

# Production of Heavy Fuel Oil Fly Ash (HFO)-based Geopolymers for Passive Cooling Systems

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## Abstract

This work aims to investigate the production of heavy fuel oil fly ash (HFO)-based geopolymers for passive cooling systems. The processing technique entails adding HFO as the porous filler material to a geopolymer matrix derived from metakaolin. A weight ratio of 10% —compared with the powder precursor (metakaolin)— was added to the metakaolin-based geopolymer. X-ray diffraction (XRD) analysis showed that the HFO-based geopolymer comprised two amorphous phases: gel and HFO particles. The HFO-based geopolymer cement exhibited a flexural strength of 7.5 MPa, and compressive strengths of 31 MPa and 28 MPa, respectively under dry and immersed conditions. The geopolymer featured high surface humidity compared with reference geopolymers. Experimental results prove that introducing HFO particles as porous filler will lower the heat rate of the chamber at 40°C. The general evaluation of the HFO-based geopolymer cement produced from metakaolin and HFO porous particles indicates its potential for a number of applications, including passive cooling systems.

**Keywords:** Geopolymers, Metakaolin, Construction, Heavy oil fly ash, Passive cooling system

## INTRODUCTION

Heavy fuel oil fly ash (HFO) is produced in large quantities from power plants and desalination plants that use oil as fuel. The output of this type of powder residue amounts to over 4000 metric tons in Egypt, making it one of this country's greatest sources of waste [1,2]. In Saudi Arabia, water desalination operations and power plants consume around 40 million metric tons of oil, resulting in vast quantities of heavy oil flying ash [1]. The fact that most of it becomes landfill can mean a dispersion of heavy metals in the surrounding groundwater and soil. Because the dispersion of fine particles of HFO may cause serious contamination, the disposal of HFO is a major environmental challenge for thermal power plants.

The chemical composition of HFO is characterized by a high carbon content of up to 95%, while this percentage does not exceed 50% in fly ash [3,4]. HFO also contains S, Zn, Pb, V, Fe and Ni [2-6]. Zn and Pb from dissolved

metals are known to have a toxic effect on health [7-10]. Soluble metal ions attached to the surface of HFO particles cause the induction of allergic responses in the respiratory system through suppressing receptor 4, innate immunity receptors, and degradation [11-13]. Therefore, HFO as powdered waste should be monitored to prevent contamination of the environment and reduce its negative impact on public health.

As one possible means of partly counteracting the global warming trend, we investigate the development of functional construction materials capable of passive cooling. These passive cooling systems rely on the evaporation of water absorbed by porous geopolymers [14]. The term "passive solar energy" thus describes certain methods of utilizing the solar heat available to buildings. Passive design can be understood as an attitude towards the construction process, representing sophisticated responses to environment and dynamic interactions that allow a building to store energy that may be used to cool or heat itself. This study aims to produce geopolymer cement using HFO ash as porous granules for passive-cooling system applications. To do so, we take advantage of the pore characteristics of a wide variety of HFO granules in conjunction with the geopolymer cement matrix.

## MATERIALS AND METHODS

### Sampling

A sample of HFO was collected from an electric power plant. The HFO sample was dried in an oven at 105°C for one day, and then sieved, taking the particle size fraction of less than 300 µm for study.

### Production of geopolymer and HFO-based geopolymer cements

A series of geopolymer cement samples was prepared. Firstly, a reference specimen (SK) was prepared with metakaolin, and without HFO. Secondly an HFO-based geopolymer cement (GA) was prepared by adding HFO as a filler, without reducing the original weight ratio of the precursor (metakaolin); in this case the mass percentage of HFO used was 20% of the metakaolin.

The geopolymer binder materials were prepared using HFO, kaolinite and alkali solutions based on sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and sodium hydroxide (NaOH). The kaolinite came from a natural deposit located in the Ar Riyad-Al Kharj area, specifically at Khushaym Radi [21]; it was heated at  $750^\circ\text{C}$  for 4 h in a laboratory furnace to obtain the respective metakaolinite.  $\text{Na}_2\text{SiO}_3$  and NaOH solutions were used as alkaline activators for the dissolution of aluminosilicate phases. The sodium silicate solution (Merck, Germany) contained 27%  $\text{SiO}_2$  and 8%  $\text{Na}_2\text{O}$ . The hydroxide solution, at a concentration of 6.0 M, was prepared using sodium hydroxide (NaOH) flakes of 98% purity (Merck) and distilled water.

