PROPERTIES OF ALKALI ACTIVATED MORTARS WITH COMBINATIONS OF DIFFERENT STARTING MATERIALS

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Abstract

Alkali-activated cements are rather new binders that are produced by the activation of pozzolans with different alkali solutions. The utilization of these types of materials might solve an important ecological problem in terms of the use of an industrial sub product. Among the precursor materials used, blast furnace slag (BFS) and fly ash (FA) has been prominent ones because of their favorable chemistry. Turkey is rich in natural pozzolans and has extensive deposits of pumice. Pumice may contain up to 75% SiO_2 and has a high pozzolanic activity. There are limited numbers of studies about using pumice powder (PP) as a binder in alkali activated mortars. In this study, alkali activated mortars were produced with using different amount of BFS, FA and PP. The mortar mixture proportions were 1:2.5:0.5 by weight of binder, sand and water respectively. BFS to binder ratio was kept constant as 0.5. PP was replaced with FA by 10, 20 and 30% by weight. Sodium hydroxide (NaOH) was chosen as the alkaline activator. Compressive strength development, physical properties and abrasion resistance of mortars were determined. Compressive strength increased with the increase in PP ratio and NaOH amount. Physical properties did not change considerably. Abrasive resistance improved by increase in the NaOH amount.

Keywords:

Alkali activated mortars; compressive strength; physical properties; abrasion resistance; blast furnace slag; fly ash; pumice powder

1 INTRODUCTION

Alkali activated materials have been shown to offer an environment friendly and technically competitive alternative to Ordinary Portland cement (OPC), and are increasingly being employed in various applications [Davidovits 2008; Duxson et al. 2005; Duxson et al. 2007; K. Komnitsas and Zaharaki 2007]. Compared with conventional concretes, the production of alkali-activated concretes is associated with low energy consumption and low CO_2 emission, along with the potential to reach high mechanical strength at early ages of curing, high stability in aggressive environments and resistance to elevated temperatures, among others [Roy 1999; Wang et al. 1995; Shi et al. 2006].

Theoretically, any material composed of silica and aluminum can be alkali-activated. So far, the investigations performed, the following prime materials have been used such as blast furnace slag, metakaolin, fly ash, kaolinitic clays and red mud. Depending on the composition of prime materials, [Roy 1999] the binding systems can be divided into two groups: $Me_2O–MeO–Me_2O_3–SiO_2–H_2O$ and $Me_2O–Me_2O_3–SiO_2–H_2O$. Palomo et al. [Palomo et al. 1999],

also established two models of alkali-activated binding systems. The first one is the case of the activation of blast furnace slag (Si+Ca) with mild alkaline solution, having CSH as the main reaction products. In the second model of alkali activation (Si+Al), the general example is the alkali activation of metakaolin or class F fly ash with medium to high alkaline solutions, and the reaction products are zeolite like polymers. Davidovits named the second group as "Geopolymer" since they have polymeric structure [Davidovits and Krivenko 1994].

These new cements are characterized by their high mechanical strengths and also high energy costs are not required during their manufacturing process. Depending on the nature of the raw materials to be activated, different reaction products are formed with different microstructures [Roy 1999].

The slag is a byproduct material obtained from the manufacturing of pig iron in the blast furnace and is formed by a combination of the earthy constituents of iron ore with limestone flux. Granulated blast furnace slag, which contains a large amount of silica and alumina, shows pozzolanic properties when it is finely ground. There are various uses of granulated blast furnace slag (BFS) as a binding material, and it can be used as a mineral admixture in concrete production

[Yazici et al. 2010]. Due to its high content of silica and alumina in an amorphous state, BFS shows binding property in an alkaline medium.

Fly ash (FA) is a byproduct of thermal power plants. Around one billion tons of FA is produced annually worldwide in coal-fired steam powder plants. Production of fly ash-based geoploymer requires approximately 60% less energy and has at least 80%less CO_2 emissions than OPC [Duxson et al. 2007].

Pumice is a highly vesicular material derived from acidic lavas and produced in very large quantities, and substantially contains amorphous silica (SiO_2). Turkey received over 3 billion cubic meters of pumice, which is 14% of the world deposits [Ozkan and Tuncer 2001]. The SiO_2 ratio (up to 75%) contained in the rock gives it an abrasive property, and the Al_2O_3 composition makes it heat and fire resistant [Binici et al. 2012].

