

FLY Ash Cenosphere Waste Formation In Coal Fired Power Plants And Its Applications As A Structural Material- A Review

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ABSTRACT

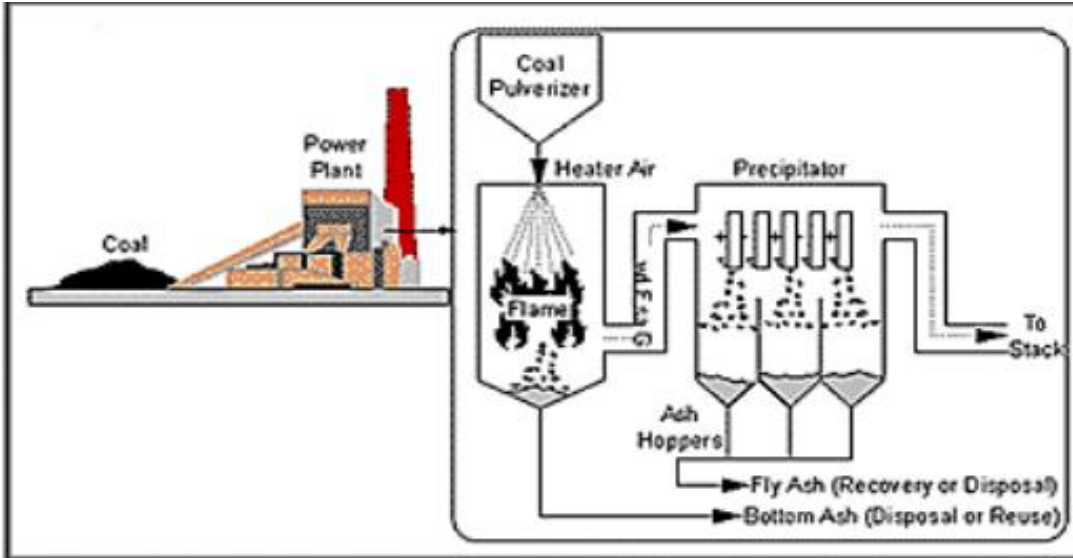
Ash cenosphere is part of fly ash exhibiting spherical shape. It is produced from pulverized coal combustion in coal-fired power stations. The term cenosphere was originated from Greek kenos (hollow) and sphaira (sphere), firstly used by Sinnatt's research group, to describe hollow char particles formed during coal pyrolysis. Ash cenospheres refer to ash particles that are hollow, of a low bulk density (lower than that of water), and is typically collected from the surface of ash lagoons. India produces a considerable amount of fly ash from the coal-fired power generation industry and is one of the countries with the lowest ash utilization. Only 10% of fly ash produced is used, mainly in the building and construction industry. The large quantities of fly ash impose significant pressure on environment and waste management. The impact, however, could be minimized by effective ash utilization. A range of potential industry applications of cenosphere is reviewed in this article

(key words- cenosphere, coal, pulverized, construction, pyrolysis)

1 Introduction

Ash cenospheres are hollow lightweight micro-spheres (see Fig1(a)) as part of fly ash produced during pulverized coal combustion for power generation.³⁻⁶ They have superior properties including a light weight, good packing factor, enhanced insulation, improved flow characteristics, reduced shrinkage, less water absorption, excellent mechanical strength, chemical inertness, good thermal resistance, and good electrical properties. Ash cenosphere utilization offers significant manufacturing advantages, product improvement, and cost reduction in a wide range of industrial processes. Ash cenospheres can be used to produce various lightweight construction products, including lightweight cements,⁷ aggregates in lightweight concrete,⁸⁻¹⁰ and porous glass crystalline molded blocks for the removal and solidification of liquid and other hazardous wastes.¹¹ They have also found extensive applications in manufacturing lightweight composites, including polyurethane composites,¹² polyester composites,¹³ functionally gradient materials,¹⁴ poly(vinyl chloride) composites, nylon composites,¹⁷ syntactic polymer foam,¹⁸⁻²¹ metal-matrix composites,²²⁻²⁴ glass fiber/epoxy resin composites,²⁵ and conducting polymers.²⁶⁻²⁸