The following ratios were used in the alkaline activation process:

- $\text{SiO}_2$  (in sodium silicate solution)/ $\text{Al}_2\text{O}_3$  (in metakaolinite) with a molar ratio of 1.
- $\text{Na}_2\text{O}$  (in sodium silicate and NaOH solutions)/ $\text{Al}_2\text{O}_3$  (in metakaolinite), molar ratio of 1.
- The  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  molar ratio was 13.

The geopolymer production method involves mechanical mixing, for 1 min, of an aqueous solution composed of  $\text{Na}_2\text{SiO}_3$ , NaOH and  $\text{H}_2\text{O}$  (see Figure 1). Afterward, the metakaolin was mixed with the sodium hydroxide and sodium silicate solutions for 15 minutes. The final pulp was poured into three rectangular molds to carry out, in triplicate, mechanical and physical characterizations ( $160\text{mm}\times 15\text{mm}\times 30\text{mm}$  each). Specimens were cured in a ventilated oven (Binder-ED115, Germany) at  $40^\circ\text{C}$  for one day; after curing, they were removed from the molds and cooled at room temperature [22]. In addition, three discs ( $2\text{cm}\times 2\text{cm}\times 1\text{cm}$ ) were prepared from each mixture to carry out microstructural and mineralogical analyses.

## Testing methods

### *X-ray Diffraction studies*

X-ray Diffraction (XRD) was carried out on the HFO sample and on powdered samples of kaolin geopolymer (SK) and heavy oil fly ash cement (GA) to analyse the HFO microstructure and identify major crystalline and potentially newly formed phases after geopolymerization process. We used a Shimadzu diffractometer-6000 (Japan) with a Co tube and a scanning range from  $5^\circ$  to  $80^\circ 2\theta$ , at a scan rate of  $2^\circ/\text{min}$ . Qualitative analysis was carried out on the crystalline phases, identified by detecting and analyzing the positions of the peaks using the software package supplied with the instrument.

### *Scanning Electron Microscopy and Energy-dispersive X-ray spectroscopy (SEM/EDX)*

A Scanning Electron Microscope (Inspect F50, The Netherlands) combined with Energy-dispersive X-ray spectrometry (SEM/EDX) was used for the elemental analysis, chemical characterization and morphology of HFO

particles and stabilized HFO particles, after geopolymerization.

Samples were mounted in epoxy resin and the surfaces were ground flat using 600 grit abrasive paper. The samples were then polished to achieve a smooth surface and placed in a vacuum for etching with argon gas for 20 minutes. The microstructures of the samples were examined by SEM and photographs were taken.

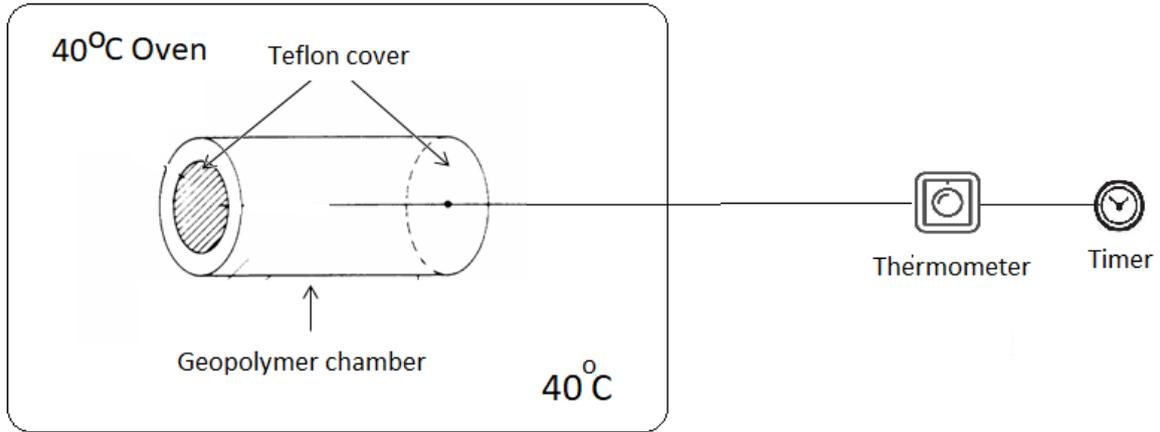
### *Mechanical characterization of HFO*

