Journal of Materials, Processing and Design (2024)
Clausius Scientific Press, Canada
DOI: 10.23977/jmpd.2024.080205
ISSN 2516-0923 Vol. 8 Num. 2

# Study on the effect of using carbon coated fly ash cenospheres on the performance of thermal insulation coatings

**Rui Shen[1,a], Ping He[1,b,*], Sorachon Yoriya[2,c], Naichao Chen[1,d], Jiang Wu[1,e]**

[1]*College of Energy and Mechanical Engineering, Shanghai University of Electric Power, Shanghai, 200090, China*

[2]*National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency (NSTDA), 111 Thailand Science Park, Phahonyothin Road, Khlong Nueng, Khlong Luang, Pathum Thani, 12120, Thailand*

[a]*shenrui0224@163.com*, [b]*heping@shiep.edu.cn*, [c]*sorachy@mtec.or.th*, [d]*yeiji_chen@126.com*, [e]*wjcfd2002@163.com*

[*]*Corresponding author*

***Keywords:*** Cenospheres, fly ash, thermal insulation coatings, surface modification

***Abstract:*** Cenospheres are widely used in industry because of their unique properties such as low density, low thermal conductivity, good thermal stability and impact resistance. This paper focuses on the effect of fly ash cenospheres on the thermal insulation performance of coatings in coal-fired power plants. Using polyacrylic acid as the substrate, the effect of particle size and filling amount of fly ash cenospheres on the thermal insulation performance of thermal insulation coatings was investigated. The results show that the smaller the particle size of fly ash cenospheres, the more significant the effect on the thermal insulation performance of the coatings; at the same time, within a certain reasonable range, increasing the filling amount of fly ash cenospheres can effectively improve the thermal insulation effect of the coatings. We100-200 fly ash cenospheres were selected and their filling amount in the coatings was adjusted to 30% to prepare carbon-coated fly ash cenospheres, and composite heat-insulating coatings were prepared to study the effect of carbon-coated fly ash cenospheres on the composite heat-insulating coatings. The carbon coated fly ash cenospheres showed advantages in enhancing the thermal insulation performance of the coatings. Through the thermal conductivity test and thermal insulation performance experiments, the modification strategy effectively reduces the thermal conductivity of the material by introducing a layer of carbon with high thermal resistance on the surface of fly ash cenospheres, and the reduction of thermal conductivity is about 20.4%, which achieves the optimization of the thermal insulation effect.

## 1. Introduction

In the contemporary era of rapid technological development, the surge in global energy consumption and the consequent rise in carbon emissions have caused a significant exacerbation of the greenhouse effect, which in turn has driven drastic changes in the global climate. In view of this, and in response to the international community's general call for energy conservation and emission reduction, this study proposes the application of thermal insulation coating technology to the building envelope. This technology aims to effectively reduce the building's dependence on heating, ventilation and air conditioning (HVAC) systems by optimizing the thermal performance of the building to achieve thermal insulation in winter and cooling in summer. This is expected to significantly reduce energy consumption and greenhouse gas emissions, thereby promoting the green transition and low-carbon development of the building industry.

Fillers play a central role in optimizing the performance of thermal insulation coatings. Cenospheres, as a class of highly efficient fillers for thermal insulation, show great potential in the development and application of military and civil thermal insulation materials due to their unique physical structure. Cenospheres have a low thermal conductivity, and the addition of cenospheres into thermal insulation coatings can improve the thermal insulation performance of thermal insulation coatings. Li[1] Titanium dioxide-coated cenospheres, a new type of heat-insulating filler, were prepared by sol-gel method and found to have good heat-insulating effect. Wang[2] Silica microspheres were prepared by the template method and compounded with silicone resin to prepare thermal insulation coatings with excellent thermal insulation and hydrophobicity, which extended the application field of cenospheres. Over the past few decades, cenospheres have been shown to be effectively dispersed in a wide range of matrix materials, including polymers[3], cements[4], and nickel alloys, and are widely used in the manufacture of industrial composites and coated foams. In view of their unique physicochemical properties, cenospheres as fillers in polymer-based products show great application potential and significant performance advantages. Although there is a wide variety of thermal insulation materials, only a few are used in thermal insulation coatings, and most of them are added with unmodified cenospheres or aerogels, whose thermal insulation performance needs to be further improved and functionality needs to be further expanded, and the current research on the surface modification of cenospheres is still relatively small, which provides a broad research space for future material innovation and performance optimization.

Fly ash cenospheres, as a high value-added material extracted from fly ash, have a hollow spherical shape with physical properties such as low density, smooth surface, excellent thermal stability, and excellent thermal insulation performance[5,6]. These properties give fly ash cenospheres significant advantages in enhancing the performance of thermal insulation materials, which predicts that their application in the field of thermal insulation technology has far-reaching research and development value[7]. Fly ash cenospheres are extracted from thermal power plant fly ash, which can effectively improve the reuse of fly ash, as well as effectively deal with the waste by-products of thermal power plants, thus reducing the pollution of fly ash to the environment[8-10].