The properties and performance of the lightweight products utilizing ash cenospheres depend largely on ash cenosphere characteristics, particularly ash cenosphere physical structure such as diameter, particle size distribution, wall thickness, and shape.^{8,13-19,21,29} For example, when used as fillers, ash cenospheres of thicker walls are favored to increase the mechanical strength of the finished products.^{8,21} On the other hand, the shape of ash cenospheres may also be an important factor¹⁶ In comparison to other shapes, spherical ash cenospheres have the lowest surface area to volume ratio and, thus, require less binder, and water to wet the surface. Besides, spherical particles offer the advantages of reduced shrinkage as well as improved workability and ease of use.^{19,29} Apart from these properties, the particle size distribution of ash cenospheres affects the mechanical properties of the manufactured products.^{13,14,18} Therefore, a good understanding of ash cenosphere characteristics and its formation mechanisms is essential for development of effective strategies to enhance and optimize ash cenosphere production in power plants, without affecting the main business of electricity generation. In practice, "floaters", that is, ash particles that have a bulk density less than that of water and therefore float on the top of ash ponds, are collected as ash cenospheres.^{3,34,35} In other words, regardless of whether the particles are of spherical shapes or nonspherical, of a network structure, inorganic particles which have apparent density less than that of water are all considered to be ash cenosphere products. Therefore, it becomes essential to carry out a systematic study on the structure of the collected "ash cenospheres" as the quality of the products utilizing these collected "ash cenospheres" are largely determined by the structure of these "ash cenospheres"



Production of fly ash in a dry-bottom utility boiler with electrostatic precipitator.

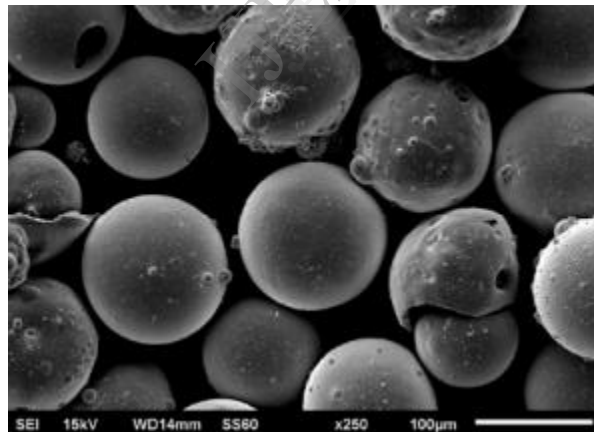


Fig1(a)- Spherical particle shape formation in fly ash cenospheres

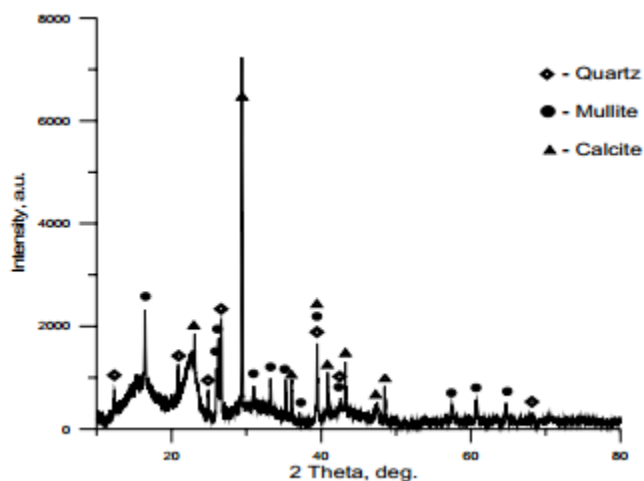


Fig 1(b) - Xray Diffraction analysis of Fly ash cenospheres

2. Sample Collections and Preparations of Fly ash samples

Ash cenosphere samples were collected from five power stations, In practical applications ash cenospheres are harvested from the surface of ash lagoons and have a density less than that of water. Therefore, usually, a sink–float method using water as the medium is employed to separate ash cenospheres from the bulk fly ash samples. The float samples are then heated to 830°C and held at that temperature for 1hr in a furnace, with air continuously flowing through the furnace to remove unburnt carbon. The yield of the float samples after density separation and heat treatment is taken as the ash cenosphere yield. Further sample preparation may also be carried out to sieve ash cenospheres from different liquid media (µm flotation and subsequently with different size fractions. (25–45µm, 45–63µm, 63–75µm, 75–90µm, 90–106µm, 106–125µm, 125–150µm, 150–250µm, and >250µm) for subsequent characterization

2.1. Sample Characterization

2.1.1 Properties of Ash Cenospheres

The properties of ash cenospheres are generally characterized into four aspects: physical (and morphological) structure, mineralogy, chemistry, and thermal properties.

(a) Physical (and Morphological) Properties.

