World Academy of Science, Engineering and Technology
International Journal of Civil and Environmental Engineering
Vol:9, No:5, 2015

Effect of Fly Ash Fineness on Sorption Properties of Geopolymers Based On Liquid Glass

M. Zelinkova, M. Ondova

Open Science Index, Civil and Environmental Engineering Vol:9, No:5, 2015 publications.waset.org/10001338/pdf

***Abstract*—**Fly ash (FA) thanks to the significant presence of SiO_2 and Al_2O_3 as the main components is a potential raw material for geopolymers production. Mechanical activation is a method for improving FA reactivity and also the porosity of final mixture; those parameters can be analysed through sorption properties. They have direct impact on the durability of fly ash based geopolymer mortars. In the paper, effect of FA fineness on sorption properties of geopolymers based on sodium silicate, as well as relationship between fly ash fineness and apparent density, compressive and flexural strength of geopolymers are presented. The best results in the evaluated area reached the sample H1, which contents the highest portion of particle under 20μm (100% of GFA). The interdependence of individual tested properties was confirmed for geopolymer mixtures corresponding to those in the cement based mixtures: higher is portion of fine particles < 20μm, higher is strength, density and lower are sorption properties. The compressive strength as well as sorption parameters of the geopolymer can be reasonably controlled by grinding process and also ensured by the higher share of fine particle (to 20μm) in total mass of the material.

***Keywords*—**Alkali activation, geopolymers**,** fly ash, particle fineness.

I. Introduction

GEOPOLYMERS are amorphous aluminosilicates, which can be produced by the reaction between silica and aluminosilicate in alkaline medium. Due to its simple, energy efficient and eco-friendly production method, good durability and mechanical properties of geopolymers can replace conventional materials from low tech application (building industry, waste immobilisation) to high tech industry (ceramics with special properties, composites) [1], [2]. Several materials are suitable for geopolymer production, which contains silica and alumina bearing phases, like primary (metakaolin) or secondary (fly ash, slag, red mud, etc.) raw materials [3], [4]. Fly ash (FA) thanks to the significant presence of SiO_2 and Al_2O_3 as the main components is a potential raw material for geopolymers [5].

The primary effect of mechanical activation is the comminution of mineral particles, which results in changes in a great number of physicochemical properties of a particular system. During mechanical activation, the crystal structure of a mineral usually becomes disordered and the generation of defects or other metastable forms can be registered [6]. It has been reported that the application of high energy mills like planetary mills and vibratory mills allow dramatic change of the structure and surface properties of solid materials [7], [8].

The most important consequence of transformation that occurs in material during the mechanical activation is its enhanced reactivity. Mechanical activation, as a method which can improve FA reactivity, is often applied for different applications of this material. Improved reactivity is primarily the result of increased particle fineness. Finer particles of FA represent more reactive material even without extra mechanical impulse. It is known that particles below 45 μm, obtained through various methods of separation, tend to improve mechanical strength of mortar when used as a supplementary cementitious material [9]. Although there are numerous data relating to the mechanical activation of FA, the literature concerning the application of mechanically activated FA for the geopolymer synthesis is rather scarce. The main advantage of using mechanically activated FA in synthesis of geopolymers is the possibility of in bulk utilization of FA, and not only its specific (finer) fraction.

Suresh et al. [10] have conducted the study on the effect of water absorption, apparent porosity and sorptivity on durability of fly ash based geopolymer mortars. The results in this study found that water absorption, porosity and sorptivity of geopolymer mortars specimens influence the durability of geopolymer mortars. The samples with higher water absorption, porosity and water sorptivity have lowest compressive strength. Farhana, Z. F. et al. [11] describe the relationship between water absorption and porosity for geopolymer paste. The geopolymer paste samples at day 90 showed the lowest percentage of water absorption and porosity while the geopolymer paste samples at day 7 showed the highest water absorption and highest porosity. This is due to the structure of samples becomes denser, harder and improved crystallinity from day 7 until day 90. The pore size decreases and the structure became denser. It can be proved by Scanning Electron Microscope (SEM) morphology. The porosity and permeability also decreased hence the durability potentially be improved.