The binary combinations of slag-fly ash have been investigated in previous studies [Puertas et al. 2000; Chi and Huang 2013; Zi et al. 2014]. However, the number of reports in the literature assessing usability of pumice powder (PP) as a cementitious material in alkali activated mortars is currently limited [Kilic and Sertabipoglu 2015; Özodabaş and Yilmaz 2013] and study on ternary combination of BFS-FA-PP has not been reported yet.

Based on the above, this paper reports the results of an investigation on the strength development, physical properties and abrasion resistance of alkali activated mortars with different contents of BFS, FA and PP activated with different concentrations of NaOH.

2 EXPERIMENTAL DETAILS

2.1 Materials

BFS, F type FA and PP were used as the binders in this study. The primary raw materials used in this study were provided by local suppliers. The chemical compositions and properties of BFS, FA and PP are given in Table 1. BFS and FA are well known to show pozzolanic property, on the other hand PP was tested according to EN 196-5 and its pozzolanic activity was experimentally verified.

Pumice, called pumicite in its powdered form, is a natural material of volcanic rock created by the release of gases during the solidification of lava. The cellular structure of pumice is formed by depressurization and rapid cooling of the molten lava flowing from volcanoes [Khandaker 2004; Neville 1995].

The pumice aggregate was initially crushed and sieved to achieve fraction finer than 63µm. CEN standard sand was used as fine aggregate in all mortar specimens. Sodium hydroxide (NaOH) was used as the alkaline activator solution. The 4M and 8M NaOH solutions were prepared by dissolving 98% purity NaOH flakes in distilled water and then cooling the solution for 2 h. A modified polycarboxylate polymer type superplasticizer was used to maintain the workability of the mortars.

Tab. 1: Chemical composition of starting materials

Materials	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	K_2O	Na_2O
BFS	41.0	13.2	33.8	1.2	7.2	0.4	1.1	0.3
FA	53.6	24.0	5.1	8.0	2.5	1.0	1.5	0.7
PP	77.5	13.0	0.1	1.5	0.4	0.52	0.1	1.0

2.2 Mixes design and specimens preparation

A total of 8 mixtures were produced. The composition of mortar mixtures were 1:2.5:0.5 by weight of binder, sand and water respectively. The ratio of BFS to the total binder by weight was kept constant as 0.5. PP was used by substituting FA by 10, 20 and 30% by weight.

Sodium hydroxide concentration in the mixture proportions were chosen as 4M and 8M.

All test batches were mixed by using an electrically driven mechanical mixer conforming to the requirements of ASTM C305. Initially, binder and fine aggregate were mixed in dry state for 1 minute and then the activator solution was gradually added while mixing continued for 1 minute at slow speed and another minute at high speed. Flow test was performed according to ASTM C1437-13. Fresh mixtures were cast into steel cubic molds with dimension of 50 mm. After casting, the samples were sealed and kept at 20±3°C and RH 55±3 % for 24 h for 'resting' and then moved to an oven and cured at 80°C for another 24 h. The samples were then de-molded and moved back to the laboratory conditions and kept there at 20°C and RH 55% until the time of testing.

Mixtures were coded according to their composition and the molarity of the activator in the form of WS-WF-WP-XM; where ''W'' represents the proportion of each binder by weight and ''X'' represents the molarity of NaOH solution. The details of the mix proportions are given in Table 2.

Tab. 2: Mix proportions of mixtures

Mixtures	Slag (%)	Fly Ash (%)	Pumice (%)	Molarity (NaOH)
50S50F-4M	50	50	-	4
50S40F10P-4M	50	40	10	4
50S30F20P-4M	50	30	20	4
50S20F30P-4M	50	20	30	4
50S50F-8M	50	50	-	8
50S40F10P-8M	50	40	10	8
50S30F20P-8M	50	30	20	8
50S20F30P-8M	50	20	30	8

2.3 Methods

Fresh mortar samples were subjected to flow test according to ASTM C 1437-13 after the mixing.

Mortar samples were tested for compressive strength following the standard procedure in ASTM C109. Test

was conducted at 3, 7 and 28 days, and the test results were presented in Figure 1 and 2, where each value represents the average of three cubic specimens.

Physical properties such as total volume of permeable voids (VPV) and water absorption were calculated according to ASTM C642-06 at 28 days. The dried (100˚C for 48h in oven), and submerged (for 48h) samples, were boiled at 100˚C for 5h to obtain VPV and water absorption.

Ultrasonic pulse velocity was determined according to BS1881 on 3 cubic (50x50x50 mm) specimens.

