Room-temperature Acid-Base Ceramics Produced Using a High-Calcium Fly Ash

Mahdi Mahyar¹, Sinan T. Erdo an¹

¹METU, Middle East Technical University, Department of Civil Engineering Dumlupinar Bulvari, Ankara, Turkey

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Abstract

The Af in-Elbistan (AE) thermal power plant in Kahramanmara , Turkey produces more than 3 million tons of a high-calcium fly ash that does not meet standards for use in the cement and concrete industry due mainly to its high sulfur and free lime content.

The chemical composition of AE fly ash indicated its potential for use in the production of chemically-bonded phosphate ceramics (CBPC). CBPCs can provide certain advantages over ordinary portland cement products such as better mechanical strength, better durability, shorter setting time, better high temperature resistance and a lower carbon footprint. This study investigated the mechanical behavior and microstructure of acid-base phosphate ceramics produced at room temperature using coal fly ash from were investigated. The main goal was to introduce a novel application for this industrial waste which does not meet the standards for use in the cement and concrete industry.

Activation of the fly ash was done using a phosphoric acid solution. Various solution concentrations and solution-to-powder ratios were used. Compressive strength was measured up to age 28 days. The microstructure and morphology of reaction products were investigated using scanning electron microscopy (SEM). X-ray fluorescence spectrometry (XRF) was used to determine the chemical analyses of raw materials and x-ray diffraction (XRD) was used to investigate the crystalline reaction products.

The main crystalline reaction products appeared to be Brushite and Monetite, both calcium phosphates. Pastes with 28-day compressive strengths as high as 30 MPa could be made with room-temperature curing.

Introduction

Turkey, like many countries, meets a majority of its electricity demand with coal-fired power plants, due to a combination of their relatively low investment and energy production costs. As such, over 15 million tons of fly ash are produced annually and this amount is expected to keep increasing [1, 2]. A small fraction of this ash is used for secondary purposes and more than 80 % goes to landfills.

The Af in-Elbistan (AE) thermal power plant is situated in the biggest lignite basin of the country. About 46 % of Turkey's total reserves (~3.4 billion metric tons) are in this basin [3, 4]. The AE power plant annually produces more than 3 million tons of a high-calcium fly ash. Although the cement and concrete industry is the main user of fly ash [5], AE fly ash does not meet the standards for use in this way due mainly to its high sulfur and free lime contents [6]. This greatly limits the use of AE fly ash. While fly ash can be used in other applications, such as soil stabilization [7], or production of glass-ceramics [8], these can present environmental, energetic, and economical challenges.

An alternative and rather new way in which fly ash can be used is the production of chemically-bonded phosphate ceramics (CBPC). CBPCs are produced at room temperature by reacting a powder base, typically magnesium oxide (MgO) or wollastonite (CaSiO₃), with a solution of phosphoric acid or an acid phosphate salt. The acid-base reaction can yield a fast-setting crystalline and/or amorphous product with high strength and better high-temperature resistance and durability than Portland cement pastes [9]. The incorporation of high volumes of fly ash in CBPCs has already been suggested. However, the use the use of fly ash as the sole powder binder in the production of CBPCs has not been reported. Also, the fly ashes used are commonly low-calcium fly ashes [10].

This paper discusses the production of CBPCs using AE fly ash as the sole powder binder. The compressive strength development and microstructures of various formulations are presented.

Materials and Methods

The fly ash used in this study was obtained from Af in Elbistan A power plant. It is mostly dark brown with some particles that are only white. The specific surface area of the "as received" fly ash, determined using the Blaine fineness method [11], was 1800 cm²/g. Its specific gravity was measured as 2.41. Table 1 provides the chemical composition of the fly ash, determined using X-ray fluorescence spectroscopy.

Oxide	Amount (wt. %)				
SiO ₂	19.40				
CaO	33.30				
Al_2O_3	9.50				
Fe ₂ O ₃	5.64				
MgO	1.88				
SO ₃	12.90				
B ₂ O ₃	5.65				
CO ₂	9.42				
K ₂ O	0.68				
Na ₂ O	0.23				
P_2O_5	0.41				
TiO ₂	0.60				

Table 1 Oxide composition of the fly ash used

The particles are 1 to 100 μ m in diameter, mostly irregular in shape, with some cenospheres of ~20 μ m diameter. Scanning electron microscope (SEM) images of the fly ash, taken at two different magnifications, are shown in Figure 1.



Figure 1 SEM images of the "as received" fly ash

Energy-dispersive x-ray analysis (EDX) revealed that some of the particles were rich in CaO and SiO₂ while others were rich in SiO₂ and Al₂O₃. Some carbon was also detected, suggesting the presence of unburnt material. The white particles were determined to be calcium sulfate. Figure 2 shows the x-ray diffractogram (XRD) of the as received fly ash. The fly ash contains calcium oxide, anhydrous calcium sulfate, quartz, calcite, and possibly some hematite and gehlenite.



Figure 2 XRD pattern for the "as received" fly ash

The orthophosphoric acid (H_3PO_4) used was an 85 wt. % aqueous solution, a colorless, odorless, non-volatile, slightly viscous liquid. H_3PO_4 is a weak acid, since its ionization is incomplete. However it can be corrosive prior to dilution with water. The pH of the 85 % solution is 0.50 and its density is 1.68 g/cm³. In contrast, the 50 % solution has a pH of 0.67, a density of 1.33 g/cm³, and lower viscosity [12].

