Utilizing Fly Ash Cenosphere and Aerogel for Lightweight Thermal Insulating Cement-Based Composites

Asad Hanif, Pavithra Parthasarathy, Zongjin Li

Abstract—Thermal insulating composites help to reduce the total power consumption in a building by creating a barrier between external and internal environment. Such composites can be used in the roofing tiles or wall panels for exterior surfaces. This study purposes to develop lightweight cement-based composites for thermal insulating applications. Waste materials like silica fume (an industrial by-product) and fly ash cenosphere (FAC) (hollow micro-spherical shells obtained as a waste residue from coal fired power plants) were used as partial replacement of cement and lightweight filler, respectively. Moreover, aerogel, a nano-porous material made of silica, was also used in different dosages for improved thermal insulating behavior, while poly vinyl alcohol (PVA) fibers were added for enhanced toughness. The raw materials including binders and fillers were characterized by X-Ray Diffraction (XRD), X-Ray Fluorescence spectroscopy (XRF), and Brunauer–Emmett–Teller (BET) analysis techniques in which various physical and chemical properties of the raw materials were evaluated like specific surface area, chemical composition (oxide form), and pore size distribution (if any). Ultra-lightweight cementitious composites were developed by varying the amounts of FAC and aerogel with 28-day unit weight ranging from 1551.28 kg/m³ to 1027.85 kg/m³. Excellent mechanical and thermal insulating properties of the resulting composites were obtained ranging from 53.62 MPa to 8.66 MPa compressive strength, 9.77 MPa to 3.98 MPa flexural strength, and 0.3025 W/m-K to 0.209 W/m-K as thermal conductivity coefficient (QTM-500). The composites were also tested for peak temperature difference between outer and inner surfaces when subjected to heating (in a specially designed experimental set-up) by a 275W infrared lamp. The temperature difference up to 16.78 °C was achieved, which indicated outstanding properties of the developed composites to act as a thermal barrier for building envelopes. Microstructural studies were carried out by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) for characterizing the inner structure of the composite specimen. Also, the hydration products were quantified using the surface area mapping and line scale technique in EDS. The microstructural analyses indicated excellent bonding of FAC and aerogel in the cementitious system. Also, selective reactivity of FAC was ascertained from the SEM imagery where the partially consumed FAC shells were observed. All in all, the lightweight fillers, FAC, and aerogel helped to produce the lightweight composites due to their physical characteristics, while exceptional mechanical properties, owing to FAC partial reactivity, were achieved.

Keywords—Sustainable development, fly ash cenosphere, aerogel, lightweight, cement, composite.

I. INTRODUCTION

The use of thermal insulating composites in building structures is persistently encouraged due to its beneficial effects in reducing the power consumption for maintaining comfortable internal building environment. The thermal insulating behavior of cement-based materials depends largely on the type of filler aggregate and unit weight of the resulting concrete [1]. Concretes and mortars possessing lower unit weight lead to better thermal insulating performance [2]. Therefore, the choice of a suitable lightweight filler aggregate (LFA) for producing lightweight cementitious composite (LCC) becomes imperative. Previously, many researchers investigated different LFAs for their suitability in producing thermally insulating LCCs. Some of these LFAs are expanded perlite [3], [4], expanded shale [5], [6], pumice [5], [7], expanded clay [8], and expanded glass [9]. Although these materials prove to be beneficial in improving the thermal insulation of the resulting LCCs, some inherent properties of these LFAs hinder their use in structural applications. Firstly, most of these LFAs are produced by mechanical and heat treatment which not only increases the production cost but also contributes towards the CO₂ emissions; and secondly, these LFAs are too weak to produce a strong structural element resulting in poor mechanical properties of these composites. In order to address these issues, selection of a suitable LFA is needed which not only promotes sustainable development but also provides adequate strength to the resulting LCCs thereby creating opportunity for its applications structural applications.

Recently, FAC [10]–[17] and aerogel [18] have been studied for producing LCC. FAC is produced as a residue byproduct of coal burning during power production process [19]. It is lightweight having loose bulk density of about 800 kg/m³ and cost effective. Wu et al. [20] performed an extensive experimentation with numerous amounts of FAC in cement composites and established that FAC is an exceptional LFA for producing LCC. It was shown that FAC has the ability of producing LCC without substantial strength decrease. They could produce LCC with compressive strength of 49 MPa at 1240 kg/m³ density. Also, Demirboga [21, [22] presented that the thermal conductivity is affected due to the nature of the FAC which makes them an optimal choice for thermally insulated concrete as well. Moreover, aerogel is
another exceptionally light (bulk density less than 100 kg/m³) and nano-porous material made of silica with a high volume (about 95%) being the air voids [23]. Gao et al. [18] experimented with it to produce LCC and found that, using 60% of aerogel (by volume), the strength could reach merely 8.3 MPa with the density being 1000 kg/m³; which might be attributed to the low mechanical strength of the aerogel particles [24]. Although the properties of FAC and aerogels on the cementitious composite have been earlier investigated, the thermal properties of the resulting composites with emphasis on the co-effects of these LFAs in cementitious binder have been scarce. The aim of current research is to develop an ultra-lightweight cement-based composite by incorporating green materials (silica fume and FAC) and aerogels that possess not only excellent thermal insulation properties but also superior mechanical properties so that it can be effectively used in building structures for energy conservation.