Abrasion test was performed according to BS EN 1338 at 28 days. Test was performed on three specimens for each mixture. The specimens were initially dried to constant mass at a temperature of 105 ±5°C and then placed on the test track of a 750 mm diameter rotating disc on which 8 g of standard abrasive (artificial corundum) was poured. Before testing, the weight of each specimen was recorded to determine the amount of the abrasion. The density of the specimens (ρ) was determined by measuring the dimensions of specimens to the nearest 0.1 mm, and by weighing them to the nearest 0.1 g. The specimens were then subjected to abrasion for 22 revolutions under a constant load of 294±3 N and 30 rev/min rotation speed. The specimens were tested for 16 cycles, each consisting of 22 revolutions. The abrasive wear was calculated after 16 cycles by determining the loss in specimen volume by the following equation.

$$\Delta V = \Delta m / \rho \qquad (1)$$

where ΔV (cm^3) is the loss in volume after 16 cycles; Δm (g) is the loss in mass after 16 cycles and ρ (g/cm^3) is the density of the specimen.

The scanning electron microscopy analysis was conducted on mortar samples with a magnification range of 1000-2500. The samples were broken into the desired sizes for the test.

3 RESULTS AND DISCUSSIONS

3.1 Flowability

Slump values of the mortar mixes are presented in Table 3. All slump values are ranged between 160 and 210 mm.

Tab. 3: Flowability results

| Mixtures | Flowability (mm) | |
	4M	8M
50S50F	210	210
50S40F10P	200	200
50S30F20P	170	190
50S20F30P	160	180

In this study, generally, replacement of FA with PP caused a decrease in the flowability. It was observed that while FA improves the flowability, PP causes a decrease due to its rough surface, high water absorption capability and fineness.

3.2 Compressive Strength

Figure 1 and 2 shows the compressive strength and standard deviation results of mortars determined at 3, 7 and 28 days. The compressive strength of mortars

increased due to the increase in curing time. This trend was more apparent when the NaOH molarities increased from 4 to 8 M (Figure 1 and 2). Increase in the amount of PP, increased the compressive strength of mortar samples at all ages. Maximum compressive strength of 26 MPa was achieved in 50S20F30P series at 28 days.
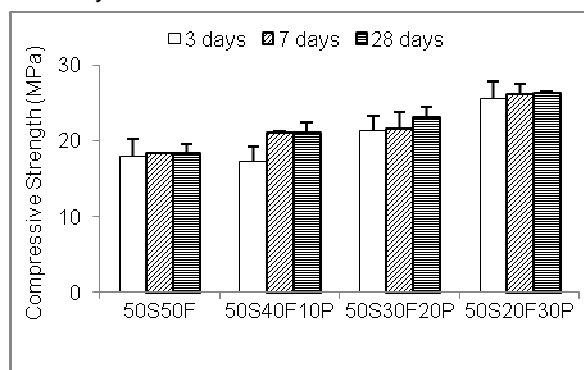

Fig. 1: Compressive strength results for 4M series.

The compressive strength of 8M NaOH-activated mortars containing different replacement levels of PP varied between 18-28 MPa, 27-30 MPa and 26-34 MPa at 3, 7, 28 days respectively. Increase in the amount of PP, increased the compressive strength in all series, the exception was however 50S30F20P series. 50S20F30P series possessed the maximum compressive strength of 34 MPa at 28 days. The reason of higher strength achievement by using higher amount of PP might be attributed to the higher alkali activity of PP. The increase in the amount of NaOH (from 4M to 8M) resulted in an increase in compressive strengths of mortars.
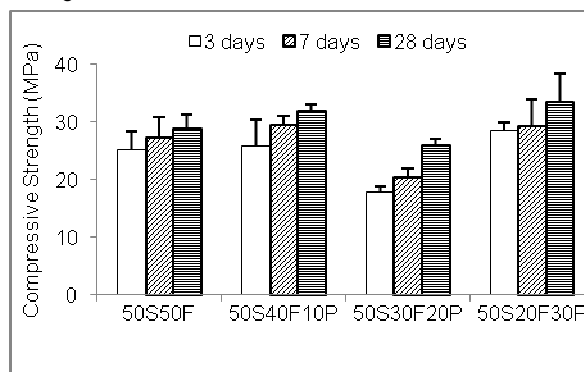

Fig. 2: Compressive strength results for 8M series.