The aim of this study is to investigate the thermal insulation coating system using polyacrylic acid as the base material and composite filled fly ash cenospheres (FAC). The research focused on analyzing the specific effects of particle size and filling amount of FAC on the thermal insulation performance of coatings. In addition, in this study, hydrothermal synthesis method was used to prepare carbon spheres capping layer on the surface of FAC to realize the modification of FAC surface. Further, the effect of surface-modified FAC on the thermal insulation performance of composite thermal insulation coatings was explored to enhance the thermal resistance of the material and optimize its thermal insulation effect in practical applications.

## 2. Materials and Methods

### 2.1. Materials

In this experiment we used a series of chemical reagents, which include: polyacrylic acid ($[C_3H_4O_2]n$), alcohol ester dodecyl film-forming additive, PTF acrylic thickener, antifoam agent, sodium hydroxide titrant (NaOH), and anhydrous glucose. All of the above chemical reagents are of experimental analytical grade and require no further processing. Fly ash cenospheres (FACs) were obtained from Henan Datang Power Plant, and there were three different sizes of FACs (We20-40, We40-100, and We100-200). Table 1 shows the specific compositions of the FACs, in which SiO2 has the largest percentage.

Table 1: FAC composition table (in wt.%).

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Na_2O$ | $TiO_2$ | $K_2O$ | MgO | CaO | $SO_3$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|
| 52.663 | 41.037 | 1.818 | 1.013 | 0.923 | 0.86 | 0.604 | 0.531 | 0.275 | 0.13 |

### 2.2. Experimental System

In this study, a thermal insulation performance test device was designed and constructed as shown in Figure 1. The device consists of four main parts: a thermal insulation box, a thermometer, a test plate, and an infrared irradiation lamp. The thermal insulation box consists of ceramic fiber board with dimensions of 293 mm × 220 mm × 200 mm and is not provided with a top. The fiber boards were bonded using a high temperature resistant sealant to form a lidless, hollow and airtight thermal barrier, where the thickness of the ceramic fiber boards was set at 10 mm to ensure good thermal insulation. On one side of the insulated box, a hole with a diameter of 5 mm was precisely drilled for inserting and firmly fixing the probe of the air temperature sensor for temperature measurement. The test board was made of asbestos cement board and was placed on top of the insulated box. At a distance of 10cm above this, a 375W adjustable infrared heat lamp was installed to simulate an external heat source and provide consistent heat radiation.

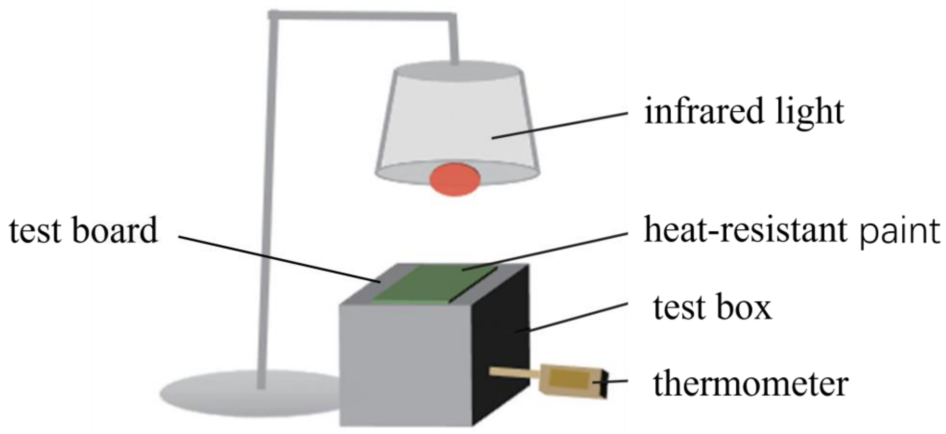


Figure 1: Thermal insulation test equipment.

### 2.3. Methods of Preparing Coatings

Proportionally weighed polyacrylic acid and deionized water mixing, mixing uniformly after adding FAC, the process of using a magnetic stirrer to make the dispersion more uniform, in the mixing process, add a certain amount of antifoam agent, thickening agent and film-forming additives in turn, stirring for 10min, and again add a small amount of antifoam agent, to eliminate the mixing process of the tiny bubbles generated, mixing uniformly to produce the coating, the basic formula is shown in Table 2.

Table 2: Basic formulation for thermal barrier coatings.

| Raw materials | wt% |
| --- | --- |
| polyacrylic acid | 40~60 |
| FAC | 15~30 |
| Defoamer | 0.1~0.3 |
| Thickener | 0.1~0.3 |
| Film forming auxiliaries | 0.1~0.3 |
| Deionized water | appropriate amount |

## 3. Results and Discussion

### 3.1. Study on the Effect of FAC Pore Size on the Thermal Insulation Performance of Coatings

In this study, a standardized coating preparation process was used to control the doping ratio of FAC to 15 wt% of the total coating mass. Three kinds of FAC with different particle size specifications, namely We20-40, We40-100 and We100-200, were sequentially doped to prepare three kinds of thermal insulation coatings with different particle size distributions of microbeads. These coatings were uniformly coated on standard test substrates and ventilated and dried at ambient temperature for 36 hours. Figure 2 illustrates the surface morphology of the dried thermal barrier coatings, where (a), (b) and (c) correspond to thermal barrier coatings containing We20-40, We40-100 and We100-200 FAC, respectively.