The aim of the presented research is to study the effect of FA fineness on sorption properties of geopolymers based on sodium silicate, as well as to examine the relationship between fly ash fineness and geopolymer´s apparent density, compressive and flexural strength. This paper is engaged to possibilities of preparing of geopolymer mixtures based on modified (ground) fly ash, which was used in specific percentage combinations with unground (original) fly ash.

M. Zelinkova is with Technical University of Kosice, Faculty of Civil Engineering, Vysokoskolska 4, 040 02 Kosice, Slovakia (phone: +421 55 602 4174; e-mail: miroslava.zelinkova@ tuke.sk).

M.Ondova is with Technical University of Kosice, Faculty of Civil Engineering, Vysokoskolska 4, 040 02 Kosice, Slovakia (phone: +421 55 602 4125; e-mail: marcela.ondova@ tuke.sk).

Open Science Index, Civil and Environmental Engineering Vol:9, No:5, 2015 publications.waset.org/10001338/pdf

A. List of Abbreviations

GFA – ground fly ash
OFA – original fly ash
M60 – mortar based of fly ash with milling time 60 min.
Ms – silicate module
d – diameters
d_m – mean particle diameter
ΔS – specific surface area
w/s – water/solids

II. Materials and Methods

A. Materials

In the experimental part of the research, tested mixtures were based on original (OFA) and ground fly ash (GFA), to variations in the amount of GFA. Proposed mixture design consisted of two materials: fly ashes (OFA and GFA) and basic alkali activator (sodium silicate - liquid glass) for the improvement of mechanical properties of fly ash compacts. Chemical composition of fly ash is presented in Table I. As can be seen, the calcium oxide content in fly ash is less than 10% therefore it is classified as Class F fly ash according to ASTM 618 standard.

TABLE I
Chemical Composition of Original Fly Ash

Oxide composition	SiO_2	CaO	MgO	Fe_2O_3	Al_2O_3
Amount [%]	51,84	4,99	2,95	7,70	21,19
Oxide composition	SO_3	P_2O_5	TiO_2	K_2O	
Amount [%]	0,62	0,30	0,93	1,73	

Sodium silicate, also known as water glass or liquid glass, is a versatile inorganic chemical made by combining sand and soda ash at high temperature. It is also the common name for compounds with the formula $Na_2(SiO_2)_nO$. In industry, the various grades of sodium silicate are characterized by their SiO_2:Na_2O weight ratio, which can vary between 2:1 and 3.75:1 [12]. Grades with this ratio below 2.85:1 are termed 'alkaline' activator, which after mixing with fly ash causes a chemical process that allows obtaining new cementing materials (alkali activation).

B. Methods

Experimental course consisted of two phases: modification (grinding) of fly ash, than mixing and testing of samples. Process of fly ash modification by grinding was carried out as follows:

- grinding time: 60 minutes and
- grinding ratio 1/17 (mass of grist to mass of grinding balls).

The granulometric compositions of fly ash (modified and unmodified) is expressed by grain diameters d (0.1) – indicates that 10% of the whole amount of investigated sample is under measured value of the particle size; d (0.5) – 50% and d (0.9) – 90%. Also mean particle diameter (d_m) and specific surface area (ΔS) were monitored. Overview of above mentioned particle fineness parameter is shown in Table II.

TABLE II
Particle Size of Original and Ground Fly Ash

Fly ash	Grain diameter [μm]				
	d(0.1)	d(0.5)	d(0.9)	d_m	ΔS [m^2/g]
OFA	6.053	43.415	182.114	68.45	0.392
GFA	1.642	7.349	44.839	45.47	1.46

Mixtures were prepared by mixing the fly ash with alkaline activator (sodium silicate). The composition of liquid glass used for experiments was as follows: 30.5 % SiO_2; 12.25% Na_2O; 57.25 % H_2O with Ms = 2.5. Five binder mixtures (H1 – H5) with ratio w/s = 0.35 were prepared. All the recipes of mixtures are presented in Table III. Increase/reduction of FA fineness is expressed by amount of particles under and above 20 μm. As it is shown in the table, a maximum amount of fine particles was in the mix H1 (100% of the GFA). Conversely, decreasing portion of GFA in the mixture is reflected in the declining portion of particles up to 20 um (H5).

