

EFFECT OF COMPOSITION ON FLY ASH GEOPOLYMERS

¹Cansu Kurtuluş*, ²M. Serhat Başpınar

¹Afyon Kocatepe University, Engineering Faculty, Materials Science and Engineering Dept., Turkey

²Afyon Kocatepe University, Faculty of Technology, Metallurgy and Materials Science Engineering Dept.,
Turkey

ABSTARCT

The geopolymer technology provides a new good and green solution to the utilization of fly ash, avoiding its negative impact on environment and ecology. The aluminasilicate minerals in fly ash can be activated with alkali silicate solution to form geopolymer. In this study highly porous fly ash based geopolymer foams (GFs) were fabricated by a gelcasting technique using hydrogen peroxide as a pore former in combination with stearate based surfactant at different compositions. Moreover, factors that the influence amount of porosity and cell size distribution were investigated. We found that porous geopolymers with density values 620kg/m^3 by this method. Interesting results will be reported.

Key words: Geopolymer, Fly Ash, Peroxide, Foam

1.INTRODUCTION

Fly ash is one of the solid residues composed of the fine particles that are driven out of the boiler with flue gases in coal-fired power plants. It is generally captured from flue gases by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys [1]. Depending upon the source of the coal being burned, the components of fly ash vary considerably. In general, the components of fly ash typically include SiO_2 , Al_2O_3 , CaO and Fe_2O_3 , which exists in the form of amorphous and crystalline oxides or various minerals. In addition to Si, Al, Fe, and Ca, usually fly ash also contains many other trace metal elements, such as Ti, V, Cr, Mn, Co, As, Sr, Mo, Pb and Hg. The concentrations of the toxic trace elements in fly ash could be 4-10 times higher than those in coal [2]. Thus, fly ash is considered as a hazardous material, and the improper disposal of fly ash will not only increase the occupation of land but also deteriorate the environment and ecology [3].

Fly ash (FA) is the most used and suitable waste material in geopolymerization due to the huge amount produced worldwide, estimated to be around 780 million tons annually and its great workability [4]. The geopolymer technology provides a new good and green solution to the utilization of fly ash, avoiding its negative impact on environment and ecology. The alumina and silica in fly ash can be activated with alkali to form geopolymer. Moreover, the toxic trace metal elements can be trapped and fixed in the geopolymer structure [5].

Geopolymer is a synthetic material produced from the reaction of aluminosilicates with an alkaline hydroxide or silicate solution, rendering amorphous polymeric structures with interconnected $-\text{Si}-\text{O}-\text{Al}-\text{O}-\text{Si}-$ bonds. The aluminosilicates can be obtained from natural sources such as kaolin and volcanic ash or from industrial wastes such as fly ash and blast furnace slags [6]. Among many products that are based on geopolymer precursors, geopolymer foams appear to be a very promising material since they are formed at temperatures below 100°C and possess properties similar to foamed glass or foamed ceramics, both of which are produced at highly elevated temperatures, above 900°C [7].

There are two main constituents of geopolymers, namely the source materials and the alkaline liquids. The source materials for geopolymers based on alumina-silicate should be rich in silicon (Si) and aluminium (Al). These could be natural minerals such as kaolinite, clays, etc. Alternatively, by-product materials such as fly ash, silica fume, slag, rice-husk ash, red mud, etc could be used as source materials. The alkaline liquids are from soluble alkali metals that are usually sodium or potassium based. The most common alkaline liquid used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate [8]. Research studies carried out on the development of porous geopolymer were mainly oriented for the development of insulating materials for potential building applications and, some of the foamed agents used included air foaming generator, sodium perborate, hydrogen peroxide, aluminum powder, and biomass materials [9]. Hydrogen peroxide is a well-known blowing agent while the redox reaction of Al in alkaline solution induces porosity by H₂ evolution [10].

Shrinkage of concrete at early age is generally considered as a critical parameter for durability design of concrete structures [11]. Drying shrinkage is a time-dependent deformation due to loss of water by hydrostatic tension from the small capillary pores of the hydrated concrete specimens and may cause severe cracking in concrete that eventually allow the ingress of aggressive agents inside the concrete [12]. Several factors such as aggregate properties, alkaline liquid and water content, binder materials and the curing environment are considered to affect shrinkage behavior of geopolymer concrete [13].