3.3 Physical Properties

The UPV values of mortar samples are shown in Figure 3 and 4. UPV values of all series ranged between 2.9-4.5 mm/μs. In this study, it has been investigated whether there is a possibility of correlation between CS and UPV in mortars containing different types of alkali activated binders. According to obtained data from this study, it is not possible to speak of absolute correlation between CS and UPV; decrease in UPV doesn't induce increase in compressive strength in all mixtures (Figure 3, 4). As it can be seen from Figure 1-4, CS and UPV graphics are inconsistent. However, in general, higher UPV indicates higher compressive strength. To forecast the strength of alkali activated materials (ie. Portland concrete) by UPV results, it's required to produce numerous series using different types of binders and activators and conduct experiments.
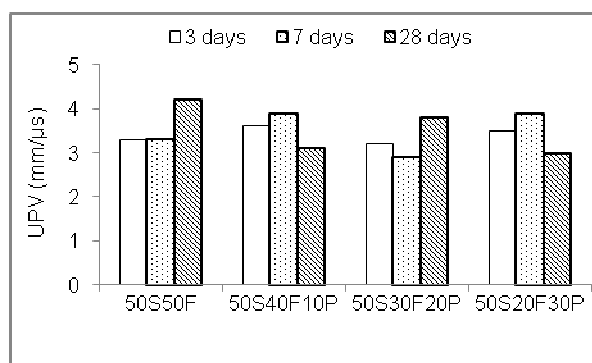
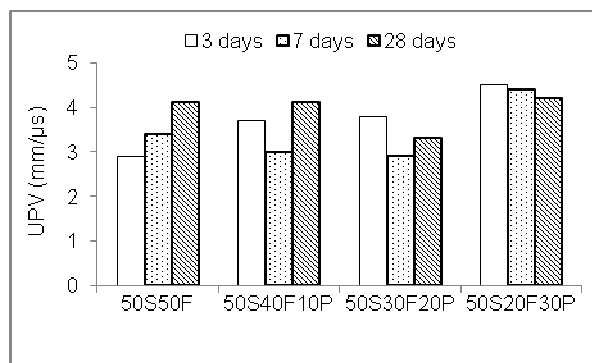*Fig. 3 Ultrasonic pulse velocity results for 4M series.*

Fig. 4: Ultrasonic pulse velocity results for 8M series.

The average VPV and water absorption values of all series are shown in Figure 5 and 6. The volume of permeable voids of 4M NaOH-activated series varied between 20.3 and 25.8 %, where 50S50F possessed the maximum value and 50S20F30P possessed the minimum. All series had more or less the same amount (25 %) and increase in NaOH amount did not cause any considerable increase or decrease in the amount of VPV (Figure 5).
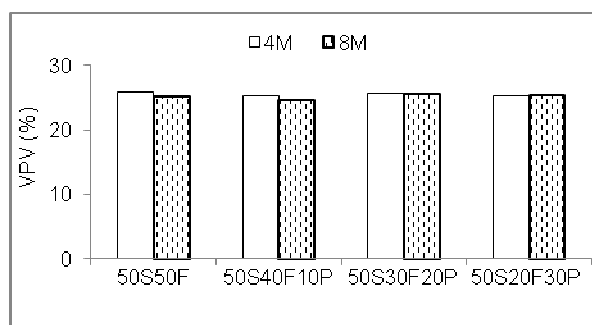

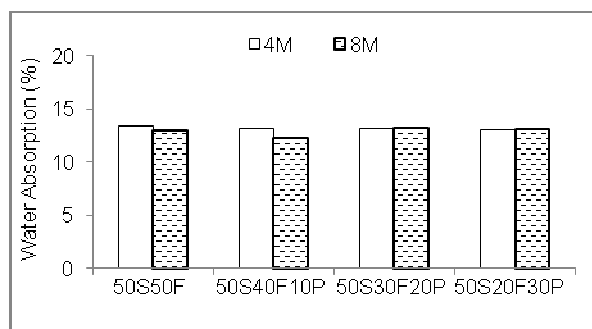*Fig. 5: Volume of permeable voids results for 4 and 8M series.*

Fig. 6: Water absorption results for 4and 8M series.

Water absorption results (Figure 6) of series followed a similar trend with VPV. In all series, the water absorption results ranged between 10.4 and 13.4%. It can be noticed from Figure 6 that the water absorption of mortars did not decrease with an increase in the NaOH content.

3.4 Abrasion

Figure 7 shows the abrasion test results.

The abrasion amount of 4 and 8M NaOH-activated mortars containing different replacement levels of PP varied between 4.6-6.6 and 3.5-5.2 cm^3, respectively. As it can be seen from Figure 7, maximum abrasion amount was seen at 50S50F-4M specimens, while minimum was obtained from 50S50F-8M. It is obvious that increase in molarity of NaOH, decreases the abrasion amount.