The mechanical characteristics of the fabricated specimens were assessed in terms of flexural strength and compression strength. These tests were performed according to the ASTM C78/C78M-16 (Standard Test Method for Flexural Strength of Concrete, Using Simple Beam with Third-Point Loading) and ASTM C116-90 (Test Method for Compressive Strength of Concrete Using Portions of Beams Broken in Flexure). Both tests were run at room temperature and with a universal testing machine. The bending specimen's dimensions were: height=15 mm, width=30 mm and length=160 mm; the distance between the supports was 120 mm and the speed of the machine head during testing was 0.1 mm/minute. Compression tests were performed on the failed bending specimens, placed on their side with a loading area= $40\times 15\text{ mm}^2$  and height=30 mm. The speed of the machine head during testing was 2 mm/minute.

### *Preliminary evaluation of HFO-based geopolymers for passive cooling systems*

As displayed in Figure 1, the following heat procedure for preliminary evaluation of HFO-based geopolymers for passive cooling systems was used in this research:

1. A cylindrical chamber with internal diameter 2.5 cm and internal height 10, and 1 cm thickness was prepared from HFO-based geopolymers and geopolymers without HFO (reference geopolymers).
2. The chamber was left open at ambient conditions for one day.
3. The surface humidity was measured and recorded.
4. A thermometer was installed in the chamber, and sealed with tape.
5. The chamber was placed in the oven at  $40^\circ\text{C}$ .
6. The required temperature was maintained during the specified period of time (4 hours).
7. The temperature of the chamber was measured and recorded every 30 minutes for 240 minutes.
8. After the exposure period, the chamber was removed from the oven, and then brought back to room temperature.