Efflorescence is the formation of white salt deposits on or near the surface of concrete. For geopolymers, as they contain much higher soluble alkali content than conventional cement, efflorescence can be a significant issue when the products are exposed to humid air or in contact with water [14]. Although geopolymer foam concretes are not predominantly intended for structural applications exposed to the weather, efflorescence is still a potential problem. Further investigations to prevent efflorescence, or at least to reduce its rate, are required [15].

The aim of this study was to develop geopolymer by preventing drying shrinkage and also efflorescence in view of potential applications in the field of thermal insulation. The geopolymeric matrices were prepared using different proportions of fly ash and blast furnace slag as the aluminosilicate raw powder and also fiber and perlite as a healing element. To prepare alkali aqueous solutions NaOH and Na₂SiO₃ were preferred.

2. EXPERIMENTAL PROGRAM

2.1. Materials

In the present study, class F fly ash and blast furnace slag were used as binder materials and chemical compositions are listed in Table 1. Sodium silicate solution and 6M NaOH solution was used as an alkali activator. H₂O₂ (50% concentration) was used in experiments as foaming agent. Foam stabilizer (FS) was used in order to obtain foam stabilization. Chopped short polypropylen fiber and expanded perlite were used also.

Table 1. Chemical Composition of Binder Materials (%)

	Fly Ash (FA)	Blast Furnace Slag (BFS)
SiO₂	50,3	35
Al₂O₃	19,1	12
Fe₂O₃	12,4	1
CaO	4,55	40
MgO	4,67	1,5
SO₃	1,8	9,8
K₂O	2,16	0,4
Na₂O	0,786	0,3

2.2. Mixture and Specimen Preparation

The sodium hydroxide flakes were dissolved in water to make a solution. The sodium hydroxide and the sodium silicate solutions were mixed together and then added to dry materials and mixed for about five minutes. After mixing in shear type mixer, samples were casted into the 100x100x100 mm plastic moulds. Samples were cured at 60 °C for 24 hour to obtain faster geopolymerization. Four types of samples were produced based on low and high FA content. Mix design of the samples are given at Table 2. Additive amounts were given as percent weight of total weight of FA+BFS. In this study, BFS is incorporated at %0, %10, %30, %50 level to the total binders and the codes were given B0, B10, B30, B50 respectively. In addition B30 and B50 mixtures were prepared without superplasticizer also. The codes were given BS30 and BS 50. Bulk density of the samples was calculated by simply dividing weight of the samples to volume.

Table 2. Mix design of the samples and measured properties.

Main Components	% wt
FA	50-100
BFS	0-50
Total	100
Additives	Wt % of Main Components
FS	0,75
Sodium silicate sol.	50
6 M NaOH	63
Polypropylene fiber	0,2
Perlite (expanded)	0-2,5
Super plasticizer	5,5
H ₂ O ₂	0,85
Bulk density Kg/m³	620-710

3. RESULTS AND DISCUSSION

It has been observed from this experimental investigation that fluidity of geopolymer paste increased significantly with the increment of the BFS in the mixes. For that reason, O₂ gas which is produced by decomposition of H₂O₂, escaped from the slurry. The pore amount in the fresh geopolymer paste strongly depends on the fluidity of the mixture. The cells are closed and almost spherical.

Bulk density of the samples depends on type of aluminosilicate raw material. Bulk density increased with the increment of BFS content. Porosity nature is also affected from composition. Increment of BFS distort the homogeneity of pore structure and also main structure. In the samples B30 and BS30 separation started approximately 1-2mm from bottom (Figure 1a) and the samples of B50 and BS50 foams separated into two parts (Figure 1(b)). Bottom parts of them has non-porous and dense structure and the top part is porous. The only difference between mixtures was superplasticizer. However, noticeable difference was not observed other than dense part volume decrease.

