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Fly ash cenospheres – A resourceful material for engineering applications.

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In India, about 60% of the total power generation comes from thermal power stations operating on fossil fuels like coal and lignite [1]. Presently about 400 million tons of coal and lignite is consumed annually for power generation. Typically, Indian coals have an average ash content of about 45%, thereby leading to generation of around 180 million tons of ash annually as an industrial by product.

Out of the total ash generated, 70 % of this ash comprises of fly ash and the remaining are bottom ash, economizer ash, air-preheater ash, etc. Presently, dry fly ash is being utilized in a big way in value added products like bricks, blocks, pavers, etc., while bulk volumes of fly ash is consumed in blended cement manufacture, different types of concrete, construction of dams, roads, river embankments, etc.

Fly ash also contains about 1.0 % hollow particles called as 'Cenospheres' generated during combustion of the pulverized coal at high temperatures in the thermal power plant boilers. Cenospheres is a useful by-product of coal combustion which can be harvested from the ash ponds or by any other methods such as tribo-electric separation, slurry precipitation, pond skimming etc., from fly ash. Fly ash cenospheres are unique in the way that they possess excellent properties such as lightweight, low density, non-metallic, high melting points. These unique properties make cenospheres a prospective raw material to produce value added products for use in engineering applications. The paper discusses the work carried out at Central Power Research Institute on cenospheres characterization and development of value added products for various applications.

Keywords: *Fly ash cenospheres, microspheres, ash pond, alumino-silicate, comprehensive characterization, engineering applications.*

1.0 INTRODUCTION

Pulverized coal fired thermal power stations generate enormous quantity of fly ash, as a primary by-product due to coal combustion in boilers, and are carried away along with the flue gas from the boiler to the chimney. The fly ash is in the form of fine suspended particulate matter which is to be captured efficiently before the flue gas is let off to the atmosphere. This fly ash is collected in the electrostatic precipitator (ESP) hoppers which is presently evacuated and stored in silos for further use in order to avoid environmental pollution. Fly ash is effectively being used in building materials, cement and concrete, roads and embankments, etc.

Fly ash particles are composed of two different types- precipitator ash which are solid spherical particles and the other 'cenospheres' (< 1% of

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the total fly ash) which are hollow particles with density less than 1.0 g cm^{-3}. Fly ash is primarily composed of the crystalline compounds such as quartz, mullite, hematite, magnetite and certain amorphous materials such as silica glass and glasses of other oxides. The ESP fly ash, which has a density in the range 2.0-2.6 g cm^{-3} are used as fillers to improve various properties of the matrix materials in composites contributing to its stiffness, strength, wear resistance and reduced density of the product [2].

Another study by V. B. Fenelonov et al [3] shows that there are two main classes of microspheres- empty spheres, in which the cavity are filled with gas only called the 'Cenospheres' and the other 'Plerospheres' in which the cavities are filled with small mineral particles, foam, spongy and other porous frameworks.

The term 'Cenospheres' comes from the Greek word 'kenos' (hollow) + 'spheres' and reflects the most important feature of the cenospheres- the presence of a cavity surrounded by solid or a perforated mineral shell. The latter of microspheres are often called as network structured cenospheres or 'Plerospheres' from the Greek 'pleres'(filled) + spheres.

Traditionally, only particles having densities < 1 gm/cm have been called 'cenospheric'. This terminology is probably because cenospheres float on water, allowing harvesting from wet ash impoundments. In the formation of fly ash, the relative amount of cenospheres is typically around 1%. However, cenospheres are really gas bubble-containing particles and their bulk density can be greater than 1 gm/cm^3 and their concentration in combustion ash can be greater than 1%. Cenosphere particles having bulk densities < 2 gm/cm, also can be effectively separated from combustion fly ashes by the use of a specially- designed, pneumatic transport, tribo-electric separators [4].

The aim of the present study is to bring out the work carried out on the characterization and value added products developed at Central Power Research Institute using Cenospheres. These cenospheres which have been harvested from the ash ponds of thermal power stations have been characterized for its physical, chemical, morphological, mineralogical, thermal and other end use oriented properties and to ascertain the behavior of different sources of cenospheres and their suitability for applications in various material schemes. Similar works carried out by other researchers with regard to cenospheres are also being documented in this paper.