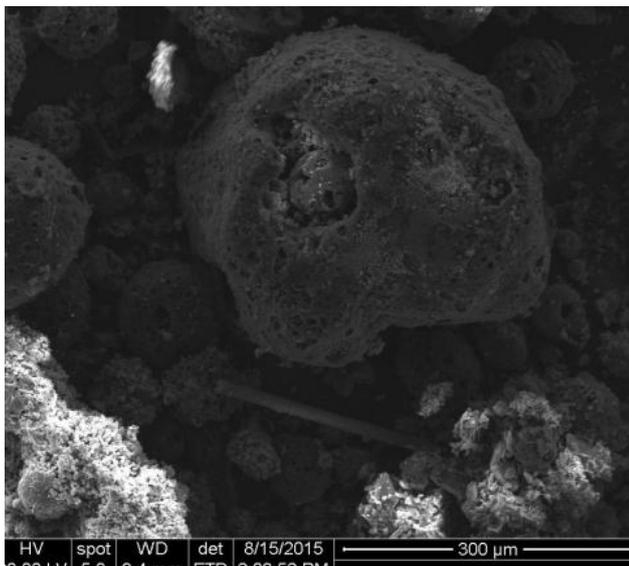


**Figure 1:** Schematic diagram of preliminary evaluation of HFO-based geopolymers for passive cooling systems

**RESULTS AND DISCUSSION**

**Porous aggregates of fuel oil fly ash (HFO)**

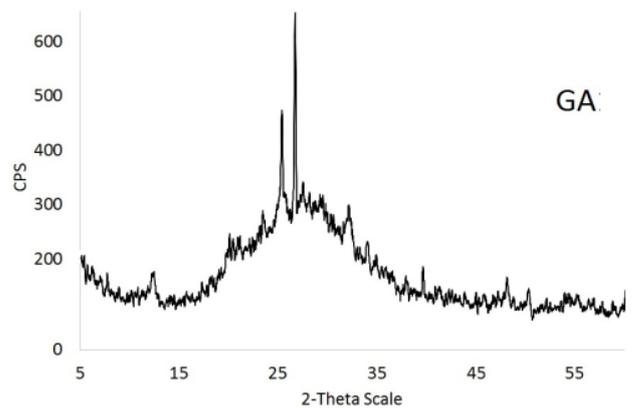
The chemical composition and physical properties of HFO have been investigated by several researchers [23-26]. The chemical analysis of this study found the HFO samples to be mainly composed of C, S, heavy metals (particularly V, Fe and Ni), and residue ash. Additional contents included Pb, Al, Ca, Mg, Si, and Na [2-6]. HFO is very high in carbon content, around 95%, whereas coal fly ash has 20%-50% of carbon [24]. Furthermore, the chemical composition of HFO clearly differs from that of coal fly ash. The SEM micrograph of HFO in Figure 2 reveals that the surface of the HFO aggregate is not smooth, but rather characterized by the presence of hollow voids and macropores that measure several microns in diameter. These hollow voids and pores were formed by the eruption of gas during combustion. Accordingly, this waste was selected as a porous functional filler for geopolymer cement to improve its humidity adsorption capacity for passive cooling systems.



**Figure 2:** SEM image of HFO aggregates

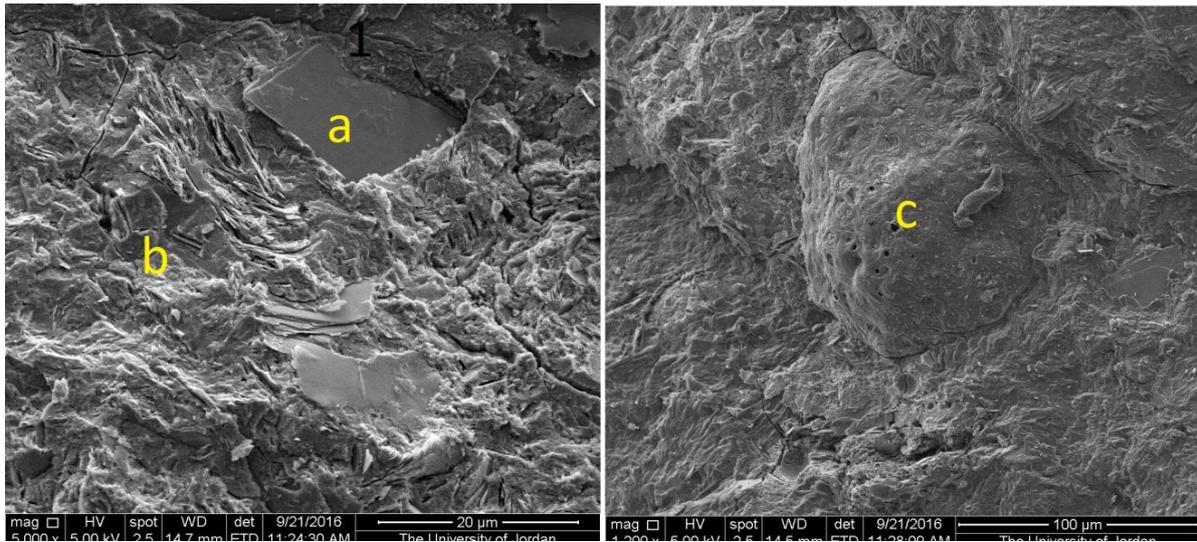
**Microstructural characteristics**

The geopolymer precursors and fillers were transformed into solid and hard matrix through the geopolymerization reactions. The XRD patterns (Figure 3) of the resulting materials show high humps between 17° and 37°. The hump with a few peaks indicates that the main phases of the resultant products are largely amorphous [27-31]. The XRD peaks correspond to the mineral anatase (TiO<sub>2</sub>), which already existed in the precursor (kaolin), as previously reported [24]. In general, no significant change in the mineral composition was observed with the addition of HFO particles (GA cement). This is indication that HFO can be considered as functional porous filler particles, lending a limited contribution in setting reactions of the geopolymer matrix.