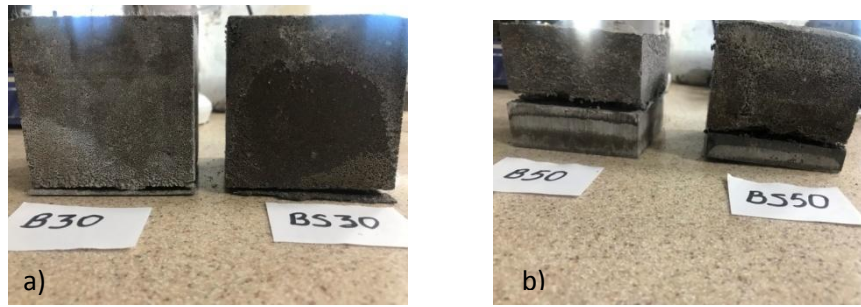


Figure 1. (a) Sample B30 contains %30 BFS and Sample BS30 contains %30 BFS without superplasticizer (b) Sample B50 contains %50 BFS and Sample BS30 contains %50 BFS without superplasticizer

Geopolymerization temperature was also important factor for the production of defect free geopolymer foam samples. Geopolymerization temperature higher than 60 °C increased the risk of drying crack formation and resulted in higher shrinkage. On the other hand lower geopolymerization temperatures decreased the foaming ability of the mixtures and lower geopolymerization rate. It is well known that the foam generation ability of the H_2O_2 increases with increased temperature.

Shrinkage of concrete is a critical parameter for durability of concrete structures. Drying cracks can occur inside geopolymer foam and decrease mechanical properties. By using large aggregate and fiber, drying shrinkage was prevented. BS30 and BS50 samples shrank more as per B30 and B50. In addition that increment of BFS increased drying shrinkage of samples.

Efflorescence is a problem for fly ash geopolymers. Efflorescence potential of samples in different compositions were investigated. Although they contains different amounts of FA and BFS, meaningful results could not achieved. Temperature increase was effective to eliminate efflorescence. It was tried with sample B10. High temperature eliminate the production of white particulates on the samples noticeably (Figure 2).

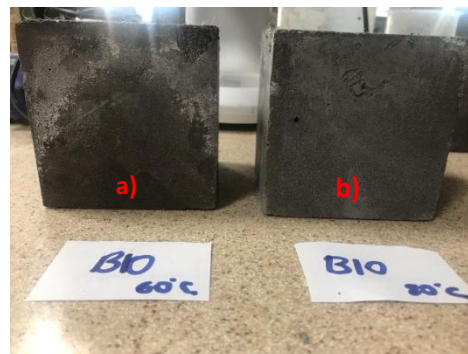


Figure 2. Sample a) was cured at 60°C and sample b) was cured at 80°C

All samples were dried at the laboratory conditions. Every day weight of the samples was measured. All samples showed similar drying curve. Calculated density vs. time graphic was drawn (Figure 3).

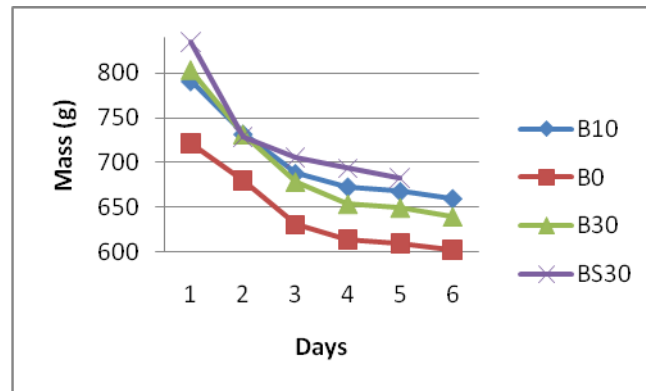


Figure 3. Drying rate of samples

4. CONCLUSION

Based on the above study the following conclusions can be drawn:

