Part 3

ASH AND SLAG HANDLING

3.5. Use of ash and slag from power coals

3.5.1. Beneficiation of ash and slag from power industry in Russia

3.5.1.3. High strength Portland cement free cementitious mortar

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ABSTRACT

The aim of this study is to product a fly ash based binder without Portland cement. Type C fly ash was activated by NaOH with different molar ratios and cured in three different curing conditions (standard, steam and autoclave). Flexural and compressive strength values of mixtures were compared with conventional Portland cement mortars. In the second stage of this study, mechanical properties of fly ash based binders were improved by using silica fume and ground granulated blast furnace slag. Test results showed that the low early strength of FA based geopolymer can be improved by slag replacement and high performance geopolymer mortars can be produced by autoclave curing. Incorporation of fly ash by 50 % ground granulated blast furnace slag and 10% silica fume was significantly increased the mechanical properties of autoclaved mortars. Drying shrinkage and swelling of geopolymer mortars were similar to Portland cement mortar. Both steam curing methods were effective in terms of reducing drying shrinkage and swelling of geopolymer mortars.

Keywords: geopolymer, fly ash, ground granulated blast furnace slag, silica fume, thermal treatment, mechanical properties, dimensional stability.

1. INTRODUCTION

Geopolymers can be classified as a new class of synthetic alumino-silicate materials formed by the reaction between alumino-silicates and oxides in alkaline media [1]. Various naturally occurring and industrially produced aluminosilicate solids are used for geopolymer synthesis. Recently there has been a growing trend to use fly ash in geopolymers due to their easy availability, good workability during processing and improved durability in the final product [2]. The alkali activation of fly ashes (AAFA) is a special procedure by which the grey powder (FA) is mixed with certain alkaline activators and then the mixture is cured under a certain temperature to produce solid materials. The glassy constituent of the fly ash transforms into a well-compacted cement. The main reaction product formed in AAFA is an amorphous aluminosilicate gel [3, 4]. This product also considered as a "zeolite precursor" [5]. This new type of cement can be used especially in precast concrete industry, since, when thermally cured, it reaches compressive strength values up to 50 - 60 MPa in a short period [6]. Thus, the demoulding and storage stages can be shortened, consequently raising the factory output. Furthermore, these materials, which adhere extraordinarily well to the reinforcing steel, and have a highvolume stability, fire resistance and durability in aggressive environments. Finally, they may be competitively priced with respect to Portland cement based materials [7]. Due to easy, energy efficient, eco-friendly processing and excellent mechanical properties, geopolymers are fast emerging materials of choice for a range of construction and building materials, fire resistance ceramics, composites, and provides a matrix suitable for stabilization of toxic wastes [2].

The process of activation of fly ashes allows to obtain of a material with similar cementing features with ordinary Portland cement. Also this process brings important economical and environmental benefits compared to the traditional manufacture of Portland cement. The emissions of CO_2 to the atmosphere decrease, the energy consumption also decreases, the destruction of natural quarries would be attenuated, etc. [8].The limiting factor which has hindered the use of fly ash in geopolymers is its low reactivity. The low reactivity characteristic of fly ash leads to slow setting and early strength development [2].

The present paper reports the mechanical properties of type C fly ash based geopolymer mortars under different curing conditions. And the main aim of this study is to develop a high strength fly ash based geopolymer by incorporation of ground granulated blast furnace slag and silica fume.

2. MATERIALS AND EXPERIMENTATION

The chemical compositions of type C fly ash (FA), ground granulated blast furnace slag (GGBFS) and silica fume (SF) used in this study are shown in Table 1. FA and GGBFS have been procured from Soma power plant and Ereğli steel plant from Turkey, respectively. Blaine fineness values of FA and GGBFS were 390 m²/kg and 485 m²/kg, respectively. The specific surface area of the commercial SF is 20000 m²/kg (BET nitrogen adsorption method).

Portland cement (CEM I 42.5N) with Blaine fineness of $368 \text{ m}^2/\text{kg}$ has been used as the reference binder. The chemical composition of Portland cement (PC) is also given in Table 1.

-		SiO_2	Fe ₂ O ₃	Al_2O_3	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Free CaO
-	FA	42.14	4.64	19.38	26.96	1.78		1.13	2.43	1.54
-	GGBFS	35.71	0.80	14.52	32.13	9.39				
-	SF	92.26	1.97	0.89	0.49	0.96	0.42	1.31	0.33	
-	PC	19.55	2.11	5.91	63.31	1.11	0.19	0.79	2.42	1.37
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Table 1. Chemical compositions (%) of FA, GGBFS and SF

Crushed limestone sand (0–4 mm) was used as aggregate in all mortar specimens. The alkaline solution used in this study was sodium hydroxide in flake form (NaOH with 98 % purity). The activator solution was used in the mixtures in cold state.