TABLE III
Mix Design and Proportion of Particle Size of Both Fly Ashes

Mixture	OFA/GFA [%]	Fly ash [g]		Alkali activator [g]	Particle size [%]	
		OFA	GFA	Na_2SiO_3	< 20 μm	> 20 μm
H1	0/100	0	785		78	22
H2	25/75	196	589		70	30
H3	50/50	393	393	650	61	39
H4	75/25	589	196		52	48
H5	100/0	785	0		44	56

Following the mixing, samples (40x40x160mm prisms) were prepared for individual tests. Samples were kept at the laboratory temperature and the relative humidity of 50% for 28 days; subsequently, the water absorptivity, capillarity, water absorption coefficient, apparent density, compressive and flexural strength were determined. Sorption properties were tested in the view of the intended function of tested materials: protective coating of concrete structures.

Capillarity and **Water absorptivity** were tested under national standard [13]; Capillarity test begin with sample drying. After drying to constant mass, one face of the specimen is immersed in 5 to 10 mm of water for a specific period of time and the increase in mass is determined. Standard periods are 10 min and 90 min. Measurements following intervals: 5, 15, 25, 35, 45, 55, 65, 75, 85, 90 minutes were performed in this experiment. Capillarity was calculated using (1):

$$\nu_r = \frac{m_s - m_d}{m_d}.100 \quad [\%] \tag{1}$$

where: ν_r is capillarity, m_s is weight of saturated samples [g], m_d is weight of dry sample [g].

In addition, in the absorptivity test all dried samples were immersed in water for one hour in laboratory conditions. Absorptivity was determined according to (2):

$$\nu = \frac{m_s - m_d}{m_d}.100 \quad [\%] \tag{2}$$

Open Science Index, Civil and Environmental Engineering Vol:9, No:5, 2015 publications.waset.org/10001338/pdf

where: ν is water absorptivity, m_s is weight of saturated samples [g], m_d is weight of dry sample [g].

Water absorption coefficient due to capillary action [14] was measured using mortar prism specimens under prescribed conditions at atmospheric pressure. After drying to constant mass, one face of the specimens was immersed in water to a depth of 5 to 10 mm for a specific period of time. The increase in mass was determined. Standard periods are 10 min and 90 min, for this experiment were determined and measured following intervals: 5, 15, 25, 35, 45, 55, 65, 75, 85, 90 minutes. Capillarity is characterized by absorption coefficient Aw – this parameter was calculated using (3):

$$A_w = \frac{m_t - m_i}{A \times \sqrt{t}} \quad [kg\ /\ m^2.h^{1/2}] \tag{3}$$

Results can also be evaluated due to capillary moisture content m_c using (4):

$$m_c = A_w \times \sqrt{t} \quad [kg.m^{-2}] \tag{4}$$

where Aw is absorption coefficient [kg/m^2.h $^{1/2}$], m_c is capillary absorption [kg/m^2], m_t is mass of sample in time „t“ [kg], m_i is initial mass of sample [kg], A is area exposed to water [m^2], t is time [hour].

Compressive and flexural strength [15]; specimens were tested after 28 days of curing. Load was applied gradually up to strength limit. The compressive strength of samples R_c (MPa) were determined according to (5):

$$R_c = \frac{F}{A_c} \quad [MPa] \tag{5}$$

where F is maximal load breaking force [N], A_c is sectional area of the test specimen [mm^2]

The test of flexural strength was provided using the three point loading. The result of measurement is the maximum value of the force (F) obtained in breach of the body (specimen). Strength of the concrete flexural strength R_f (MPa) is determined according to (6):

$$R_f = \frac{F.l}{d_1.d_2^{\,2}} \quad [MPa] \tag{6}$$

where: F is maximal load force, l is the distance between the support rollers (mm).