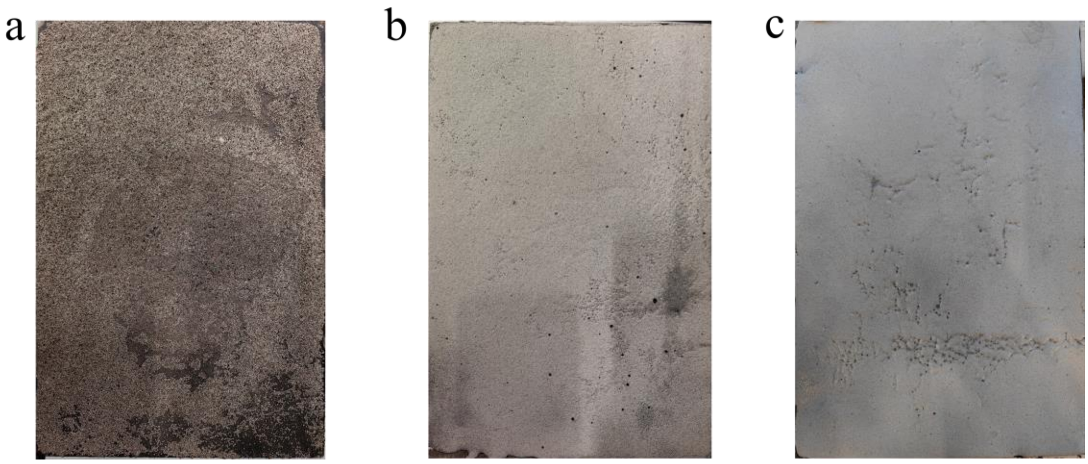


Figure 2: Insulation coatings with different FAC particle sizes (a for W20-40, b for We40-100, c for We100-200).

Observing the image shown in Figure 2, it can be clearly pointed out that FAC with smaller particle size (i.e., high mesh size) exhibited more uniform and continuous coating characteristics on the asbestos-cement substrate, while forming a thicker coating layer. Specifically, when the FAC has a mesh size of We20-40, although full coverage of the substrate is achieved, particle aggregation and cascading occurs on the coating surface due to the interfacial roughness caused by its larger particle size, which results in the creation of gaps. Upon further increasing the size of FAC to We40-100, unevenly distributed pore structures were observed after the coating dried. Poor interfacial compatibility between the larger particle size FAC and the polyacrylic acid matrix can be observed. This interfacial incompatibility is believed to be due to the mismatch between the surface energy of the larger particle size beads and the polymer matrix, which in turn could potentially affect the overall insulation effectiveness of the coating. When the FAC specification was upgraded to We100-200, the homogeneity and smoothness of the coating improved significantly, and the surface of the coating showed a more consistent morphology than the previous two specifications.

Subsequently, these coatings were subjected to a pre-determined thermal insulation performance test setup for thermal insulation performance assessment. At the beginning of the experiment, when the temperature sensor recorded that the baseline temperature reached 35 ℃, a timer was started and the temperature changes inside the thermal barrier were continuously recorded at 5-minute intervals until the total test time reached 60 minutes. The continuously monitored and recorded temperature data during the 60-minute test period are presented in the form of a line graph in Figure 3. The graph reveals a trend: as the particle size of the FAC decreases (i.e., the number of mesh increases), its thermal resistance performance in thermal barrier coatings is significantly improved.

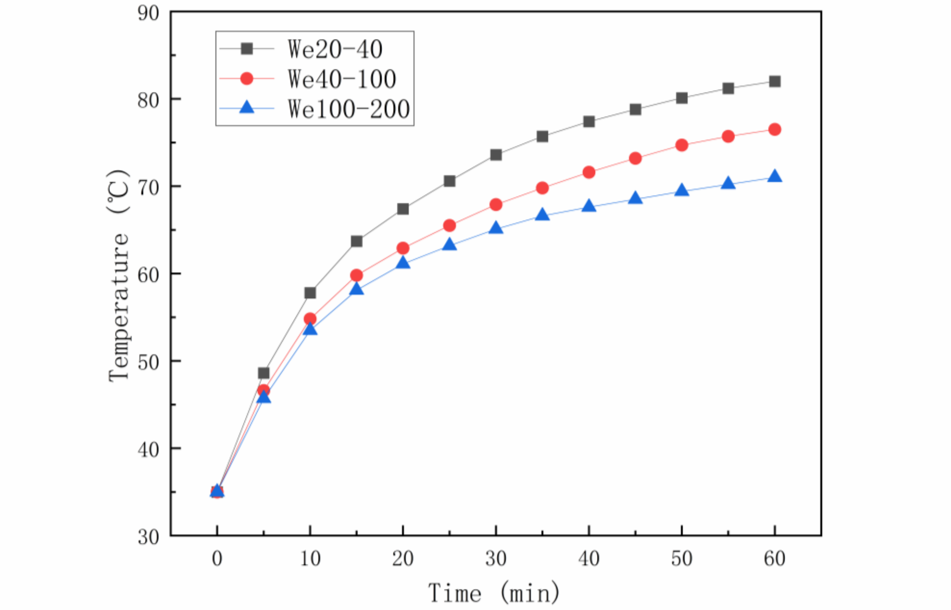


Figure 3: Temperature variation of FAC with different particle sizes.