While the real density of ash materials in ash cenospheres is $> 2.0 \text{ g cm}^{-3}$, the apparent density of ash cenosphere is generally in the range of 0.4 to 0.8 g cm^{-3} and the bulk density varies from 0.2 to 0.5 g cm^{-3} (much lower than that of water).^{13, 17, 20, 21, 26, 30, 40-48} Therefore, ash cenospheres can be easily separated and collected from fly ash in ash lagoons as ash cenospheres have low apparent density and float on the lagoons' surface.^{20, 24, 25} Ash cenospheres may have particle sizes ranging from 5 to $500 \mu\text{m}$, typically 20 – $200 \mu\text{m}$,^{13, 17, 19-22, 25, 30, 42, 43, 45, 46, 48-53} The particle surface is generally smooth, with uneven texture or having blisters. The shell thickness of ash cenospheres can vary from 1 to $20 \mu\text{m}$. The apparent ratio of wall thickness to particle diameter is 3 – 16% , (calculated based on the estimation of bulk ash cenosphere samples).^{20, 21, 30, 45, 48, 51, 53, 54} However, the direct measurement of true diameter and shell thickness of ash cenospheres on a particle-by-particle basis via a novel technique developed recently show that such a ratio is limited between an upper bound of $\sim 10.5\%$ and a lower bound of $\sim 2.5\%$, irrespective of ash cenosphere size.¹⁹

The common perception is that ash cenospheres are generally hollow with thin shells so that the cross-section of an ash cenosphere has a ring structure.^{19, 20, 30, 43, 44, 48, 54} However, the recent study¹⁹ has shown that the ash cenospheres separated from fly ash via density separation using water as a media consist of two different types of structures. One is spherical and of a single-ring structure (see Figure 2-1a) and the other is irregular and of a network structure (see Figure 2-1b)

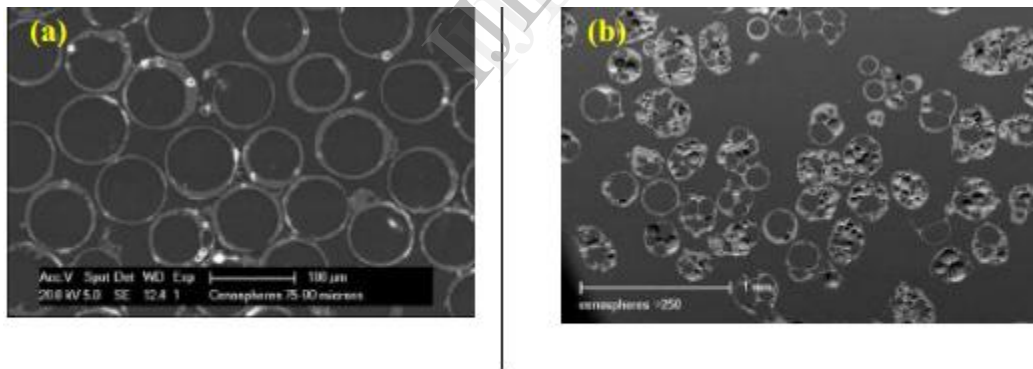


Figure 2-1: Morphology of ash cenospheres with (a) spherical shape with a single-ring structure; (b) non-spherical shape with a network structure.¹⁹

(b) Mineralogy.

The mineralogy of ash cenospheres varies from sample to sample. It is reported that mullite and/or quartz are the main crystalline phases identifiable in the shells of ash cenospheres, based on XRD analysis.^{17, 41, 44, 46, 50, 55} (See Fig-1(b)) The minor or accessory mineral phases in the shells of ash cenospheres are plagioclase, K-feldspar, dolomite and some gypsum and Fe

oxides.²² However, ash cenospheres from the combustion of solid fuels are generally amorphous aluminosilicate glass phases (70-90 wt%).

(c)Chemistry.

The chemical composition of ash cenospheres also varies from sample to sample, depending on the power station where the sample was collected. Table 1 lists the chemical compositions of bulk ash cenospheres and fly ash reported in the literature.

