Cenospheres Recovery from Fly Ash

Subjects: Crystallography

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Coal fly ash (CFA) is a major global pollutant produced by thermal power plants during the generation of electricity. A significant amount of coal fly ash is dumped every year in the near vicinity of the thermal power plants, resulting in the spoilage of agricultural land. CFA has numerous value-added structural elements, such as cenospheres, plerospheres, ferrospheres, and carbon particles. Cenospheres are spherical-shaped solid-filled particles, formed during the combustion of coal in thermal power plants. They are lightweight, have high mechanical strength, and are rich in Al-Si particles. Due to cenospheres' low weight and high mechanical strength, they are widely used as ceramic/nanoceramics material, fireproofing material, and in nanocomposites.

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1. Introduction

Coal fly ash (CFA) is one of the major pollutants of the 20th and 21st centuries. It has drawn global attention regarding its safe management, optimized generation, and utilization [1]. Globally, a million tons of CFA are generated per year, in thermal power plants (TPPs), from the burning of pulverized coal, during the production of electricity [2]. The huge amount of generation of CFA leads to air, water, and soil pollution. Every year, a huge amount of CFA is dumped in the near vicinity of the TPPs, in fly ash ponds, which ultimately leads to water and land pollution. These fly ashes contain heavy metals, which can leach out once they contact water [3]. Besides heavy metals, CFA also contains minerals, such as magnetite, calcite, mullite [4], cristobalite, and silica [2]. These minerals contribute to the silica (40–60%), alumina (20–40%), and ferrous (5–15%) that rely on the source and types of coal used [2].

Since TPP furnaces are operated at very high temperatures (1000–1800 °C), the organic matter of coal becomes decomposed into a molten slag, which attains morphologically variable shape and size [5]. This variation leads to structurally different types of particles in CFA, namely, plerospheres, ferrospheres, and cenospheres (CS) [6]. The plerospheres are encapsulated particles that have numerous smaller particles within them, along with gases and minerals [7]. While, as the name suggests, ferrospheres are ferrous-rich spheres or "spherical particles" [8], and cenospheres are Al-Si rich spheres or "spherical particles" [2]. These Al-Si-rich particles are also known as aluminosilicate spheres or CFA microspheres [2]. As well as these spherical particles, there are varying amounts of irregular-shaped organic and inorganic carbon particles, i.e., unburned carbon soot and chars.

Among all the spherical particles, CS have been a focus in the field of ceramics, construction, lightweight materials, agriculture, etc., due to their unique physical and mechanical features. The word "cenospheres" is derived from the two Greek words—cenos, meaning "hollow", and spahira, meaning "spheres" [9]. Due to the hollow nature of CS, their density is near 2.3 g/cm^3, whereas the buoyancy of a CS is provided by its density. The bulk density of CS is around 400 kg/m^3 [10][11], and the true density is ca. 2.3 g/cm^3 [12]. Their high mechanical strength, high porosity, and thermal shock-resistance have encouraged scientists to use them in ceramics, the preparation of nanocomposites (decorating micron-sized CS with nanomaterials), and for environmental cleanup [13].

2. Morphological Properties of CFA Extracted Cenospheres

Based on the morphology, viscosity of liquid composition of slag, and elemental composition, some investigators have classified the CS into two broad types—namely, nonmagnetic CS and magnetic CS. The formation of magnetic CS depend upon the melts of A-Si and Fe-Al-Si [9]. High viscosity type cenospheric particles have more tendency to trap gases and increase in diameter of the particle, resulting in the thinner shell with the complete absence of pores [14].

Certain cenospheres have high Fe deposition on their surface that exhibit magnetic properties, while others are mainly rich in Al and Si (along with Na and Ca). In numerous pieces of literature, CS with small Fe deposition have been widely in the petroleum cracking, catalysis, ceramic, nanocomposites, and steel or iron-based industries [2].

Based on some physical parameters, i.e., texture, shell thickness, and shape, cenospheric particles are either transparent, grey, and dark type [15]. The former type of particle is thin-shelled, smooth-surfaced, grey type are translucent, porous, thick, and rough-surfaced [9]. While the dark-type CS have numerous perforations on their surface, their porosity is much greater than the grey CS. Dark CS scatters the light completely, which is passed through them and acts as an opaque particle. Ferrous-rich CS can be divided into two types: One having a porous shell, while the other with a spotty nonuniform surface, containing grey, black, brown, and white inclusions, along with dark black or brown spheres with a bright and smooth surface [16]. The Al content contributes a valuable role in the average size of a nonmagnetic CS, i.e., more Al equals higher mullite, and ultimately results in a decrease in the average diameter [9][17][18].

CS can be divided into two main groups, based on their magnetic features, which are acquired by the presence of Fe_2O_3/Fe_3O_4 minerals in the shell [19]. The shell of CS is a complex, layered structure (which is covered by a nano-size film externally), and internally [16][20] (which is 30–50 nm thick and contains Fe_2O_3). When the ferrous oxide percentage varies from 3 and 4 wt.% in the alumino-silicate glass, then two types of Fe^{3+} are present, i.e., single ions and nanoparticles with a diameter of 3 to 5 nm. These particles consist of a superparamagnetic phase with a spinel structure whose sublattices are diamagnetically diluted with Mg^{2+} and Al^{3+} ions. CS, having about 7 wt.% of Fe_2O_3 content, also involves a magnetic phase, based on defective magnetite [21].