2.0 CENOSPHERES

Cenospheres is a highly useful by-product with properties par excellence to produce novel products. Fly ash cenospheres as alumino silicates have unique properties such as very low density (lightweight), smooth and mostly spherical in character, hard, non-porous, inert, thermally, electrically and sound insulating. Because of these unique properties, cenospheres help to produce value added products for engineering applications in an economical way. The particle size of cenospheres varies from few microns to 200μm with their mean particle diameter is of 90-200μm in size.

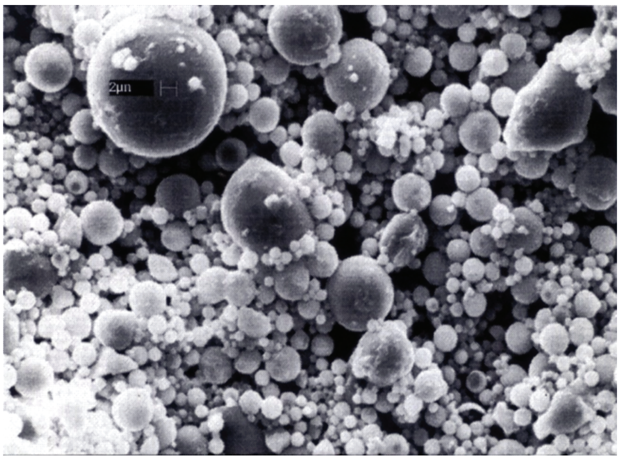


FIG. 1 FLY ASH PARTICLES WITH CENOSPHERES

Their color ranges from white to light grey. They are also referred to as microspheres, hollow spheres, hollow ceramic microspheres, micro balloons, or glass beads [5].

The thickness of cenospheres walls may be very small - < 10 % of the particle diameter, typically in the range of 2 – 10 microns.

2.1 Formation of Cenospheres

Cenospheres are formed from coal combustion ash when it is in molten state. Flowing with the combustion gas stream, the temperature of the molten particles is rapidly quenched, thereby 'freezing in' a spherical shape. Any gas bubbles within the molten particles are also trapped inside the spheres. These bubbles cause the production of light weight sphere-cenospheres; bubbles may occur in multiple forms within the 'frozen' particles, or as single concentric forms and their thickness that are nearly as great as the diameter of the particles.

Various researchers have undertaken studies on cenospheres and their properties mainly to focus on the relationship that exists between the cenospheres chemical composition, its mineralogy, density, fired properties, water absorption characteristics and the morphology on the processed products. The influence of processing parameters like milling, compaction pressures, sintering temperature and time on the properties, microstructure and mineralogical changes of the sintered products have also been investigated [6].

The Scanning Electron Micrograph shown in Figure 1 depicts the cenospheres dispersed in fly ash particles as received from the thermal power plant.

3.0 CHARACTERIZATION OF CENOSPHERES

4 samples of Indian coal ash cenospheres were harvested from the ash ponds of two thermal power stations, for evaluating their properties. The details of the characterization carried out using various techniques are reported:

3.1 Morphology

The morphology of cenospheres was observed using the Scanning Electron Microscope (SEM), Leica make Q500MC Model. The Energy Dispersive X-ray spectroscopy (EDAX) attached to the SEM was usedfor chemical constituents' analysis.