Table 1. Chemical Composition of Fly Ash Samples from Different Power Stations (bulk fly ash (wt %))

Chemical composition	A1	A2	A3	A4
SiO ₂	54.00	65.10	68.60	62.60
Fe ₂ O ₃	10.50	2.00	1.30	0.54
Al ₂ O ₃	28.30	27.30	25.50	34.90
TiO ₂	1.70	1.20	1.10	1.90
P ₂ O ₅	1.10	0.14	0.10	0.04
CaO	1.70	0.37	0.22	0.03
MgO	1.20	0.35	0.25	0.11
Na ₂ O	0.28	0.36	0.37	0.05
K ₂ O	0.73	3.20	2.50	0.19
V ₂ O ₅	0.03	0.03	0.04	0.03
BaO	0.35	0.06	0.04	0.03
SrO	0.26	0.04	0.03	0.03

Table 2. Chemical Compositions of Ash Cenospheres from Different Power Stations cenospheres (wt %)

CHEMICAL COMPOSITION	A1	A2	A3	A4	A5	A6
SiO ₂	51.60	57.90	58.10	67.40	62.40	60.60
Fe ₂ O ₃	5.10	1.20	0.73	0.94	0.49	0.50
Al ₂ O ₃	36.20	34.80	36.70	26.20	34.60	36.80
TiO ₂	1.50	1.10	0.85	1.08	1.31	1.43
P ₂ O ₅	0.84	0.10	0.04	0.01	0.03	0.04
CaO	0.88	0.29	0.19	0.03	0.04	0.04

MgO	0.87	0.88	0.22	0.01	0.02	0.04
Na ₂ O	0.23	0.31	0.23	1.30	0.30	0.01
K ₂ O	1.70	3.50	2.70	0.03	0.35	0.35
SO ₃	<0.1	<0.1	<0.1	BDL	BDL	BDL
BaO	0.25	0.23	-	-	-	-
SrO	0.13	0.20	0.20	ND	ND	N.D

The chemistry of ash cenospheres varies from power plant to power plant. Such variations in the chemistry of ash cenospheres are expected, depending on mineralogy of ash-forming species in the parent coals and combustion conditions. Secondly, Si and Al oxides are dominant (> 80% by weight) in the chemistry of ash cenospheres, with SiO₂ / Al₂O₃ ratio varying from 1.3 to 2.5. Such chemistry is in accordance with the mineralogy of ash cenospheres which contain commonly aluminosilicate glass phases plus mullite and quartz as the main crystalline phases

Lastly, there has also been debate on whether iron species are essential to ash cenosphere formation. Raask²⁰ suggested that a minimum ~5% ferric oxide (Fe₂O₃) is essential to ash cenosphere formation, as it provides the required source of oxygen for gas generation inside the molten silicate particles for expansion. This conclusion appears to be suggested by the majority of the published data in the literature. However, there were several studies^{19,51}, in which it is clearly shown that high yield of ash cenospheres were produced when iron oxide was very low (<0.5%). It is therefore clear that during pulverized fuel combustion, there are different mechanisms responsible for ash cenosphere formation. Iron may be one of the important factors for enabling gas generation within the molten precursor droplets. Other possible sources of gas generation including decomposition of carbonates, dehydration and dehydroxylation of clay minerals, evaporation of pore water and fusion of silicates should be considered as suggested in the literature.^{20, 21, 25, 56}

(d) Thermal Properties.

Various methods were used to investigate the thermal behaviour of ash cenospheres from solid fuel combustion, such as TGA/DTA analysis,^{22, 50} DTA/DTG analysis⁵⁸ and a Leitz heating microscope.²⁰ De crepitation of ash cenospheres was observed to take place at 230 –330 °C, due to the release of water dissolved in the silicate glass^{20, 22, 50} and/or some gases escaped from the hollow ash cenospheres,²² as suspected. Therefore, ash cenospheres should be finely ground for thermal analysis to avoid the samples loss due to the decrepitation. Additionally, an exothermic effect may also take place at 260 –600 °C and cause weight loss,^{22, 58} due to the oxidation of residual unburnt carbon materials in the ash particles. This fact also suggests that ash cenospheres harvested from ash lagoons are necessary to be heat-treated under oxidizing atmosphere to remove possible unburnt carbon materials for further analyses.^{19, 52} Thermal

analysis on several ash cenospheresamples by Raask²⁰ also indicated that the sintering of ash cenospheres commenced at 1200 °C –a temperature higher than the sintering temperature of dense fly ash. For other ash cenosphere samples, Vassilev and co-authors²² found that the sintering and softening started at 1010 – 1330 °C while complete fusion was reached at 1315 – 1450 °C.

2.1.2 Key Factors Influencing the Formation of Ash Cenospheres

The formation of ash cenospheres during pulverized coal combustion can be governed by a number of important factors, summarized below.