Five alkali-activated fly ash mortar mixtures and a control PC mortar mixture were prepared based on previous studies. In the first stage of this study, the effect of molar NaOH ratios on the mechanical properties of fly ash based geopolymer was investigated with 4, 5 and 6 M NaOH solutions. At the second stage, the fly ash was replaced with 50 % ground granulated blast furnace slag and 10 % silica fume and effects of these mineral admixtures on the mechanical properties and dimensional stability were determined. 5 M NaOH solution were used in these tests. The aggregate to binder ratio of 2.75 and solution to binder ratio of 0.60 were kept constant for all geopolymer mixtures. The water to cement ratio of PC mortar was 0.45. All test batches were mixed by using an electrically driven mechanical mixer conforming to the requirements of ASTM C305 [9]. Initially, binder and aggregate were mixed in a dry state for a minute and then the activator solution was gradually added while mixing continued for about 3 minutes. Fresh mixtures were cast into steel moulds and kept in a humidity cabinet (20 °C temperature and 90 % relative humidity). One group of specimens was kept in the humidity cabinet for 4 h before steam curing of 70 °C for 6 h. After steam curing, the specimens were demoulded. The other group of specimens was kept in the humidity cabinet for 24 h. After demoulding, the specimens were autoclaved at 210 °C and under 2.0 MPa pressure for 6 h. The specimens, which were subjected to heat treatment, were kept in laboratory atmosphere for cooling after completion of their curing periods. The heat-treatment cycles are shown in Fig. 1. The remaining specimens were cured in standard conditions (water curing at ~20 °C) up to testing periods.

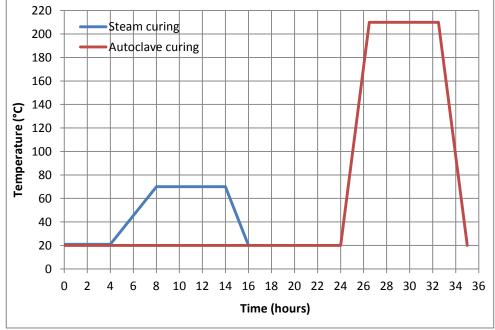


Fig. 1. Heat treatment cycles

Three prismatic specimens (40x40x160 mm) from each mixture were subjected to flexural strength test according to ASTM C348 [10]. The specimens were loaded from their mid-span and the clear distance between simple supports was 120 mm. The compressive strength tests were performed following the flexural tests on two broken pieces left from flexural test according to ASTM C349 [11].

Shrinkage values were measured on mortar bars (25x25x285 mm) according to ASTM C596 [12]. The first reading of length was taken after demoulding for standard cured mortars and for steam and autoclave cured mortars at the end of the heat treatment periods. Then the prisms were kept in laboratory conditions (~20 °C temperature and about 55 % relative humidity). The length change values of specimens were recorded periodically.

3. TEST RESULTS

Mechanical properties and dimensional stability of standard cured, atmospheric and high pressure steam cured geopolymer mortars are given below.

3.1. The mechanical properties of geopolymer mortars

The compressive and flexural strength values of standard cured mortars are given in Fig. 2 and 3, respectively. The compressive strength of PC mortar was higher than all geopolymer mortars at all ages. Maximum compressive strength at 1-day for 100 % FA mortars was obtained for 4M NAOH solution. For 3 and 7 days, maximum compressive strength values were obtained for 5 M NaOH case and for 28-day 6 M NaOH solution gave the highest values. In other words, higher molar NaOH gives higher later age strength values. The replacement of FA by GGBFS resulted in significantly increase in compressive strength for both early and later ages. However, SF replacement did not have a positive effect on early age strength. Similar trend was seen in flexural strength case as shown in Fig. 3.