Magnetic CS have heterogeneous regions of ferrospinels on their outer surface. An increase in the concentration of iron increases the crystallite size of the ferrospinel phase in the magnetic CS, and decreases the degree of iron substitution (Mg and Al) [9][17].

In general, CS size falls in the range of 20–300 microns, with a shell thickness of 1–18 microns, but the average size is 5–500 microns [22]. In comparison to the CFA particles, CS are much larger, and can vary from 5 to 500 µm [23].

3. Properties of Cenospheres Recovered from CFA

Structurally, cenospheres are hollow spherical-shaped particles that resemble glass beads, micron-balloons, or hollow ceramic micron-sized spheres [24]. Their size is 5–500 microns [25], and an average size is 30 µm to about 350 µm [26][23]. The cenospheric weight in a CFA comprises approximately 0.1–4.8% of the total weight of CFA [16], as shown in the literature.

There might be slight variation in the weight fractions from different parts of the world. As far as chemical compositions are concerned, CS contains elements, such as Ca, Mg, K, Na, Ti, Al, Mg, Si, Fe, C, and O [25], which may be present as different mineral phases [27]. Moreover, several investigators have also reported a trace of elements like V, Zr, Ba, Sr, S, P, and Rb. Strzałkowska and Adamczyk, 2019, reported all the above-mentioned elements in the CS recovered from three different TPPs (Dolna Odra, Opole, and Kazakhstan) [25]. Furthermore, Danish and Mosaberpanah, 2020, analyzed the chemical composition of CFA from 12 different TPPs, from various parts of the world, and found that all of them have Si, Al, and Fe as major elements, while Ti, Ca, Mg, Na, S, and Mg were present in smaller quantities [28]. The common elements were Al, Si, Fe, O, and Ca, whose composition may vary, but the presence of the other elements depend on the type of coal, source of coal, geographical origin, and furnace temperature during the burning of coal in the TPPs. When water or rain comes in contact with these toxic elements, it may leach out from there and may have a negative effect on the material [29][30].

Since CS have two surfaces, i.e., inner and outer, which are covered by a nano-thin film whose thickness is between 30–50 nm [21]. The inner surface is mainly composed of a glass of alumina and silica, and the skeleton is comprised of crystalline minerals like quartz, mullite, and magnetite [31]. Both of these surfaces make a shell composed of a crystalline phase and amorphous glass phase. The thickness of the crystalline phase is 2–30 microns, while for the amorphous glass phase, it is 50–90 microns [16]. The major crystalline phase is dominated by mullite, magnetite, calcite, cristobalite, feldspar, and hematite [32], which play a role in the morphology and elemental composition of CS. The average gas pressure inside a CS is below one atm within the range of 0.172–0.227 atm, which decreased in larger particles, since more gases would be required for expansion [33][34]. The stability of the hollow spheres is dependent on the equilibrium of surface tension forces on melt drops and intrinsic pressure of the internal hot gas [14]. The CS are bestowed with numerous physical properties like lightweight, low thermal conductivity (TC) [35], thermal shock-resistant [35], ultra-low density [22], highly porous [36][37], fire-proof [38], resistant to acid and bases [39], resistant to oxidation and corrosion [40], excellent mechanical strength [26], and protected from electromagnetic interferences [9][41][42][43][44]. The thermal shock-resistant properties in the CS are added from the mullite content [45], which is chemically inert. Furthermore, the porous nature of the CS enhances their water absorption capacity, thus it is considered a potential candidate as an absorbent for wastewater treatment and environmental cleanup [46].

4. Methods Used to Recovery Cenospheres from CFA

The recovery of CS from CFA is possible by both dry- and wet-based methods [47]. As the name suggests, the wet method involves a liquid media like water and or any organic solvent, whereas the dry-based method utilizes either air stream or size-based screening. Among all the techniques for recovery of CS from CFA most common methods are magnetic separation, sedimentation, flotation, or sink float method [12]. All these recovery methods are carried out in a separation tank which contains water (1 g/cc) and acetone (0.789 g/cc), which is fitted with agitation or stirring, and consequently, heavier particles settle down, while lighter particles float at the top. The dry-based method mainly uses air classifiers to separate CS particles [12][48].

5. Applications of Cenospheres in Ceramics and Environmental Cleanup

CS finds applications in all the fields which include building/construction materials [49], ceramics [50], plastics [19], construction [26], lightweight construction material [51], recreation [52], coating [22], automotive [19], paints and coatings [53], energy storage devices [54][55], polymer fillers [56], buoyancy and as low dielectric constant substrates [28]. They are best fitted for adding into silicone rubber to increase the conductivity. Besides this, it also increases rubbers' suitability as an electromagnetic wave absorbing material [56][57], which can be used in electronic, as a broad band microwave absorber, and radar-based applications [58].

6. Conclusions

CFA is considered hazardous waste, due to the presence of numerous heavy metals. However, it has been categorized into useable materials in the last decade, due to their minerals and structurally important structures, such as cenospheres, plerospheres, and ferrospheres. Cenospheres possess unique and remarkable physical, chemical, and mechanical properties; thus, it has drawn the attention of the scientist from all parts of the world in ceramics, environmental cleanup, and lightweight materials. Cenospheres could be either magnetic or nonmagnetic, based on the Fe content. The cenospheres could be recovered from CFA by both dry and wet-based methods, but the wet-based method is preferred because of their economical nature [59]. The efficient recovery of cenospheres was least affected by the morphological properties of the cenospheres. To date, cenospheres are successfully used in the field of ceramics, wastewater treatment, agriculture, and electronics, and soon they will be considered a material of the future.

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