Coal Properties. These include three aspects: particle size, properties of coal organic matter and properties of coal inorganic matter. Coal particle size was reported to be an important factor in the formation^{20, 22} and size^{14, 37} of ash cenosphere. According to Raask,²⁰ mineral particles smaller than 10 µm are incapable of expanding to stable cenospheres. The speculated reason is that carbonaceous matter is completely separated from ash particles due to extensive milling, or as results of excessively vigorous gas evolution and expansion inside small ash droplets, resulting in their bursting to form dense particles. The properties of coal organic matter are also believed to be critical in ash cenospheres formation because they have very different organic properties, resulting in substantial difference in their devolatilization behavior. This includes the swelling characteristics of coal particles, thus influencing the combustion condition hence ash cenospheres formation. The properties of mineral matter in coal, including the content and mineralogy of mineral matter play important roles in the formation of ash cenospheres. Ghosal⁷⁹ showed that ash cenosphere yield appears to be positively correlated with the total ash content of coal. In addition, it was also indicated by the studies that the mineral type present in coal, such as clay mineral, mica, zeolite, feldspar and anauxite, will favor the cenosphere formation.^{17, 22, 25, 55, 79, 83, 85, 86} Furthermore, Kruger and Toit¹⁷ claimed that alkalis in the mineral matter can act as precursors for the generation of cenospheres at the prevailing combustion

Characteristics of Ash Droplets -. Generally speaking, these include three factors, i.e. carbon in ash droplets, iron content of ash droplets, viscosity and surface tension of ash droplets. Carbon in Ash Droplets was considered to be one of the favorable conditions for cenosphere formation by Raask^{20, 21} as observed in Leitz heating microscope, it was found that a minimum of 1 % by weight of carbon should be incorporated or attached to fused silicate particles as one of the conditions for cenosphere formation along with Iron Content in Ash Droplets. The gases locked inside the ash cenospheres were found to be CO₂ and N₂ with traces of O₂ and CO. Based on ash cenosphere chemistry and the possible formation routes, Raask ruled out the possibility of dissociation of carbonates and combustion of carbonaceous matter being the origin of CO₂. Via experiments on gas evolution by heating various minerals in the Leitz heating microscope, Raask

^{20, 21} originally suggested that the presence of iron can catalyze the reactions to produce CO₂ and CO inside the fused ash particles. Rassk's estimation based on his experiments results suggested that generally, a minimal ~5% wt of iron oxide is required for the formation of substantial quantities of ash cenospheres. More than 7 % iron oxide is required for the formation of a large amount of ash cenospheres from bituminous coal combustion, while for some sub-bituminous coal, 3-4% iron oxide is sufficient. While the requirement of high iron oxide contents for the formation of substantial ash cenospheres is generally supported by the published experimental data, there have been various exceptions. For example, Ngu and co-authors¹⁹ reported the high ash cenosphere yield from an Australian power station which burns coals with negligible iron contents in ash (~0.6 wt % on average). Else, some studies^{18, 51} also suggested that high iron contents do not always lead to high ash cenospheres yield. As shown in Morrison's survey,⁵¹ there were even cases that have Fe₂O₃ contents up to 25% but do not produce a large quantity of floaters. Similar phenomenon was also reported by Lauf¹⁸ when the content of Fe₂O₃ in ash is >20%.

Viscosity and Surface Tension of Ash Droplets- Viscosity and surface tension of molten ash droplets control the expansion of the precursor ash droplet and determine the survival of ash cenospheres.^{14, 17, 18, 20-22, 33, 54, 79} The change rate of a hollow sphere radius is governed by viscous relaxation. Viscosity and surface tension of the precursor ash droplets determine the final size of ash cenospheres. In order to sustain the high intrinsic pressure of expanding gas bubble within the precursor ash droplet, the precursor droplets should have relatively high viscosity. The cenosphere precursor will collapse if the force as a result of surface tension is too low to maintain the equilibrium pressure between the internal and external gas. This was supported by the work of Lauf¹⁸ who investigated ash cenospheres produced by melts with relatively high viscosities from ash samples of seven different locations. Calculations also suggest that only those molten droplets that are sufficiently viscous can survive long enough to be resolidified into ash cenospheres. Unfortunately, there are few published data in terms of the value of viscosity and surface tension of molten precursors responsible for ash cenosphere formation.