- The foam ability was significantly affected by the mix fluidity.
- In the case of high fluidity of the mixture (high BFS) the foam ability is lower. Additionally the increment of BFS causes separation.
- Specimens with lower FA content result in lower strength and higher density.
- Increasing the content of BFS increases fluidity and the fibers uniformly distributed inside the geopolymer paste.
- Efflorescence problem can be overcome with temperature increase.
- All samples showed similar drying curve.
- Addition of higher amount of fly ash resulted in the reduction of drying shrinkage. It can also be observed that addition of higher amount of fly ash reduced mass change as well as drying shrinkage. Any sample not showed drying cracks. This result was achieved by the agency of perlite and fibers inside geopolymer paste.
- The blast furnace slag substitution upto 10% had shown a good fluidity and the samples were in good shape at the end of the process. Higher than %10 of BFC content causes separation.
- Compressive strength was adversely affected by increment of BFS. Max strength was achieved with the sample of B0 and the lowest one with B30 as 1,80MPa and 1,06MPa, respectively

5. REFERENCES

- [1] Ahmaruzzaman M., "A review on the utilization of fly ash," *Prog. Energy Combust. Sci.*, vol. 36, no. 3, pp. 327–363, Jun. 2010.
- [2] Neupane G. and Donahoe R. J., "Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests," *Fuel*, vol. 104, pp. 758–770, Feb. 2013.
- [3] Zhuang X. Y. *et al.*, "Fly ash-based geopolymer: Clean production, properties and applications," *J. Clean. Prod.*, vol. 125, pp. 253–267, 2016.
- [4] Duan P., Yan C., and Zhou W., "Influence of partial replacement of fly ash by metakaolin on mechanical properties and microstructure of fly ash geopolymer paste exposed to sulfate attack," *Ceram. Int.*, vol. 42, no. 2, pp. 3504–3517, Feb. 2016.
- [5] Li Q. *et al.*, "Immobilization of simulated radionuclide $^{133}\text{Cs}^+$ by fly ash-based geopolymer," *J. Hazard. Mater.*, vol. 262, pp. 325–331, Nov. 2013.
- [6] Duxson P., Fernández-Jiménez A., Provis J. L., Lukey G. C., Palomo A., and Van Deventer J. S. J., "Geopolymer technology: The current state of the art," *J. Mater. Sci.*, vol. 42, no. 9, pp. 2917–2933, 2007.

- [7] Srinivasan K. and Sivakumar A., "Geopolymer Binders: A Need for Future Concrete Construction," *ISRN Polym. Sci.*, vol. 2013, pp. 1–8, 2013.
- [8] June J. *et al.*, "Geopolymer Concrete with Fly Ash," *Second Int. Conf. Sustain. Constr. Mater. Technol.*, vol. 7, no. 6, pp. 1493–1504, 2010.
- [9] Novais R. M., Buruberry L. H., Ascensão G., Seabra M. P., and Labrincha J. A., "Porous biomass fly ash-based geopolymers with tailored thermal conductivity," *J. Clean. Prod.*, vol. 119, pp. 99–107, 2016.
- [10] E. Landi *et al.*, "Alkali-bonded ceramics with hierarchical tailored porosity," *Appl. Clay Sci.*, vol. 73, no. 1, pp. 56–64, 2013.
- [11] Bakharev T., Sanjayan J. G., and Cheng Y.-B., "Alkali activation of Australian slag cements," *Cem. Concr. Res.*, vol. 29, no. 1, pp. 113–120, Jan. 1999.
- [12] Deb P. S., Nath P., and Sarker P. K., "Drying shrinkage of slag blended fly ash geopolymer concrete cured at room temperature," *Procedia Eng.*, vol. 125, pp. 594–600, 2015.
- [13] Kong D. L. Y. and Sanjayan J. G., "Effect of elevated temperatures on geopolymer paste, mortar and concrete," *Cem. Concr. Res.*, vol. 40, no. 2, pp. 334–339, Feb. 2010.
- [14] Škvára F., Kopecký L., Myšková L., Šmilauer V., Alberovská L., and Vinšová L., "ALUMINOSILICATE POLYMERS-INFLUENCE OF ELEVATED TEMPERATURES, EFFLORESCENCE," 2009.
- [15] Zhang Z., Provis L., Reid A., and Wang H., "Geopolymer foam concrete: An emerging material for sustainable construction," *Constr. Build. Mater.*, vol. 56, pp. 113–127, 2014.