**Figure 3:** Qualitative XRD patterns of the HFO-based geopolymers

The SEM analysis indicates that HFO porous particles are embedded in the geopolymer matrix: Figure 4 shows where the particle (point c) is fully surrounded and bonded by geopolymer gel (point b), and residual metakaolin (point a).



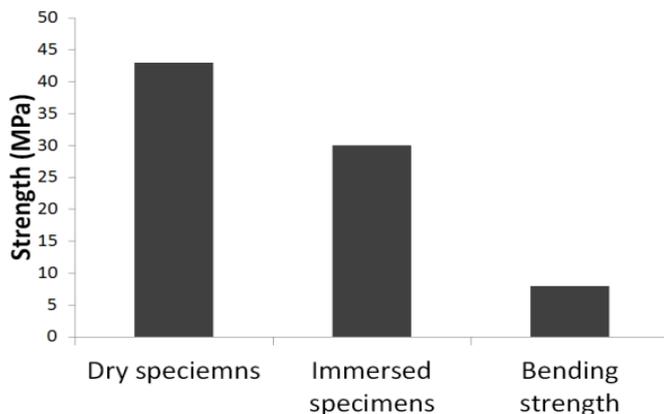
**Figure 4:** SEM image of HFO-based geopolymer; a) residual metakaolin, b) geopolymer gel, and c) HFO particle

Metakaolinite, serving as a precursor in this study, was attacked by the alkaline solution during geopolymerization as seen in Figure 4. Microstructural observations through SEM analyses reveal phase heterogeneities: HFO particles (point c), geopolymer gel (point b), and partially reacted metakaolin (point a).

The HFO particles contain 72% carbon, in addition to Na, Si, Al, and S. The low percentages of SiO<sub>2</sub> (2%) and Al<sub>2</sub>O<sub>3</sub> (3%) oxides of the HFO contents are responsible for the limited contribution of these particles to the composition of the geopolymer gel. Therefore, they undergo little morphological change after the hardening of the material, as shown in Figure 4 (point c).

**Mechanical properties**

According to the microstructural analysis, HFO particles have a limited chemical effect on the geopolymer cement, as mentioned in the previous section; however, they could bear an influence on the physical and mechanical properties because of their low density and high porosity [31].



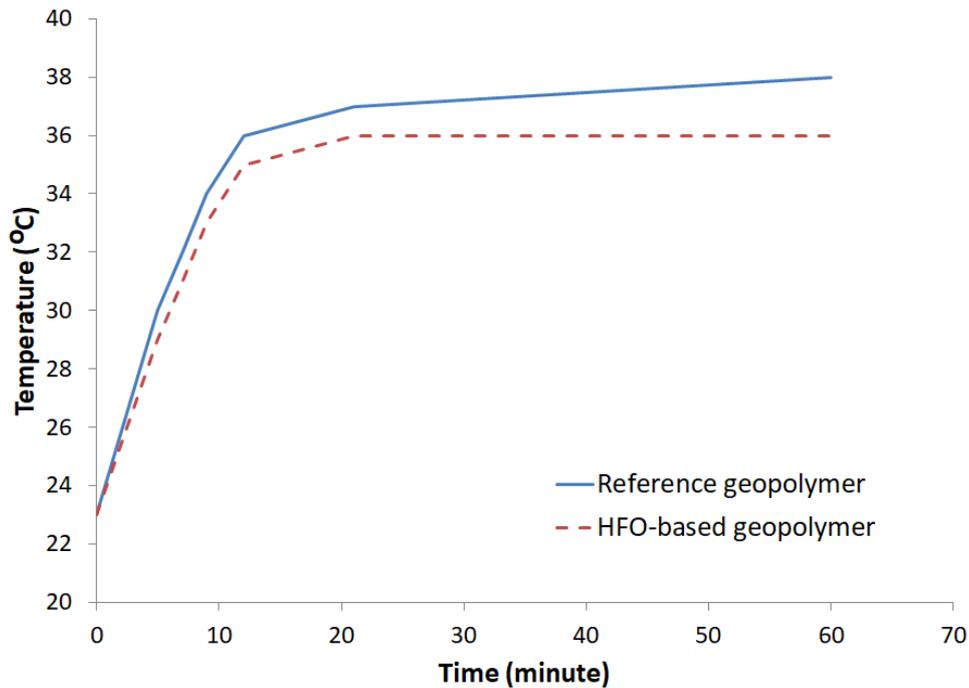
**Figure 4:** Strengths of the produced HFO-based geopolymer cement