Combustion Conditions -. These mainly include three key parameters, i.e. furnace temperature, residence time and cooling rate. Furnace Temperature is considered to be a critical factor in ash cenosphere formation during pulverised-coal combustion.^{14, 17, 19, 22, 37, 38, 87} It affects not only the rate of gas released from the ash particle, but also the formation of molten ash droplets (hence the viscosity and surface tension of these ash droplets). There is still debate on the effect of furnace temperature. For example, it was reported that the yield of ash cenospheres increased with combustion temperature and reached the highest at 1600 °C.⁸⁷ However, Vassilev and co-authors²² suggested that the suitable furnace temperature for ash cenosphere formation is 1315 –1500 °C. Considering the viscosity and surface tension of fused

silicate glass, as well as the rate of gas production, Raask²⁰ estimated that the optimal temperature for ash cenosphere formation is 1400 °C.

Residence Time. A proper residence time is required for the formation of ash cenospheres with different sizes, governed by the rate of gas evolution and viscous relaxation of the molten ash droplets. Sufficiently long residence time of ash particles in the boiler during combustion is required to enable the molten ash droplets formation and trapping an appropriate amount of expanding gas to form ash cenospheres. However, it should not be excessive as further expansion of gas inside the melt would lead to bursting before solidifying of the precursors to form ash cenospheres.

Cooling Rate- During cooling stage, ash precursor droplets of cenospheres solidify and ash cenospheres survive eventually. Upon cooling, the molten ash droplets will contract due to a reduction in gas pressure within the cenospheric particle. The viscosity and surface tension will change upon cooling. Therefore, the net balance between the internal pressure and the strength of the shell of molten droplets may lead to the breakage of the particles hence reduce ash cenosphere formation.⁸⁸ Rapid cooling of molten ash droplets is critical for ash cenospheres formation.^{22, 51} However, cooling should not be too rapid. It is logic to reason that due to the thin wall thickness of cenosphere precursor, the high internal pressure will cause the rupture of the cenospheres. Another opinion based on calculation suggested that there is no significant contraction of cenospheres upon rapid cooling to about 1000 °C in boiler flue gas.²⁰ After this rapid cooling in high-temperature flue gas, the pressure inside the frozen cenospheres will reduce steeply, causing the possible breakage of ash cenospheres, although there is no experimental evidence to support so

2.1.3 Separation of Cenospheres from Fly Ash and the Typical Yields

The most common method for separating ash cenospheres from fly ash is the sink-float method that uses water as the medium for density separation because ash cenospheres have bulk density lower than that of water (1 g cm⁻³).^{18-20, 22, 24, 48, 54, 55, 57, 76-78} Briefly the method involves dispersing the dry fly ash samples collected from the power plants in water (distilled water and/or tap water) at room temperature. After continuous stirring and settling for 24 hours, the float ash samples above water are collected via decantation followed by filtration. The float samples are then heated to 800-900 °C in a furnace with air continuously flowing through for 2 hours in order to remove unburnt carbon. The yields of ash cenospheres using this separation procedure vary strongly with the sources of fly ash, up to 35.6 % wt, with the most common values are 0.1 -5.0 % wt.^{11, 19-22, 25, 26, 48, 49, 53, 57, 63, 77, 78} It should be noted that, apart from using water as medium, other solvent liquids were also used for separating ash cenospheres from ash, such as ethanol and hexane^{55, 71, 72} acetone containing 1% triethanol amine lauryl sulphate 46 and n- heptane.⁵² The other method is centrifugal separation that can be used to determine

the amount of ash cenospheres in fly ash. Various liquid medium may be considered, including water,⁵⁰ distilled water and lithium metatungstate solutions of density 1.5 and 2.0 g cm⁻³, and liquid of density 2.2 g cm⁻³ prepared by mixing carbon tetrachloride, dibromomethane and diiodomethane in appropriate proportions.^{79, 80} However, it is obvious that the ash cenospheres separated with the last two liquids have density greater than that of water. Lastly, a combination of hydro- and aerodynamic separation can also be employed to isolate the concentrates of magnetic microspheres and cenospheres.^{13.}

3.0 Advantages and Applications of Ash Cenospheres

Ash cenospheres have unique properties such as being spherical, lightweight, heat resistant, enhanced insulation, good thermal stability and chemical inertness etc. These materials have a wide variety of applications in the area of industry, agriculture, recreation and others. Ash cenospheres can be used in manufacturing value-added products such as lightweight materials, Lightweight Construction Products. Lightweight construction products have many benefits including low density, excellent mechanical strength and reasonable cost. Ash cenospheres can be used as fine aggregate in the manufacture of lightweight concrete and as additive for producing lightweight cements.