## 3.2. Study on the Effect of FAC Content on the Thermal Insulation Performance of Coatings

In this study, We100-200 specification of FAC exhibited superior thermal insulation performance in coatings, and thus was selected as the experimental material for further investigation of the effect of FAC doping ratio on the performance of thermal insulation coatings. The doping ratios of FAC were systematically adjusted to 15 wt%, 20 wt%, 25 wt%, and 30 wt%, and the thermal insulation effects of the different formulations were evaluated using the aforementioned thermal insulation performance testing device. Figure 4 illustrates the surface morphology of the thermal insulating coatings with different FAC doping ratios, where (a), (b), (c) and (d) correspond to 15wt%, 20wt%, 25wt% and 30wt% FAC doping ratios, respectively. By carefully observing the surface of the dried coating, it can be found that the surface of the coating presents a more uniform and smooth morphology with the increase of FAC content, which indicates that the high content of FAC helps to improve the surface quality of the coating.

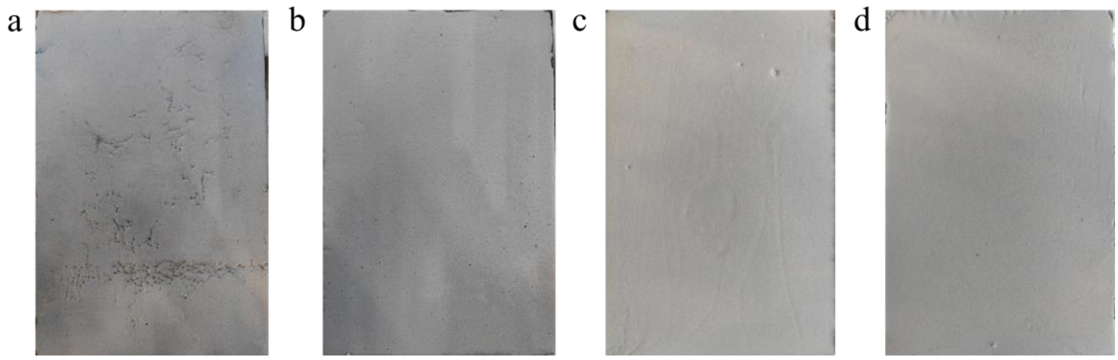


Figure 4: Thermal barrier coatings with different FAC incorporation (a 15 wt%, b 20 wt%, b 25 wt%, c 30 wt%).

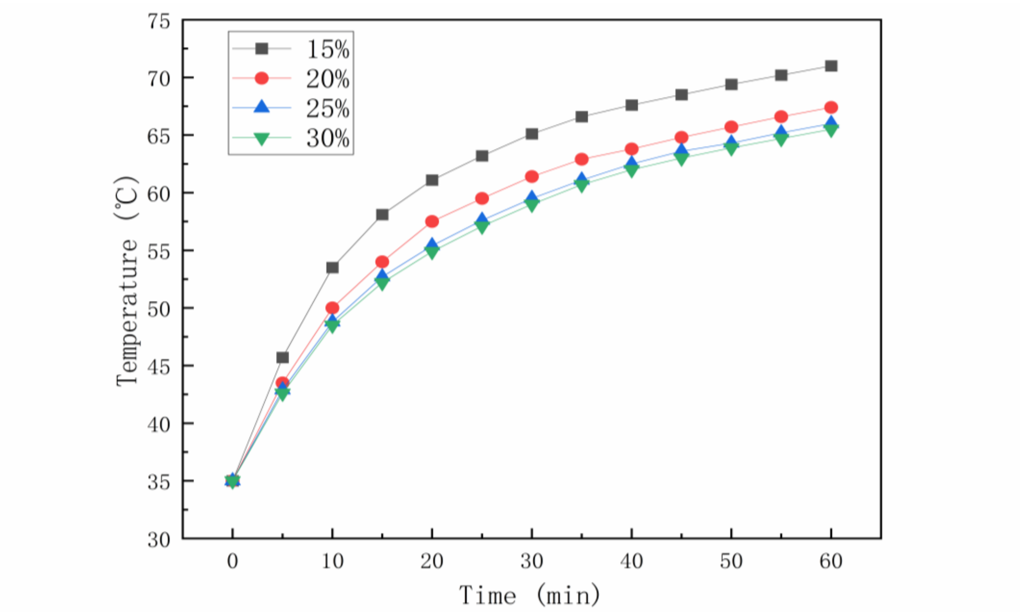


Figure 5: Temperature variation with different FAC doping levels.