In all PP series, abrasion resistance is increased as the rate of PP increased. It can be noticed that mixtures with higher compressive strength, in general, possessed lower abrasion values (Figure 1,2 and 7).
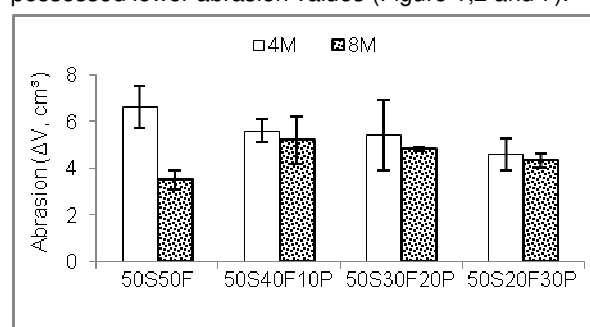

Fig. 7: Abrasion test results.

3.5 Microstructure Analysis

Fig. 8 and 9 shows the SEM images of 50S50F and 50S20F30P samples at the age of 90 days. Similar to most alkali activated cementitious materials, the hardened alkali activated mortars consists mainly of aggregated fine gel-like particles, probably of C-S-H, C-A-S-H and N-A-S-H [Puertas et al. 2011; García-Lodeiro et al. 2011; García-Lodeiro et al. 2010], which are difficult to tell from each other for their small sizes, disordered structures, variable compositions and close aggregation. Though there is no significant difference in the phase types in qualitative sense, there are significant differences in microstructure between the series produced with different solution concentrations, indicating that the solution concentrate notably affected the microstructure.

The 8M series (Fig. 8b and 9b) shows a very compact microstructure consisting of closely aggregated homogeneous gel, with no particles and pores detectable under the magnification of 1000x. This might be the possible reason of higher mechanical properties of 8M series compared to 4M ones. As it can be seen from Fig.8a and Fig.9.a, series containing 30% PP has a denser structure compared to 50S50F series. This might be an evidence of higher compressive strength and abrasion resistance of 50S20F30P series. The change of particle-aggregated microstructure to compact one with the increase of NaOH concentration is presumably resulted from the increase of the reaction degree of the starting materials. There are a fewer micro cracks in the sample of the 8M mortars (Fig. 8b and 9b), which may be ascribed to the higher content of gel like hydrates as the result of the higher degree of reaction.
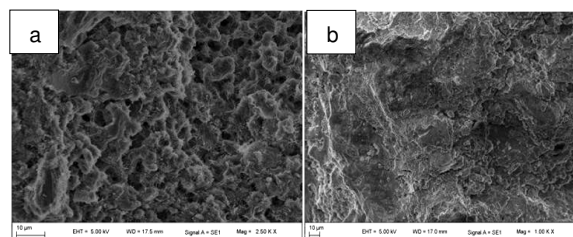
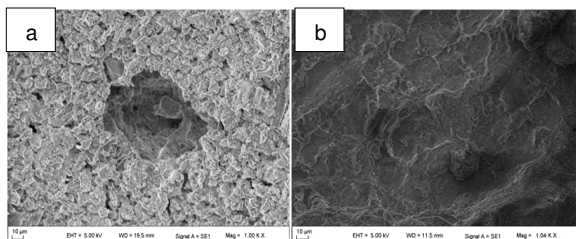*Fig. 8: SEM images of 50S50F series (a) 4M, (b) 8M.*

Fig. 9: SEM images of 50S20F30P series (a) 4M, (b) 8M.

4 CONCLUSIONS

The results obtained from this study confirm that pumice powder (PP), as binder, when used at different replacement ratios, can effectively increase compressive strength and thus can be used in production of alkali activated materials.

Based on the experimental results, the following conclusions can be drawn:

- As the amount of PP increase, compressive strength increases. Also, the increase NaOH amount resulted in significant increase in compressive strength, especially in 28th days.

- Ultrasonic pulse velocity test results are not correlated with compressive strength.

- Physical properties did not change considerably with increase in replacement ratio of pumice powder and NaOH.

- SEM observations verified the fact that increasing NaOH concentration increases the reactivity of the samples and gives higher resistance to abrasion.

- Additional studies are needed in order to better understand the activation mechanism of slag, fly ash and pumice by the alkali environment and the potential use of these materials as a means to stabilize hazardous materials.

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