Cenospheres can be used as aggregate to produce lightweight concrete, resulting in significantly improved thermal conductivity of the lightweight concrete and significantly decreased weight of products. It was also suggested that ash cenosphere additives can improve the crystallization of hydration products. The acoustic behavior of the product also does not deteriorate compared with the lightweight concrete manufactured with other aggregate. As additives of lightweight cement, ash cenosphere also leads to changes in the structure of lightweight cement and raises hardening temperature. However, the addition of ash cenosphere does lead to some strength loss. Fortunately, such strength loss can be recovered by improving the interfacial strength between the cenospheres and the cement. It should be noted that special consideration needs to be given to the excessive moisture uptake/loss by cenospheres (hence the water uptake/loss in cenosphere-concrete products) when ash cenospheres are used to replace fine sand to be the aggregates in concrete. The work of Barbare et al showed that the equilibrium moisture content of cenospheres is ¹⁸ times higher than that of sand indicating substantial water should be added prior to curing the concrete. Ash Cenosphere Formation during Solid Fuels Combustion ¹⁸ times higher than that of sand, suggesting that substantially more water should be added prior to curing the concrete.

Composites.

Polymer Composites. As results of unique properties such as spherical shape, controlled particle size, porous structure, low density, good insulation and low cost, ash cenospheres are extensively introduced as lightweight fillers into various polymer composites.

For example, ash cenosphere particles coated with Cu could be utilised for manufacturing conducting polymers for EMI shielding applications.⁵⁹ While the use of cenospheres in polypropylene and polyethylene is limited due to high-shear conditions in extrusion and injection moulding, new manufacturing techniques may be employed to address this aspect by controlling cenosphere particle size.²⁴ Lightweight, high strength polyester materials can also be produced by the incorporation of a controlled size, surface modified cenospheres into a polyester matrix.²⁷ Comparison of the mechanical properties of both epoxy resin and high density polyethylene shows the similarity with the two fillers.¹⁷ It is known that significant advantage could be achieved by filling ash cenospheres into the high density polyethylene since the wider variety of colours and more importantly, less pigment required.

Syntactic Foams.

Syntactic foams are made by mixing hollow cenosphere particles in a matrix material, achieving various advantages including excellent buoyancy, low moisture absorption, high compressive strength, high energy absorption during deformation, and high damage tolerance.^{51, 61-64} Such materials are extensively applied in automotive industries,⁶⁶ in marine and aerospace industries for core material in sandwich structured composites,⁶⁵ and as underwater buoyant structures which can withstand high hydrostatic pressures of deep ocean.⁶³ It was found that the density and mechanical properties of syntactic foam can be affected by ash cenosphere sizes and specimen aspect ratio.⁶¹ An increase in compressive strength and modulus can be achieved as the internal radius of cenospheres decreases.

Ceramic Foams.

Ceramic foam has advantages including lightweight, high compressive strength and good resistance towards gas erosion. It can be easily shaped, making this material desirable for producing high performance products, including Ash Cenosphere Formation during Solid Fuels Combustion¹⁷ sensors, heat dissipaters, thermal insulators etc.⁶⁷ Russak and co-authors⁵² demonstrated that a ceramic closed cell foam insulation material made from ash cenospheres could meet all the requirements for developing a fully reusable ceramic heat shield of space shuttle to protect the vehicle prime structure during the reentry maneuver.

Polyvinyl Chloride (PVC) and Ethylene Vinyl Acetate (EVA) Foams.

PVC foam is an insulation material with various characteristics of light, fire-proof, water-proof, heat-resistant, sound-insulating, non-flammable and non-toxic.⁴⁸ EVA foam has unique properties of lightweight, elasticity and insulation and is mainly used to make sports shoe bottoms. For manufacturing PVC foams, CaCO_3 and talc are the two major constituents. For manufacturing EVA foams, a rather high proportion of CaCO_3 is added as the filler. Considering the vast economic benefit, ash cenospheres can be added to replace the talc present in 5% of the mixture to make PVC foams. For EVA foams, ash cenospheres can be used to completely replace CaCO_3 present in the mixture. It was found that such replacement resulted in excellent strength and insulation properties compared to the original products⁴⁸

Functionally Gradient Materials.