Based on the trend of the data presented in Figure 5, it can be clearly observed that the rate of temperature increase inside the thermal barrier box shows a significant slowdown with the gradual increase in the FAC doping ratio. This phenomenon indicates that a high content of FAC in the coating can significantly enhance the thermal insulation performance of the coating. Specifically, the increase in the amount of FAC doping led to a reduction in the thermal conductivity, which enhanced the barrier effect of the coating on heat transfer, and thus achieved a more excellent thermal insulation effect. However, the improvement in the thermal insulation efficiency of the coatings slowed down when the amount of FAC added was increased from 25% to 30%. Based on this phenomenon, the doping ratio of FAC was limited to 30% in this study as an upper limit for further experiments.

### 3.3. Carbon Coated FAC

In view of the limitations of FAC emitted from thermal power plants in terms of thermal insulation performance, this study adopts a modification strategy to reduce its thermal conductivity and thus optimize its effectiveness in the application of thermal insulation coatings.

### 3.3.1. Carbon-coated FAC Preparation

In the first step of the alcohol wash treatment, the FAC was washed with an anhydrous ethanol solution aimed at removing impurities and potential organic residues adhering to the surface. As shown in Figure 6, the surface of the FAC without the alcohol wash treatment was characterized by the presence of significant impurity particles; in contrast, the surface of the alcohol-washed sample in Figure 7 exhibited superior smoothness. This step is to ensure uniformity and adhesion for subsequent surface modification or coating processes. After the alcohol wash, the FAC was dried in a drying oven at 75-85 ℃ for 20-30 hours.

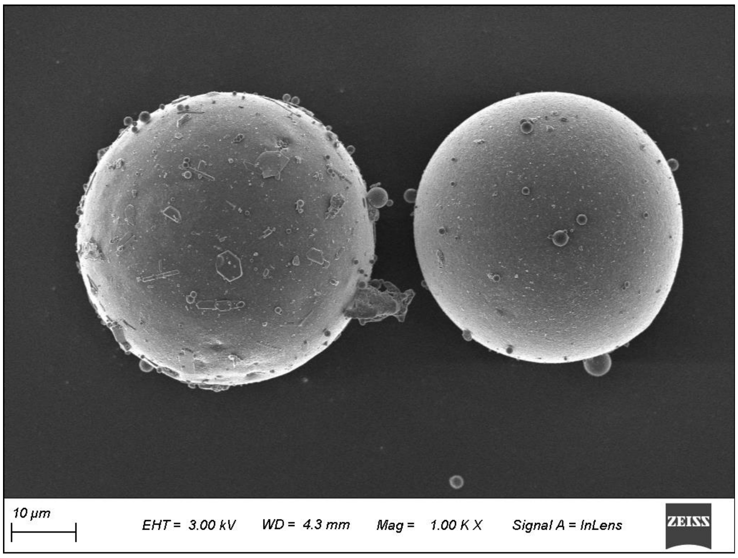


Figure 6: SEM image of unalcohol-washed FAC.

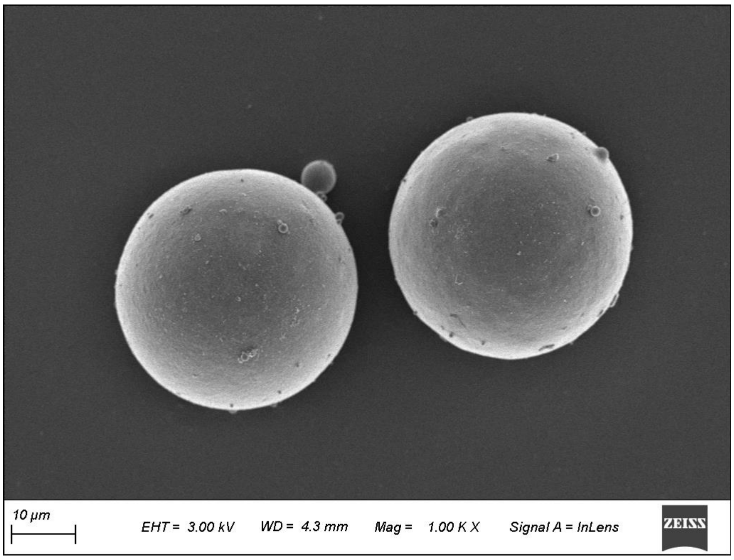


Figure 7: SEM image of the alcohol-washed FAC.

The second step of hydroxylation treatment. To hydroxylate the surface of FAC, the cleaned and dried FAC was completely infiltrated in 0.1 mol/L sodium hydroxide (NaOH) solution and uniformly stirred for 1h using a magnetic stirrer at a set temperature of 80 ℃. The FAC was then cleaned and filtered, and then washed and filtered. After the stirring was completed, filtration was carried out, and after the filtration was completed, cleaning and filtration were carried out. After cleaning, it was put into a drying oven at 80 ℃ for 24 h. The solution was then dried in the drying oven at 80 ℃ for 1 h.