II. EXPERIMENTAL METHODS

A. Materials
Ordinary Portland cement (OPC) type 52.5 (conforming to ASTM Type I) from Green Island, HK was used in the experimental study. Binder composed of OPC and locally available silica fume. FACs, having bulk density of 720 kg/m³ and particles size up to 400 microns, were acquired from Zhen Yang Mineral Powder Processing Plant, Hebei China. Fig. 1 shows the granulometric distribution of FAC particles. Aerogel particles, as obtained from Guangdong Alison Hi-Tech Co., Ltd (China), had the bulk density of 720 kg/m³, particle size range 0.1-5 mm, porosity >90%, pore diameter 20-100 nm, and specific surface area of 366.52 m²/g (measured experimentally by using Brunauer–Emmett–Teller (BET, Coulter SA 3100) analysis). The pore size distribution in aerogel is shown in Fig. 2. The PVA fiber (KURALON K-II REC15) used was 39 µm in diameter and 8 mm in length. The oxide composition (wt.%) of the powders is given in Table I.

![Fig. 1 Particle size distribution (by weight) of FACs](image)

<table>
<thead>
<tr>
<th>Description</th>
<th>Cement</th>
<th>FACs</th>
<th>Silica Fume</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.47</td>
<td>73.1</td>
<td>98.45</td>
</tr>
<tr>
<td>SO₃</td>
<td>5.71</td>
<td>0.41</td>
<td>0.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.49</td>
<td>3.94</td>
<td>0.31</td>
</tr>
<tr>
<td>Na₂O</td>
<td>---</td>
<td>2.42</td>
<td>---</td>
</tr>
<tr>
<td>CaO</td>
<td>65.4</td>
<td>1.05</td>
<td>0.77</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.26</td>
<td>0.35</td>
<td>---</td>
</tr>
<tr>
<td>MnO</td>
<td>---</td>
<td>0.05</td>
<td>---</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.86</td>
<td>16.7</td>
<td>---</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.2</td>
<td>1.95</td>
<td>0.05</td>
</tr>
<tr>
<td>MgO</td>
<td>1.58</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

B. Mix Proportioning and Specimen Casting
Two sets of mixes were prepared. Initially, only FAC was employed to cast six different composite specimens. The aim was to determine a suitable weight fraction of FAC for adequate mechanical characteristics while maintaining lower unit weight. Once and adequate weight fraction of FAC is determined, this amount was set as a basis for further modifying its properties with aerogel addition. The total 12 mix proportions (six with varying FAC amount and six with varying aerogel dosages), of the cementitious composites, in Table II. A fixed weight fraction of 1% of PVA fibers was used. Aerogel was added as percentage by weight of binder. A poly-carboxylate based super-plasticizing admixture was also used to retain the consistency and uniformity of the mixture.

The mixing procedure consisted of dry mixing of all the powders followed by addition of water and superplasticizer while continuously mixing. After a thorough mixing for about five minutes, the fibers were progressively disseminated in the mix while continuously mixing until the visual inspection revealed thorough uniform dispersion of fibers.

The mixed fibrous pastes were cast into the pre-lubricated steel molds and compacted on a vibrating table to facilitate removal of entrapped air. Specimen of size 40 mm x 40 mm x 160 mm (for flexural strength testing), 40 mm x 40 mm x 40 mm (for compressive strength testing) and 350 mm x 350 mm x 20 mm (for evaluating thermal conductivity behavior) were cast for each mix. After casting, the specimens were sealed with a plastic sheet at room temperature for one day. Later, the specimens were subjected to moist curing in curing room where the relative humidity and temperature were maintained.
at 95% and 25 °C, respectively. The curing was prolonged till the testing age which was 7 and 28 days.