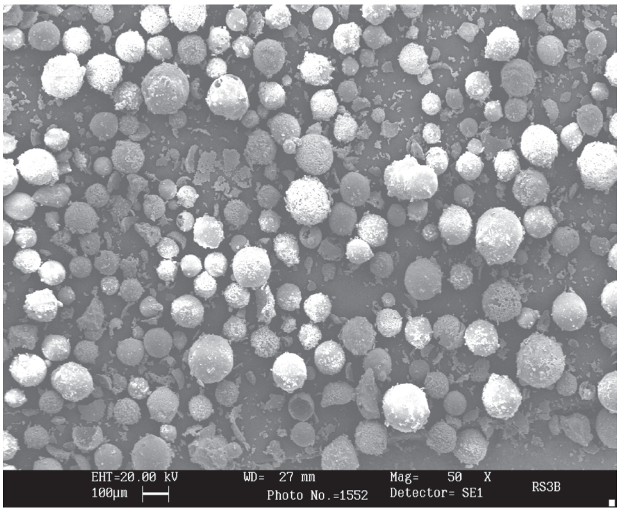


FIG. 2 AS COLLECTED CENOSPHERES SAMPLE

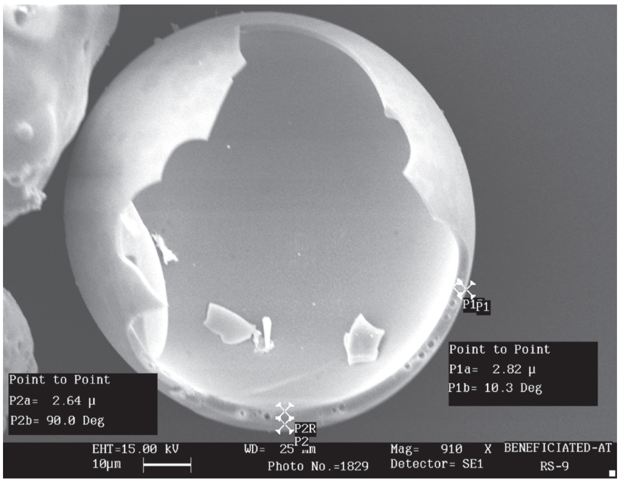


FIG. 3 HOLLOW CENOSPHERES PARTICLES

The SEM micrograph in Figure 2 depicts morphology of cenospheres particles as collected from the ash pond of the power plant and Figure 3 shows the measured thickness of the ruptured cenospheres wall which ranges from 2 – 6µm thick.

3.2 Chemical composition

The major chemical constituents of cenospheres are made up of metallic oxides like Silica (SiO_2), Iron (Fe_2O_3), Alumina (Al_2O_3) and Calcia (CaO) which forms the bulk chemical composition.

The chemical compositions of the Cenospheres are listed in Table 1.

3.3 Particle size distribution

The particle size of cenospheres varies from <45 microns to 400 microns with majority of the particles in the size range of 90-200 microns. These cenospheres have a crushing strength ranging from 4000 – 7000 psi.

TABLE 1

CHEMICAL COMPOSITION OF CENOSPHERES

Chemical Composition (%)	Samples			
	1	2	3	4
SiO_2	51.08	50.72	40.47	42.30
Al_2O_3	24.07	23.88	31.00	32.12
Fe_2O_3	2.41	3.55	5.75	5.35
CaO	17.13	15.51	1.68	1.50
Na_2O	0.65	0.87	9.70	7.00
K_2O	1.85	2.26	1.50	1.70
MgO	0.68	0.59	3.80	3.90
TiO_2	1.48	1.84	2.59	2.62
SO_3	0.32	0.39	0.08	0.10
P_2O_5	0.33	0.39	0.30	0.10

The particle size distribution of 2 samples of fly ash cenospheres of Power Station A carried out using Malvern Laser Beam Particle Size Analyzer equipment and 2 samples of fly ash cenospheres of Power Station B based on wet sieve analysis showed the following results:

TABLE 2

PARTICLE SIZE DISTRIBUTION / SIEVE ANALYSIS DATA OF FLY ASH CENOSPHERES

Particle Size (Passing through)	1	2	Particle Size (Retained on)	3	4
400 µm	96.8	98.6	250 µm	13.1	10.9
300 µm	87.8	90.3	180 µm	27.3	24.4
150 µm	24.7	27.6	106 µm	45.6	44.8
100 µm	5.2	5.6	90 µm	5.6	5.7
50 µm	3.5	3.9	75 µm	2.8	8.6
20 µm	1.1	0.02	45 µm	1.3	4.3