III. Results and Discussion

A. Absorption Coefficient Due to Capillary Action

The calculated capillarity moisture content (according to (4)) of mixtures H1-H5 in dependence on testing period is given in Table IV. It is necessary to say here that the test time is expressed as the square root of the monitored testing interval.

TABLE IV
Dependence of Capillary Moisture Content on the Time T $^{0.5}$(s$^{0.5}$)

Testing period [s$^{0.5}$]	17.32	30.00	38.73	45.83	51.96
Capillary moisture content [kg.m^{-2}]	m_c	m_c	m_c	m_c	m_c
H1	0.83	0.90	0.93	0.93	0.93
H2	0.22	0.54	0.62	0.72	0.76
H3	0.14	0.14	0.14	0.14	0.14
H4	0.56	0.97	1.11	2.50	2.50
H5	0.71	0.96	1.14	1.17	1.24
Testing period [s$^{0.5}$]	57.45	62.45	67.08	71.41	73.48
Capillary moisture content [kg.m^{-2}]	m_c	m_c	m_c	m_c	m_c
H1	0.93	0.93	0.93	0.93	0.93
H2	0.76	0.87	0.87	0.87	0.87
H3	0.14	0.14	0.14	0.14	0.14
H4	2.71	2.78	2.78	2.85	2.85
H5	1.31	1.35	1.35	1.35	1.35

Clearer, dependence of m_c (H1-H5) on the square root of time is shown in Fig. 1.

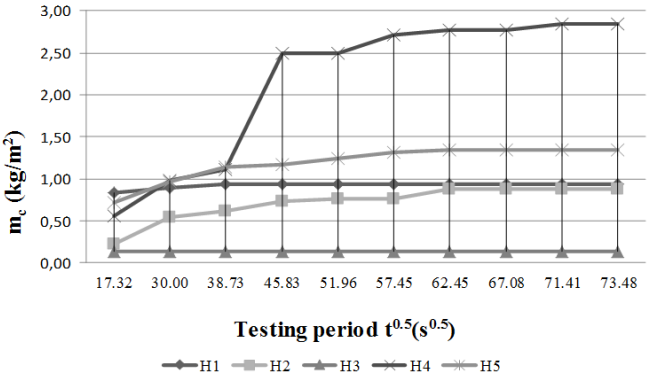


Fig. 1 Results of absorption coefficient due to capillary action by Capillary moisture content m_c

Saturation progress of sample H3 with the same proportion of GFA and OFA (1:1) seems totally linear. Similarly, the sample with 100% share of ground fly ash over the time of 25 min. was constant. Results of the mixtures H2 and H5 are very similar; with a slight increase of absorption to the 65 min. The biggest change was seen in samples H4 (75% OFA). Test interval 25-35 min. showed the highest increase in capillary moisture content (1.39kg.m^{-2}); value in the mentioned interval recorded in others mixtures was 0.03kg.m^{-2} in average.

B. Capillarity

Results of capillarity test are presented in Table V. Values are defined as saturated high [cm] of water above the base waterline in dependence on time. Progress of capillarity line of various mixtures was monitored and is shown in Fig. 2. It is evident that the highest capillarity was measured for the sample H5 containing 100% of OFA with more than 50% (56%) of particles having dimension over 20μm. On this basis (higher porosity of the material due to the low particle fineness), it can be expected that the H5 will receive lower strength values.

Open Science Index, Civil and Environmental Engineering Vol:9, No:5, 2015 publications.waset.org/10001338/pdf

TABLE V
CAPILLARITY EXPRESSED BY HEIGHT IN THE TIME

Testing period [min]	5	15	25	35	45
	v[cm]	v[cm]	v[cm]	v[cm]	v[cm]
H1	0.89	1.78	1.97	1.97	1.97
H2	1.23	2.14	2.30	2.56	2.63
H3	0.84	0.84	0.84	0.84	0.84
H4	0.88	1.30	1.55	1.56	1.56
H5	1.29	2.23	2.63	2.74	2.80
Testing period [min]	55	65	75	85	90
	v[cm]	v[cm]	v[cm]	v[cm]	v[cm]
H1	1.97	1.97	1.97	1.97	1.97
H2	2.63	2.75	2.75	2.75	2.75
H3	0.84	0.84	0.84	0.84	0.84
H4	1.60	1.69	1.69	1.75	1.75
H5	2.95	3.10	3.10	3.10	3.10