The acid solution was added to the fly ash at solution-to-powder ratios (S/P) ranging from 0.5 to 1.2. Mixing was done by hand for about 1 minute. In all cases, the resulting slurry appeared to dry shortly after the start of mixing and resemble moist sand. The mixture was then cast into molds of 50*50*50 mm cube molds and compacted using a plastic tamper. The samples were kept at 21 ± 1 C and 35 ± 5 % relative humidity.

For these acid-base mixtures, water-to-powder (W/P) ratio is calculated slightly differently than for Portland cement pastes. Both the concentration of the solution and the S/P need to be considered. As such, a mixture made with a 30 % acid solution and S/P=0.5 and a mixture made with a 70 % acid solution and S/P = 1.2 will both have W/P ~ 0.35.

Results and Discussion

Compressive Strength Development

Mixtures with combinations of acid solution concentrations from 30 % to 70 %, and S/P from 0.8 to 1.2 were made to evaluate their combined effect on strength development. 24-h compressive strength was observed to increase with increasing H_3PO_4 solution concentration up to 60 wt. %, for all S/P, thereafter decreasing abruptly.

The compressive strengths of mixtures made using a 60 % acid solution and various S/P were measured up to 28 days and are shown in Table 2. As characteristic for acid-base cement systems, strength gain was very rapid in the first 24 h and then slowed down. For some mixtures, even a slight strength loss was observed from 7 to 28 days.

Mixture	Acid solution concentration	Powder	S/P	Compressive strength (MPa)		
				1 d	7 d	28 d
1			1	14.9	20.2	22.1
2			0.9	13.1	17.1	14.0
3	60 wt. %	100 % AE	0.8	7.8	10.5	9.2
4	H ₃ PO ₄	fly ash	0.7	2.6	4.4	3.4
5			0.6	2.0	2.7	1.7
6			0.5	0.9	1.9	0.5

Table 2 Compressive strength development of the mixtures

Lower S/P gives lower strengths at all ages. This could be due in part to the W/P of the mixtures, which changes from 0.40 for an S/P of 1.0 to 0.20 for an S/P of 0.5. The amount of water in the latter case could be too low to achieve adequate compaction of the sample. In addition, the problem is exacerbated by the loss in fluidity of the sample shortly after mixing. Another explanation of this behavior could be changes in pH. Acid-base reactions take place at critical, narrow ranges of pH. The initial pH of the mixtures is 1-2 and increases as reaction products are formed. During this increase, different mixtures spend different amounts of time in certain pH intervals that allow reactions that give strength to the resulting sample. Figure 3 shows the change in pH of various mixtures in the first 24 h.



Figure 3 Increase in pH of some mixtures in the first 24 h

The mixtures that gain higher ultimate strengths have higher slopes at 24 h. A greater increase in pH generally suggests more reaction has taken place. Since the reactions require the availability of water, very rapid reactions that can increase the temperature of the mixture and evaporate some of the water can yield lower ultimate strengths than controlled-rate reactions. Well-reacted mixtures can reach ultimate values of pH~7.

Several mixtures in which the AE fly ash was partially replaced with other wastes such as soda-lime glass powder and/or calcium aluminate cement were also made. Some of these pastes attained 28-day compressive strengths of 30 MPa.

Microstructural Investigation

Figure 4 shows SEM images of the sample produced by reacting a 60 % acid solution using S/P = 1.0.



Figure 4 SEM images of the CBPC sample made using a 60 % acid solution and S/P=1.0

Fig. 4 shows two distinct microstructural features. One is a needle-shaped crystalline product (Fig. 4b) rich in calcium and phosphorus, and the other is an aluminosilicate glass (Fig. 4d). The XRD pattern for this sample is given in Figure 5.



Figure 5 XRD pattern for the CBPC sample made using a 60 % acid solution and S/P=1.0.

The calcium phosphate crystals in Fig. 4 are revealed to be Brushite $(CaHPO_4.2H_2O)$ and Monetite $(CaHPO_4)$. The disappearance of calcium oxide present in the unreacted fly ash suggests that it reacts with phosphate ions from the acid solution to form these crystalline products. Additionally, some of the quartz and calcium sulfate present in the unreacted fly ash remain unaltered after the reactions take place. Formation of a crystalline reaction product is consistent with the rapid early-strength gain observed. The amorphous hump around ~30 2 supports the observation of an aluminosilicate glass in the SEM-EDX analysis. The presence of an amorphous phase is likely responsible for the continued strength increase beyond 24 h, decreasing overall porosity.

Conclusions

A high-calcium fly ash was reacted at room temperature with solutions of diluted H₃PO₄. The compressive strength development of the paste mixtures and the reaction products formed were investigated. The following conclusions were reached:

- Pastes made by combining AE fly ash and solutions of H₃PO₄ can achieve 1-day compressive strengths of ~15 MPa, and 28-day compressive strengths in the range of 20-30 MPa.
- The final pH of the well-reacted samples is close to neutral.
- Mixtures made using a 60 wt. % solution of H₃PO₄ attain higher early and ultimate strengths than mixtures made with solutions with different concentration.
- A solution-to-powder ratio of 1.0 gave the highest compressive strength for the mixtures using a 60 wt. solution.
- The products of the reaction of AE fly ash with H₃PO₄ solution are both crystalline (Brushite and Monetite) and amorphous (aluminosilicate glass). The crystals form from the reaction of the free lime in the unreacted ash and the phosphate ions from the acid solution.

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