Figure 5 reports the maximum compressive strengths of HFO-based geopolymer (GA) —44 MPa and 31 MPa, respectively under dry and immersed conditions. These values are comparable with the reference geopolymer (SK) [1]. The flexural strength of GA is around 8 MPa.

The results of the present study show that using calcinated natural kaolinitic soil as the precursor material and HFO as a filler in the starting mixture affects the microstructure and strength of the geopolymers to a certain degree. The mechanical properties of HFO-based geopolymers are comparable with those of ordinary concrete [32]. Hence, the HFO-based geopolymers studied here satisfy the criteria for use in housing.

**Performance evaluation of using HFO-geopolymers for passive cooling systems**

This research strives to develop and assess the feasibility of a solar-thermal driven adsorption cooling system using low energy geopolymeric construction materials from local resources as the adsorbent–refrigerant pair. Thus, a preliminary study was carried out to analyze the effect of porous HFO particles on the evaporating cooling system as reflected in Figure 6. It is seen that the surface humidity at ambient conditions increases from 30% up to 38% by introducing the HFO particles as filler. This is an indication that the new product is more effective for evaporative cooling systems.



**Figure 5:** Effect of HFO on the indoor heating of the geopolymer chamber

Introducing porous HFO particles as filler for geopolymer cement reduces the heating rate of the closed chamber as shown in Figure 6. The most effective approach to cool a building is to prevent heating. The basic source of heat in a building is the sunlight energy naturally absorbed through the roof, walls and windows, as well as the heat generated by appliances and air leakages. The present study presents a sustainable method of cooling buildings by developing functional construction materials with a specific pore structure to increase the surface adsorbed water. It evaporates during hot weather, lowering the indoor temperature by means of the natural conditions that exist both in arid and semi-arid environments [1-4]. Under this approach, solar energy can be considered along with an evaporative cooling technique involving the use of a porous HFO-based geopolymer. Introducing HFO particles as the porous filler (Figure 6) increases the performance of a passive cooling system. The HFO-based geopolymer effectively reduces the air temperature of the room.

## CONCLUSIONS

In this study, HFO particles were introduced into geopolymer cement as functional fillers intended to improve the performance of passive cooling systems. One important finding resides in the possibility of using HFO for mass production of geopolymer cements offering high mechanical performance and acceptable physical properties, a sound alternative to the more conventional passive cooling system materials.

Metakaolin and HFO particles were transformed into a solid and hard matrix through the geopolymerization process. The resultant phases are largely amorphous. The HFO serves as a

functional filler with only a limited contribution in setting reactions. The HFO particles preserve their physical structure after geopolymerization, with no significant involvement in the chemical composition of the resultant geopolymer gel. The HFO pores are filled with geopolymer gel during the reactions.

HFO particles bear an influence on the physical and mechanical properties because of their low density and high porosity. The mechanical properties of HFO-based geopolymers are comparable with those of ordinary concrete. Hence, the HFO-based geopolymers studied here would satisfy the requirements for use in general construction and housing applications.

Our results demonstrate that introducing HFO particles as porous filler enhances the performance of a passive cooling system. Furthermore, the HFO-based geopolymer proves to be an effective material that reduces air temperature of the room.

## ACKNOWLEDGMENTS

Financial support for the project "Development of functional geopolymer-based construction materials for passive cooling of buildings" funded under contract number (AT-34- 211) by the King Abdulaziz City for Science and Technology KACST, within the Research Grants Program, is gratefully acknowledged.

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