The third step of carbon coating treatment. Anhydrous glucose was used as a carbon source to form an amorphous carbon spheres coating on the surface of FAC by pyrolysis method as a means of surface modification of FAC. In order to find a better ratio of anhydrous glucose to FAC, the raw materials were accurately proportioned according to the substance amount ratios of anhydrous glucose to FAC of 1:1, 1.25:1, and 1.5:1, and the proportioned raw materials were poured into a beaker, added with deionized water and stirred homogeneously, and then the mixture was loaded into a high-temperature reactor and subjected to a constant-temperature heat treatment for 12 hours at 180 ℃. The mixture was then treated by the thermolysis method for the surface modification of FAC, which was carried out by the thermolysis method. Upon completion of the reaction, the reactor was cooled down to ambient temperature, followed by transferring the reaction product to a beaker and adding deionized water for 30 seconds with stirring to facilitate the diafiltration process. The unreacted anhydrous glucose and possible impurities were removed by filtration and subsequent washing steps, and finally dried to obtain the surface-modified FAC.

### 3.3.2. FTIR Analyze

The resulting Fourier transform infrared spectra (FTIR) of the hydroxylated modified samples are shown in Figure 8. Figure 8 demonstrates two key absorption peaks: the absorption peak located at 1096 cm-1 is attributed to the stretching vibration of the C-O bond, while the absorption peak at 3438 $cm^{-1}$ corresponds to the stretching vibration of the hydroxyl (OH) group, and the presence of this characteristic peak confirms the successful implementation of the hydroxylation treatment on the surface of the FAC.

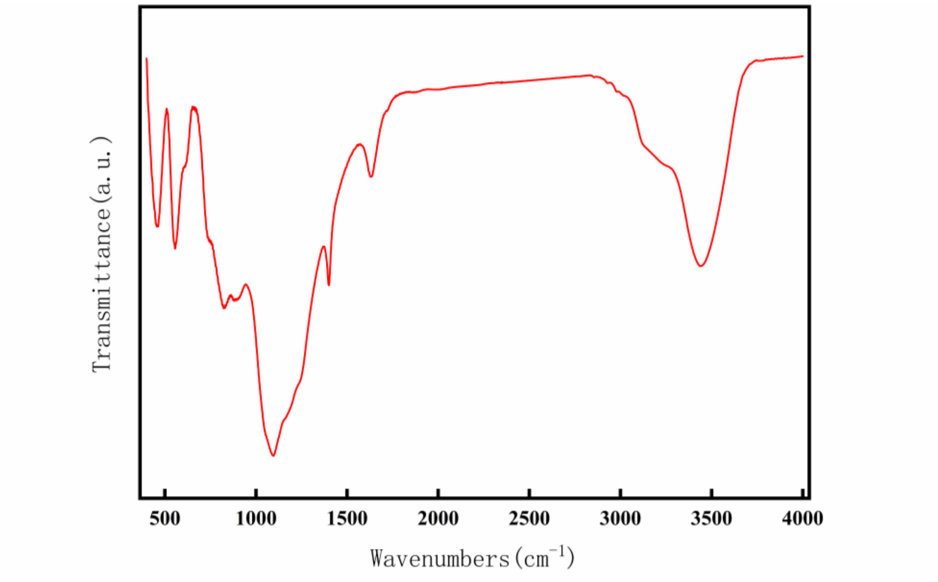


Figure 8: FTIR plot after hydroxylation.

### 3.3.3. SEM analyze

As shown in Figure 9, the scanning electron microscope (SEM) image of the carbon-coated FAC reveals that its surface is uniformly covered with a layer of amorphous carbon spheres. Further observing Figure 10, the diameter of these carbon spheres ranges from 2 to 5 micrometers. The amorphous structure of this carbon layer effectively reduces the thermal conductivity of the FAC and significantly improves its thermal insulation performance. In addition, the focused ion beam scanning electron microscopy (FIB-SEM) images shown in Figure 11 indicate that the carbon-coated FAC prepared by hydrothermal synthesis maintains its original microstructural integrity, a result that confirms that hydrothermal method, as a mild synthesis technique, is able to realize the surface modification without destroying the intrinsic morphology of FAC.

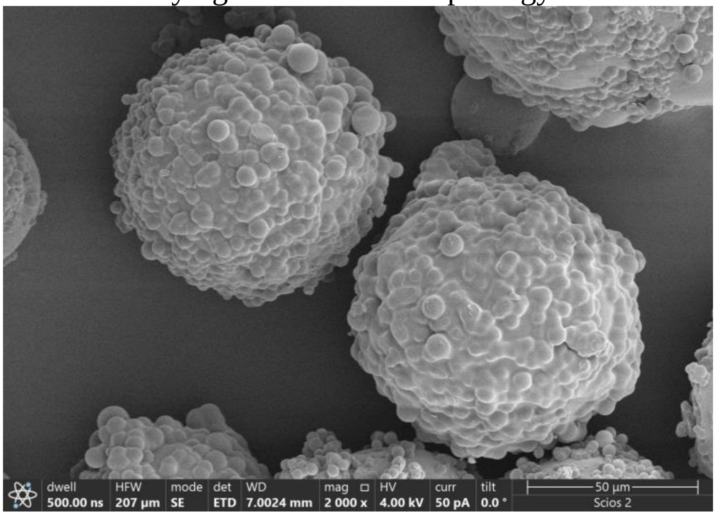


Figure 9: SEM image of FAC after carbon coating.