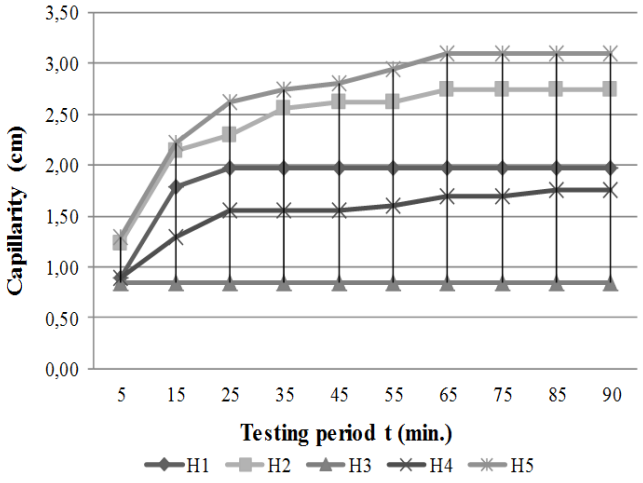


Fig. 2 Results of capillarity test

C. Test of Hardened Samples after 28 Days

Tables VI and VII present the results of the tests verified on the samples H1-H5 after curing time of 28 days.

Measured and calculated results, like in the study of Sivakumar and Tan (2013), show that by increasing share of particles finesses in the mixtures, also the strength (compressive and flexural) is increasing [16]. This was also confirmed in paper of Komljenovic (2010), who stated that the compressive strength results are predominantly affected by the content of fine particles [17].

TABLE VI
RESULTS OF COMPRESSIVE AND FLEXURAL STRENGTH AFTER CURING TIME OF 28 DAYS

Mixture	OFA/GFA [%]	Particle size [%]		Strength [MPa]	
		<20 μm	>20 μm	R_f[MPa]	R_c[MPa]
H1	0/100	78	22	3.17	6.79
H2	25/75	70	30	1.85	4.65
H3	50/50	61	39	1.72	3.84
H4	75/25	52	48	2.11	3.83
H5	100/0	44	56	1.22	3.35

TABLE VII
WATER ABSORPTION, CAPILLARITY AND APPARENT DENSITY TESTING AFTER CURING TIME OF 28 DAYS

Mixture	OFA/GFA [%]	Water absorption [wt. %]	Capillarity After 90 min. [wt. %]	Apparent Density [kg/m^3]
H1	0/100	14.42	0.34	1619
H2	25/75	16.44	0.34	1564
H3	50/50	17.77	0.05	1470
H4	75/25	17.23	1.25	1441
H5	100/0	22.58	0.57	1254

Based on the results, it was also showed that the density of materials directly related to the increase/decrease in strength. The tests confirmed that with the increasing density, the compressive and flexural strength is also increased; both in dependence with particle size (in this case, the particles size to 20μm and under 20μm).

Water absorption and capillarity after 90 min. were also monitored. It is general information about their dependence on the porosity of the material. The total porosity and capillary porosity of the blended samples containing finer fly ash (GFA) was significantly lower than that with coarser fly ash (OFA). The same principle was also retained in the context of water absorption and capillarity. Similar finding was also reported by other investigations [18].

All these statements are confirmed by mixtures H1, H2, H3 and H5. The best results in the evaluated area reached the sample H1, which contents the highest portion of particle under 20μm (100% of GFA). Conversely, the worst values were recorded in the mixture H5. However, the interdependence of individual tested properties was confirmed for geopolymer mixtures corresponding to those in the cement based mixtures: higher is portion of fine particles <20μm, higher is strength and density, lower are sorption properties and probably lower is porosity of the material). Those principles were not manifested by the sample H4. Results of tested properties are out of above mentioned dependence. Therefore results of H4 mixture should not be regarded as relevant. However, four of the five results are sufficient for confirmation of discussed dependence.