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>Binder (by weight)</th>
<th>Water</th>
<th>FAC</th>
<th>Aerogel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement</td>
<td>Silica Fume</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FAC 1</td>
<td>0.90</td>
<td>0.10</td>
<td>0.35</td>
<td>0.20</td>
</tr>
<tr>
<td>FAC 2</td>
<td>0.90</td>
<td>0.10</td>
<td>0.40</td>
<td>0.25</td>
</tr>
<tr>
<td>FAC 3</td>
<td>0.90</td>
<td>0.10</td>
<td>0.42</td>
<td>0.30</td>
</tr>
<tr>
<td>FAC 4</td>
<td>0.90</td>
<td>0.10</td>
<td>0.45</td>
<td>0.35</td>
</tr>
<tr>
<td>FAC 5</td>
<td>0.90</td>
<td>0.10</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>FAC 6</td>
<td>0.90</td>
<td>0.10</td>
<td>0.55</td>
<td>0.60</td>
</tr>
<tr>
<td>FAC - A0</td>
<td>0.90</td>
<td>0.10</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>FAC – A2</td>
<td>0.90</td>
<td>0.10</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>FAC – A6</td>
<td>0.90</td>
<td>0.10</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>FAC – A8</td>
<td>0.90</td>
<td>0.10</td>
<td>0.55</td>
<td>0.50</td>
</tr>
<tr>
<td>FAC – A10</td>
<td>0.90</td>
<td>0.10</td>
<td>0.55</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**C. Testing Methods**

Compressive and flexural strength testing: In order to evaluate the mechanical behavior of the composites, three-point bending test was performed on the specimen with size 40 mm x 40 mm x 160 mm. MTS810, with force capacity of 250 kN, was used to apply load at the center of prism specimen with a span length of 100 mm. Only the specimens with FAC only were tested for flexure. The reason was primarily the determination of suitable weight fraction of FAC for producing strong lightweight composites. Loading rate was set as 0.20 mm/min. correspondingly, mid-span load and deflections were determined, and afterwards, equivalent stress and strain values in addition to the elastic modulus were calculated by using (1) and (2) [25]:

\[
\sigma = \frac{3Pl}{2b}
\]

\[
\varepsilon = \frac{6Dd}{L^2}
\]

where, \(\sigma\) = stress in the outer fibers at midpoint, MPa, \(\varepsilon\) = strain in the outer surface, mm/mm, \(P\) = load at a given point on the load-deflection curve, \(L\) = support span, mm, \(b\) = width of beam tested, mm, \(d\) = depth of beam tested, mm, \(D\) = maximum deflection of the center of the beam, mm.

Compressive strength testing was done on 40 mm x 40 mm x 40 mm specimen, by crushing them in automatic compression testing machine (5000 kN capacity), while the loading rate was maintained at 1.0 kN/sec [26]. The modulus of elasticity was calculated by using ACI 318M – 08 [27]. The relation used is given in (3):

\[
E = Wc^{1.5}(0.043)\sqrt{\lambda} f_c
\]

where, \(E\) = modulus of elasticity of concrete, MPa, \(Wc\) = density (unit weight) of concrete, kg/m³, \(f_c\) = compressive strength of concrete, MPa, and \(\lambda\) = modification factor reflecting the reduced mechanical properties of lightweight concrete.

Thermal Conductivity Testing: Thermal conductivity of the specimen was determined by using Quick Thermal Conductivity Meter (QTM-500). Larger specimens of size 350 mm x 350 mm x 20 mm were used for the testing. The thermal conductivity coefficient was determined at multiple points and averaged to estimate the representative value for each composite. The equipment could measure the thermal conductivity values up to the range of 0.23 to 12 W/m-K. QTM500 comprises of a probe sensor with a single heating wire and thermo-couple. The temperature of the wire increases in exponential progression when electric power is given to the probe. The heating wire is allowed to rest on the surface under testing for one minute. Temperature rising curve is plotted versus time on logarithmic scale. The lower the thermal conductivity, the smaller the slope of the curve. The thermal conductivity is measured by (4) [28]:

\[
\eta = \frac{q \ln\left(\frac{t_2}{t_1}\right)}{4\pi(T_2 - T_1)}
\]

where, \(\eta\) = Thermal conductivity of the sample, (W/m-K), \(q\) = Generated heat per unit length of sample/time, (W/m), \(t_1\), \(t_2\) = measure time length, (sec), \(T_1\), \(T_2\) = Temperature at \(t_1\), \(t_2\) (K).

The performance of the thermal insulating composites analogous to real life conditions (such as exterior wall panels or roof coverings for dissipating heat from the sun) was replicated in the laboratory by an experimental setup consisting of an infra-red lamp of 275 W acting as heat source (imitating sun) placed at a distance of 250 mm from the sample surface. The light heat was intensified with ceramic cylindrical partitioning (as shown in Fig. 3) which focused heat from the lamp directly on to the specimen surface. Multiple temperature sensors/thermocouples were employed to determine the temperatures of specimen surfaces. The thermocouples were connected to a data logger through a computer which recorded the temperature at interval of one second. Each specimen was exposed to steady heating of five hours. The difference of peak temperature between outer and inner surface was determined from the results.