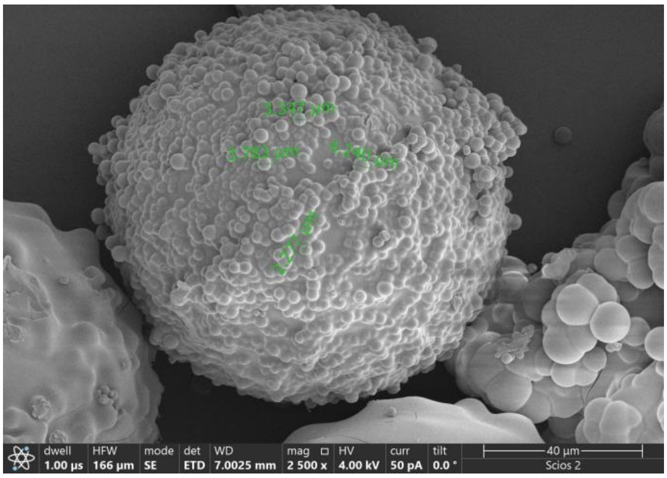


Figure 10: SEM image of a carbon pellet.

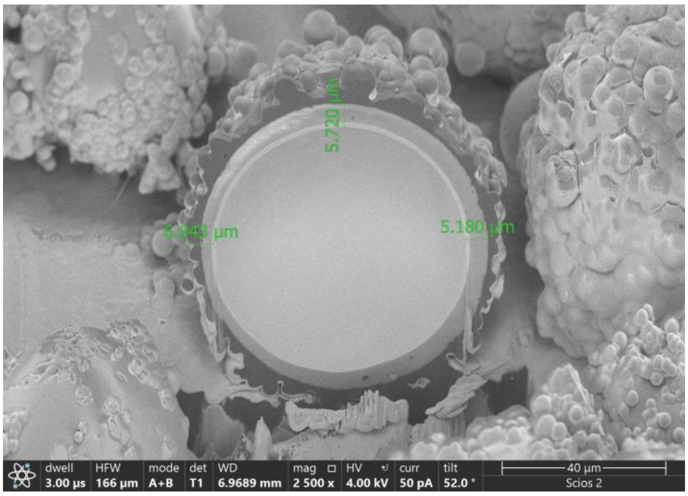


Figure 11: FIB-SEM image of FAC after carbon coating.

### 3.3.4. Thermal Conductivity Test

The thermal conductivity coefficients of unmodified FAC and FAC after surface carbon encapsulation were measured. As shown in Table 3, the lowest thermal conductivity coefficient of the prepared carbon spheres coated FAC was obtained when the ratio of anhydrous glucose to FAC was 1.25:1. The thermal conductivity of the unmodified FAC was 0.1363 W/mK and 0.1084 W/mK after modification, and the reduction of the thermal conductivity was about 20.4%, which indicated that the carbon coated FAC had a significant improvement in the thermal insulation performance.

Table 3: Thermal conductivity.

| | Unmodified FAC | Dextrose anhydrous : FAC | | |
|---|---|---|---|---|
| | | 1:1 | 1.25:1 | 1.5:1 |
| Thermal conductivity (W/mK) | 0.1363 | 0.1264 | 0.1084 | 0.1184 |

### 3.3.5. Thermal Insulation Test

According to the above coating configuration method, the modified FAC content of 30% was added to prepare a new thermal insulating coating, and the prepared coating was applied on the test plate and dried in a cool ventilated place for 48 h. As shown in Figure 12, it demonstrates the surface morphology of the thermal insulating coatings prepared by FAC after the surface carbon coating treatment presented after drying.

Figure 12: Addition of Carbon Encapsulated FAC for Thermal Insulation Coating.

Subsequently, the coatings were tested for their thermal insulation effect using the thermal insulation performance test method described above. In the graph of data presented in Figure 13, this study observed that the introduction of carbon coated FAC into the formulation of the thermal insulating coatings significantly reduced the rate of temperature rise as compared to the matrix coatings that did not contain this modified component. This phenomenon reveals the significant contribution of the modified FAC in enhancing the thermal insulation performance, thus confirming its effectiveness in enhancing the thermal resistance properties of the material.

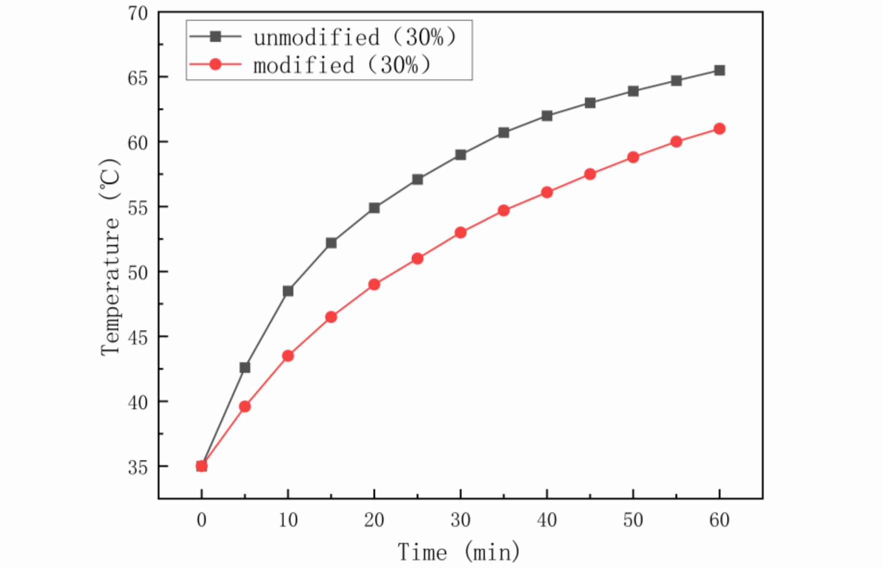


Figure 13: Temperature change of adding carbon coated FAC.

