republic, 2009.
- [9] D. P. Bentz, "Transient plane source measurements of the thermal properties of hydrating cement pastes," *Mater. Struct.*, vol. 40, pp. 1073–1080, 2007.
- [10] Y. Luo, and L. Wang, "Research on non-steam-cured and non-fired fly-ash thermal insulating materials," *J. China Univ. Min. Technol.*, vol. 18, pp. 0116–0121, 2008.