Functionally gradient materials are composites made of varied material compositions to optimize the performance so as to achieve specific applications. These materials are extensively used in applications such as internal combustion engines, insulating and thermal coatings for turbine blades, military armor and other engineering applications⁶⁹ Parameswaran and Shukla⁶⁸ developed a technique to prepare a model functionally gradient material using polyester resin and ash cenospheres. The results showed that increasing cenosphere volume fraction can reduce the density of the functionally gradient material by 20%.

Metal-matrix Composites.

Ash cenospheres have desired characteristics to be used as fillers or reinforcement in aluminium, lead, magnesium and several other nonferrous metal matrices, e.g. spherical shape, low density, especially the high melting point^{30, 31, 70} It was found that the aluminum composites with 50-60 vol.% of ash cenosphere exhibit sound microstructure except near the regions of contacting particles.⁷⁰

Other Applications. Ash cenospheres can also find applications in making catalytic supports, absorbents and catalysts,^{22, 40, 71, 72} as results of their spherical shape, chemical inertness, and thermal stability. For example, catalysts were developed based on ash cenospheres for deep methane oxidation.

Ash cenospheres are also used to manufacture special ceramics such as fire-, heat-, and sound-insulating materials, taking advantage of their heat-resistant, thermally-stable, and sound-insulation features.²² Ash cenospheres can also be incorporated into mortars as binders to produce ceramic products such as man-made marble and insulation/refractory ceramics.²⁴

Another application of ash cenospheres is for manufacturing anti-corrosive paint and wear resistant coating due to their excellent mechanical properties and chemical inertness.^{73, 74} Ash cenosphere is also a good option for producing fire retardant and insulation paints as these hollow particles are non flammable and high temperature resistant.

The gas trapped within enclosed ash cenospheres becomes an excellent insulating medium, which makes cenospheres having excellent heat insulation properties. Therefore, cenospheres are ideal materials for heat-insulating refractory products.^{17, 24, 43}

Test has shown that the mixture of ash cenospheres and clays can be used to produce various refractories for metallurgical industry.

Pearlite microspheres with low density were found as the sensitizer of emulsion explosives after investigations of the physical-chemical and explosive properties of emulsion compositions contained pearlite microspheres⁷⁵

Apart from the various industrial applications, ash cenospheres can also be used to manufacture materials used in recreation and home. For example, ash cenospheres could be used for the manufacture of sport equipment's such as kayaks, surfing boards and other floaters due to their low density and excellent buoyancy properties.⁴⁶ Interestingly, ash cenospheres combined with other floating materials are helpful to grow a special instant turf.⁵¹ This type of turf is thinner and therefore lighter than natural turf, and has an intact root system. Such instant turf also has a long duration of keeping moist and thus saves water and costs.

4. Conclusions

7.2.1 Possible Formation Mechanisms of Ash Cenospheres from a Coal-fired Power Station

Thermomechanical analysis shows that the fusion characteristics of ash cenospheres are dependent on the particle size of ash cenospheres. However, the various size-fractioned ash cenospheres do not melt at 1600 °C, suggesting that these ash cenospheres from coal-fired power station are impossible to be formed at temperatures <1600 °C. The chemistry of ash cenospheres of various size fractions is dominantly SiO₂, Al₂O₃, TiO₂ and Fe₂O₃, which comprise >99.3 wt% of the total ash chemical compositions. SiO₂/Al₂O₃ ratio decreases with increasing ash cenosphere size, accompanied with an increase in the sum of TiO₂ and Fe₂O₃ contents (i.e. TiO₂+Fe₂O₃). The gas products locked inside ash cenospheres of all size fractions are dominantly CO₂ and some N₂, with trace amount of CO. The average gas pressure inside the individual ash cenosphere particles decreases from 0.227 atm to 0.172 atm (NTP) as particle size increases from 63-75 μm to 150-250 μm. The characteristics of molten ash cenosphere precursors derived from the ash chemistry of individual cenospheres indicate that the optimum particle temperature for cenosphere formation is from ~ 1640 to 1800 °C. Under these

conditions, molten ash droplets can be formed and trap a certain amount of gas generated within the ash droplets

Ash cenosphere yield and chemistry vary across the power stations. Ash partitioning occurred in the process of ash cenosphere formation during combustion. Iron is not necessarily an essential requirement for ash cenospheres formation. This study has also developed an ash cenosphere characterization technique which is capable of measuring true ash cenosphere diameter and wall thickness on a particle-to-particle basis. It has been demonstrated that the ash cenospheres can be made use of in various areas of application like composites, foams, functionally graded materials, and metal matrix composites.

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