IV. CONCLUSION

As a result of the investigation, the effect of fly ash fineness on sorption properties geopolymers was revealed. In addition, difference in strength development was observed on samples prepared based on non-modified and modified (ground) fly ashes. A relationship was found between the geopolymer physical properties (compressive strength, density), sorption properties (water absorptivity, absorption due to capillary action, capillary) and fly ash fineness.

ACKNOWLEDGMENT

This research has been carried out within the SGA project 1/0767/13.

Open Science Index, Civil and Environmental Engineering Vol:9, No:5, 2015 publications.waset.org/10001338/pdf

REFERENCES

[1] J. Junak, N. Stevulova, "Alkali activated binder based on fly ash, "*Chemicals sheets*, Vol. 108, No. 6, pp. 620-623, 2014 (in Slovak).

[2] J. Junak, N. Stevulova, "Activation techniques of coal fly ash for its application as a partial cement replacement in concrete," *Folia Oecologica 3*, Vol. 51, No. 3, pp. 142-147, 2010.

[3] K. Komintsas and D. Zaharaki, "*Geopolymerisation: A review and prospects for the mineral industry*," Mineral Engineering 20, pp. 1261–1277, 2007.

[4] G. Mucsi, J. Lakatos, Z. Molnar and R. Szabo, "Development of geopolymer using industrial waste materials", in *Proc. The 9th International Conference "Environmental engineering,"* Vilnius, Lithuania, 2014, ISBN 978-609-457-640-9

[5] J. Davidovits, *Geopolymer Chemistry and Application*, Institut Geopolimére, Saint Quentin (France), 2008.

[6] P. Balaz and M. Achimovicova, "Mechano-chemical leaching in hydrometallurgy of complex sulphides," *Hydrometallurgy*, Vol. 84, Iss. 1–2, p. 60–68, October 2006.

[7] P. Balaz, *Extractive Metallurgy of Activated Minerals*, Elsevier, Amsterdam 2000, p. 278.

[8] Tkacova, K. *Mechanical Activation of Minerals*, Elsevier, Amsterdam 1989, p. 293

[9] N. Marjanović, Komljenović, Z. Bascarević and V. Nikolić, "Improving reactivity of fly ash and properties of ensuing geopolymers through mechanical activation," *Construction and Building Materials*. Vol. 57, pp. 151-162, 2014.

[10] S. Tokchom et al., "Effect of water absorption, porosity, and sorptivity on durability of geopolymer mortars," *ARPN Journal of Engineering and Applied Sciences*, Vol. 4, pp. 28-32, 2009.

[11] Z. F. Farhana et al., "The relationship between water absorption and porosity for geopolymer paste," *Materials Science Forum*. Vol. 803, pp. 166-172 2015.

[12] G. Lagaly, W. Tufar, A. Minihan and A. Lovell, "Silicates" *in Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, 2005.

[13] STN 73 1316, *Determination of moisture, water absorption and capillarity of concrete*, national standard, 1989.

[14] EN 1015-18, *Methods of test for mortar for masonry. Part 18: Determination of water absorption coefficient due to capillary action of hardened mortar*, 2003.

[15] EN 1015-11, *Methods of test for mortar for masonry. Part 11: Determination of flexural and compressive strength of hardened mortar*, 2001.

[16] N. Sivakumar and L. Tan, "Effect of fly ash fineness on the performance of cement mortar," *Jordan Journal of Civil Engineering*, Vol. 7, No. 3, 2013.

[17] M. Komljenovic, "Mechanical and microtructural properties of alkali-activated fly ash geopolymers," *Journal of Hazardous Materials*, Vol. 181, pp. 35-42, 2010.

[18] P. Chindaprasirt, Ch. Jaturapitakkul and T. Sinsiri, "Effect of fly ash fineness on compressive strength and pore size of blended cement paste," *Cement & Concrete Composites*, Vol. 27, pp. 425-428, 2005.