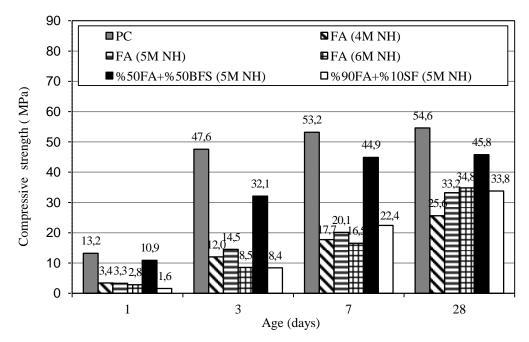


Fig. 2. Compressive strength of standard cured mortars

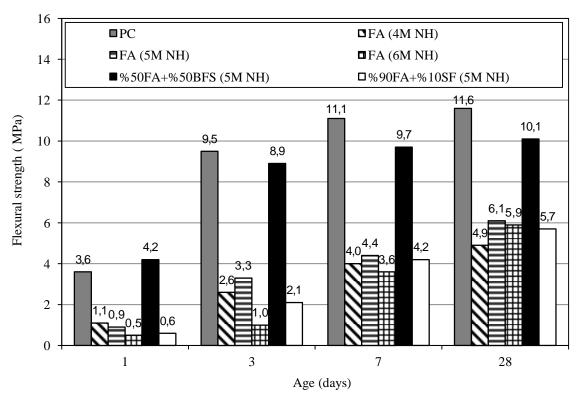


Fig. 3. Flexural strength of standard cured mortars

The variation of compressive and flexural strength values of heat treated mortars are presented in Fig. 4 and 5, respectively. As shown in Fig. 4 and 5, the strength of autoclaved PC mortar is significantly lower than the steam cured one and standard cured mortars. Under the conditions of high temperature and pressure, the chemistry of hydration has been substantially altered. C–S–H forms, however it is converted to a crystalline structure α -calcium silicate hydrate (α -C₂S) which cause an increase in porosity and reduction in strength [13-15]. This result indicates the need of extra silica source; such as silica fume, fly ash, etc., in order to obtain high strength values. Maximum compressive strength for steam cured 100 % FA mortars was obtained for 5M NaOH solution case. The compressive strength values of steam cured 100 %FA mortars were between 33.9 to 38.3 MPa depending on their NaOH ratios. In other words, similar performance with PC mortar can be obtained by steam curing application of 100 %FA mortars. However, GGBFS and SF replacement resulted in a decrease of compressive strength about 23 % and 38 % under steam curing, respectively.

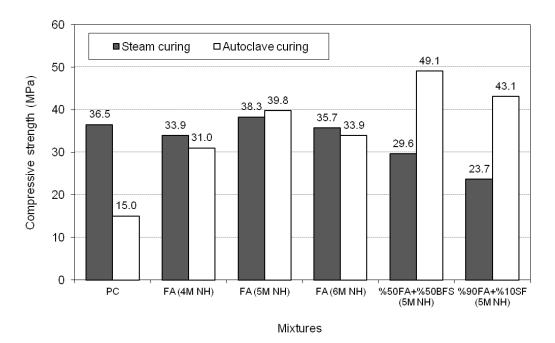


Fig. 4. Compressive strength of steam and autoclave cured mortars

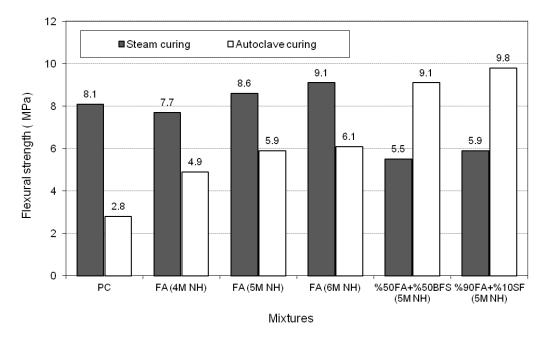


Fig. 5. Flexural strength of steam and autoclave cured mortars

The maximum compressive strength value for autoclave curing was obtained for 5M NaOH solution case for 100% FA mortars similar to steam curing. Compressive strength values were considerably similar for steam and autoclave curing for 100 %FA mortars independent from NaOH content. In case of autoclave curing, a compressive strength increase about 23 % and 8.3 % was appeared for GGBFS and SF replacement, respectively. All alkali activated mortars have considerably higher compressive strength values compared to PC mortar under autoclave curing.

Flexural strength of 100 % FA geopolymer mortars have increased parallel to increasing NaOH content both steam and autoclave curing cases. The flexural strengths of autoclave cured %100 FA mortars were found lower than steam cured mortars. Flexural strength of FA mortar was reduced by GGBFS and SF incorporation in case of steam curing in contrast to autoclave curing.

3.2. Dimensional stability of geopolymer mortars

The length changes of mortar mixtures that were stored in water and in air are presented in Fig. 6, 7 and 8 for standard, steam and autoclave curing conditions, respectively.