**Fig. 3 QTM500 (a) and (b) steady thermal conductivity behavior testing setup**

Morphological and microstructural characterization: SEM was done to characterize inner surface of the broken specimen as well as the hydration products. JSM-6390 (JEOL) was
employed for this purpose which was also equipped with the EDS for mineralogical classification in the hydration products of the composites.

III. RESULTS AND DISCUSSION

A. Density and Mechanical Properties

Density and mechanical properties of FAC modified composites are given in Fig. 4. It was found that the density of FAC composites decreases directly with FAC incorporation. The higher the FAC amount, the lower is the density. The density varied from 1551.28 kg/m³ to 1027.85 kg/m³ depending on the amount of FAC utilized in producing the composites. However, it was seen that, in order to reduce the density of the resulting composite, significantly larger quantity of FAC is desirable (i.e. 50% or 60% by weight of cementitious binder). But, the FAC addition leads to greater total air content in the composite due to the inherent hollow spherical nature of FAC particles. Fig. 4 (b) shows the declining trend of compressive and flexural strength with FAC increasing amount. The developed composites showed outstanding mechanical performance in relation to their corresponding unit weight. It can be seen that incorporating 50% and 60% of FAC leads to a drastic strength reduction, while the corresponding density also decreases favorably indicating potential viability of the resulting composite for thermal insulating applications, as thermal conductivity reduces with the density of concrete and mortar. The aim of the current study was to develop thermally insulating composites with adequate strength characteristics so that such products could be used in building and structural applications, therefore, based on results of FAC composites, FAC 5 (i.e., 50% FAC content) was selected for further modification using aerogel.

The results of the FAC-aerogel incorporated lightweight composites are shown in Fig. 5. Like FAC composites, here also the declining trend in mechanical properties with aerogel addition was observed. However, such decrease was not significant because of the lower dosages of aerogel. The aerogel incorporation led to successfully achieve the lower density as required for ultra-lightweight cement composites (i.e., less than 1250 kg/m³). The lower density of the resulting composites is the key in achieving higher thermal insulating behavior.

B. Thermal Conductivity

The results of thermal conductivity testing are given in Figs. 6 and 7 where the thermal conductivity coefficient values (using QTM500) and peak temperature difference between exterior-interior surfaces (by steady heating test) are indicated, respectively. Direct correlation of thermal conductivity
reduction with increase in aerogel content was proved, and the linear trend line equation along with coefficient of determination is indicated in Fig. 8. It was found that incorporating merely 10% of aerogel leads to the thermal conductivity coefficient of 0.21 W/m·K which is a substantial improvement over conventional cement mortars where this value exceeds 1.4. The results of temperature difference between exterior and interior surfaces of the composite specimen indicate up to 14 °C difference. This suggests that if such composites are used as roof covering, exterior wall panels, etc., then the inner temperature of the building structure can be reduced in summers and increased in winters as these panels shall act as temperature barrier surface between the external and internal environment of the building. This may help to reduce the power consumption of the buildings due to reduced heating or cooling load requirements (as the case may be).

C. Morphological and Microstructural Analyses

The micro-morphological studies of the specimen showed that FAC and aerogel incorporation in the cementitious composites leads to a porous inner structure. Pore sizes up to a few hundred microns could be seen in the SEM imagery (Fig. 8). Such pores could be due to multiple reasons: first, the hollow nature of the FAC particles; second, the greater amount of required water (for adequate workability of the fresh mixes) with increasing FAC amount; and third, the spherical nature of FAC particles leading to improper packing of the particles within the binder matrix. All the aforementioned factors may contribute towards the higher apparent porosity. The PVA fibers were seen to have adequate bonding in the matrix thus facilitating strain hardening of the composites when tested for flexural performance. The EDX analysis (Fig. 9) showed the typical hydration products as found usually in the cement-based materials. Moreover, partially consumed (not broken) FAC shells were also observed in SEM imagery indicating the partial reactivity of FAC particles.

Fig. 7 Peak temperature difference between exterior and interior surfaces of specimen subjected to steady heating

Fig. 6 Thermal conductivity coefficient (measured by QTM500) and density at 28-day age

Fig. 8 (a) General morphology of the inner surface of FAC composites and (b) SEM image of FAC-aerogel specimen (aerogel particles are identified with the letter ‘A’)
Acknowledgment

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References

[27] ACI Committee 318, Building Code Requirements for Structural Concrete (ACI 318M-08), 2007.