## 4. Conclusions

In this study, we investigated the effect of filling FAC on thermal insulation coatings using polyacrylic acid as the base material. Through a series of experiments, we evaluated the effects of FAC particle size, filler content, and carbon coating on the thermal insulation performance of the coatings. The results show that the particle size and content of FAC have a significant effect on the thermal insulation effect of the coatings, and the thermal insulation performance of the coatings can be further enhanced by carbon coating treatment. First, the experimental results revealed the importance of FAC particle size on the thermal insulation performance of the coatings. With the reduction of FAC, the thermal insulation effect of the coating was significantly enhanced. Secondly, the filling amount of FAC is also a key factor affecting the thermal insulation performance of coatings. It was found that increasing the filling amount of FAC within a certain range can effectively improve the thermal insulation effect of the coating. However, when the filling amount exceeded a certain percentage, the improvement of the thermal insulation efficiency slowed down. In addition, the hydrothermal synthesis method was used in this study to carbon coat the FAC, which significantly reduced its thermal conductivity by 20.4% by forming a coating layer of amorphous carbon spheres on the surface of the FAC, as well as optimizing the thermal insulation performance of the coating. The results of this study provide a strategy for the innovation of thermal insulation coatings and significantly advance the resource utilization of fly ash from thermal power plants. This strategy not only enhances the economic value of industrial by-products, but also helps to reduce energy consumption, which is important for promoting the construction of low-carbon economy and sustainable industrial ecology.

## Acknowledgements

This work was sponsored by the “National Key R&D Program of China” (2021YFE0109800).

## References

*[1] Xiaoyu L, Jiajie L, Dan L, Danielxian S, Xiaoling Y, Rongshuang X, et al. Preparation of hollow glass beads containing titanium dioxide and its application in heat-insulted coatings. New Building Materials/Xinxing Jianzhu Cailiao 2020; 47(2).*

*[2] Wang J. Preparation and properties of SiO2 aerogel and fabric composite based on polyurethane. Xi'an Polytechnic University, School of Textile and Materials, Xi'an, China, 71179 2018; Vol. 189(No. 1): 36-43.*
*[3] Devi MS, Murugesan V, Rengaraj K. Utilization of fly ash as filler for unsaturated polyester resin. Department of Chemistry, Anna University Chennai-600 025, India 1998;Vol. 69(No.7): 1385-1391.*
*[4] Maher A, Balaguru PN. Properties of Flowable High-Volume Fly Ash-Cement Composite. Dept of Civ and Envir Engrg, Rutgers Univ, Piscataway, NJ, 08855, United States 1993; Vol. 5(No.2): 212-225.*
*[5] Hirajima T, Petrus HTBM, Oosako Y, Nonaka M, Sasaki K, Ando T. Recovery of cenospheres from coal fly ash using a dry separation process: Separation estimation and potential application. International Journal of Mineral Processing 2010; 95(1-4): 18-24.*
*[6] Kolay PK, Singh DN. Physical, chemical, mineralogical, and thermal properties of cenospheres from an ash lagoon. Department of Civil Engineering Geotechnical Engineering Division Indian Institute of Technology, Bombay, Powai, Mumbai 400 076, India 2001;Vol. 31(NO.4): 539-542.*
*[7] Yih SM, Tu C, Kuto ST, Quo LW. Recovery Of Cenospheres And Application To The Manufacture Of Insulation Materials. Chung Yuan Christian Univ, Chung Li, Taiwan, 1988; Vol. 19(No.1): 23-29.*
*[8] Gupta N, Brar BS, Woldesenbet E. Effect of filler addition on the compressive and impact properties of glass fibre reinforced epoxy. 1Department of Mechanical Engineering,Louisiana State University,Baton Rouge,USA;2Baba Banda Singh Engineering College,Punjab,India 2001;Vol.24(NO.2): 219-223.*
*[9] Rohatgi PK, Weiss D, Gupta N. Applications of fly ash in synthesizing low-cost MMCs for automotive and other applications. 1Center for Composite Materials, Materials Engineering Department,University of Wisconsin-Milwaukee,Milwaukee,USA;2Composite Materials and Mechanics Laboratory, Mechanical and Aerospace Engineering Department,Polytechnic Institute of New York Univ 2006;Vol.58(No.11): 71-76.*
*[10] Doddamani M, Kulkarni S. Dynamic response of fly ash reinforced functionally graded rubber composite sandwiches - a Taguchi approach. International Journal of Engineering, Science and Technology 2011; Vol.3(No.1).*