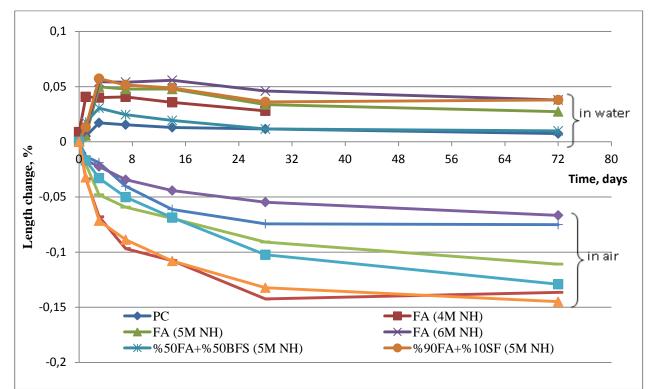


Fig. 6. Dimensional stability of standard cured mortars

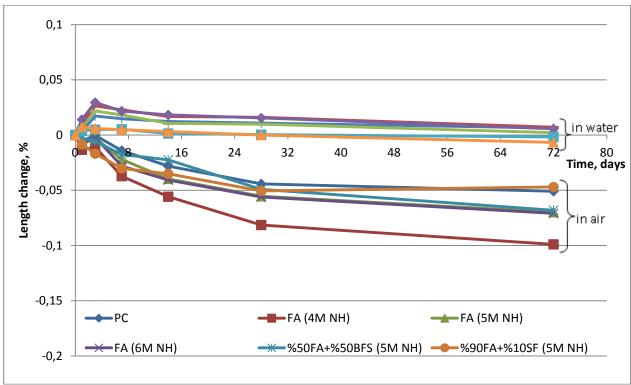


Fig. 7. Dimensional stability of steam cured mortars

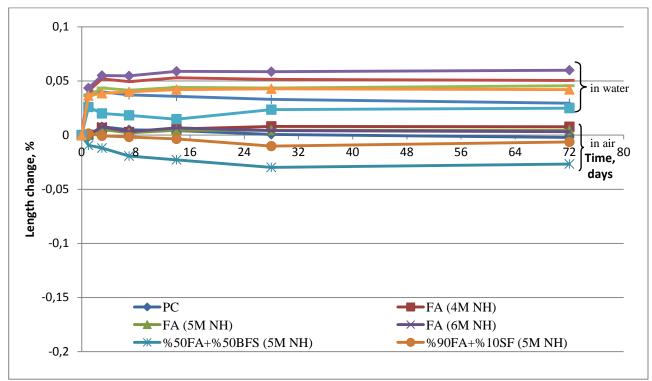


Fig. 8. Dimensional stability of autoclave cured mortars

Mortars cured continuously in water exhibited a net increase in length. This swelling is due to the absorption of water by the cement gel: the water molecules act against the cohesive forces and tend to force the gel particles further apart, with a resultant swelling pressure. Also, the ingress of water decreases the surface tension of the gel, and a further small expansion takes place [16]. In standard conditions, swelling of 100 % FA mortars increased with the increasing of molar NaOH concentration of activator solution. However, drying shrinkage of 100 %FA mortars decreased with the increasing NaOH amount. The swelling was decreased by slag incorporation. However, drying shrinkage of geopolymer mortars was increased by slag or silica fume incorporation. Nevertheless, these variations in swelling and drying shrinkage were considerably low. All alkali activated mortar mixtures displayed similar behaviour with PC control mortar in case of air and water storage conditions.

Swelling behaviour of mortars was considerably reduced by steam curing but did not significantly change with autoclaving compared to standard curing conditions. Drying shrinkage values of mixtures reduced in case of heat curing. However, autoclave curing is more effective in decreasing drying shrinkage compared to steam curing.

4. CONCLUSIONS

Based on the results of this experimental investigation, the following conclusions are drawn:

- Under standard curing conditions, mortars that have compressive strength over 30 MPa can be produced by activation of C type fly ash. However, early age strength of fly ash mortars is lower than the control Portland cement mortar. The early age strength of FA based geopolymer mortars have increased by the incorporation of ground granulated blast furnace slag.

- Similar performance with PC mortar can be obtained for fly ash based geopolymer mortar under atmospheric steam curing. Replacement of some fly ash by ground granulated blast furnace slag or silica fume has negatively affected the mechanical performance of atmospheric steam cured geopolymer mortars.

- Mortars produced by the alkali activation of fly ash showed a superior performance compared to PC mortar in case of autoclave curing. The performance of FA mortars have improved by silica fume and ground granulated blast furnace slag incorporation under this curing condition.

- Swelling and drying shrinkage behaviour of geopolymer mixtures were similar to PC mortar. Atmospheric and high pressure steam curing were effective in decreasing the drying shrinkage.

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S. Aydın, B. Baradan. High strength Portland cement free cementitious mortar // Proceedings of the International Conference "Eurocoalash 2012", Thessaloniki, Greece, September, 25–27, 2012.