3.4 Mineralogy of Cenospheres

Fly ash is primarily composed of crystalline compounds such as quartz, mullite, hematite and amorphous glassy materials such as silica glass and glasses of other oxides. Mineralogical analysis revealed that the raw fly ash cenospheres sample (RS) could be distinguished into two major matrices: the amorphous constituent of glassy alumino silicates and crystalline constituent as represented in terms of mullite, quartz, calcite, hematite, magnetite and lime. Based on the beneficiation studies carried out by washing the fly ash cenospheres in water (WT), and mild acids (AT), the mineralogy is revealed in Table 3. However, the mullite crystals are largely attributed to kaolinite and illite which contributes towards the glass and cenospheres formation [7].

Cenospheres are composed of about 30 wt% crystalline phases such as SiO2 and $3Al_2O3.2SiO2$ and 70 wt% glassy phases and the amorphous content increases on beneficiation.

TABLE 3

MAJOR MINERAL PHASES IN CENOSPHERES

XRD Phases and their content(%)	Samples			
	1	2	3	4
Amorphous (Alumino-silicates)	67.19	68.33	82.38	71.09
Crystalline	32.81	31.67	17.62	28.91
Mullite (M)	8.79	10.08	6.09	8.08
Quartz (Q)	13.42	14.88	8.67	17.21
Calcite (C)	6.08	2.99	0	0
Hematite (HM)	1.7	1.04	0.89	1.31
Magnetite (Ma)	1.14	1.52	1.27	0.79
Lime (L)	1.68	1.16	0.7	1.52

3.5 Thermal Characteristics of Cenospheres

The determination of fusion temperature of the ash Cenospheres is of prime importance to assess its high temperature behavior for refractory application. The measured Cenospheres fusion temperatures are tabulated in Table 4 below:

TABLE 4				
FUSION TEMPERATURE OF CENOSPHERES				
Fusion Temperature (^{0}C)	**Samples**			
	1	**2**	**3**	**4**
Initial Deformation Temperature	1220	1260	1300	1315
Softening Temperature	1240	1260	1315	1330
Hemi-spherical Temperature	1250	1290	1345	1400
Fusion Temperature	1260	1360	1420	1450

The other physical properties of the fly ash cenospheres are appended in the Table 5 below.

TABLE 5	
OTHER PHYSICAL PROPERTIES OF CENOSPHERES	
Particle Density (g/cc)	0.50 to 0.70
Specific Gravity	0.68 –0.72
Bulk Density (g/cc)	0.35-0.42
Hardness (Mohs)	5-6
Thermal Conductivity ($Wm^{-1}K^{-1}$)	0.10- 0.20
Melting Point (^{0}C)	1200 to 1500
Shell Thickness (microns)	2 – 6
Crushing Strength (psi)	4100 - 7000
Colour	Off-white
Shape	mostly spherical
Moisture (%)	0.2 to 0.4 max
pH in water	8- 8.5
Loss on Ignition (%)	6.0 – 8.0

4.0 CENOSPHERES PROPERTIES FOR ENGINEERING APPLICATIONS

Based on the above comprehensive characterization of fly ash cenospheres, their properties are found to be extremely suitable for development of high value products for engineering applications. These beneficial properties are:

- Spherical Morphology
- Free flowing
- Particle size distribution
- Lightweight character
- Mineralogy
- Inertness
- Hardness
- Melting point
- Water absorption
- Thermally Insulating
- Electrically Insulating
- Sound Insulating
- Oil Absorption
- Packing factor
- Product performance

4.1 Spherical Morphology

The sphere is nature's most efficient shape with the lowest surface area compared to volume. It is this shape which gives fly ash cenospheres such a wide variety of uses other than simply being used as a light weight filler. The spherical shape means that it takes less resin, binder, water, etc to wet out the surface of fly ash cenospheres than any other shaped filler. This results in low resin or binder demand which in turn allows high solids formulations, lower shrinkage and often lower cost.

Spherical fillers like fly ash cenospheres exhibit excellent flow provide a more even distribution of the filler and are easy to spray, pump, trowel, etc. Cenospheres are therefore used to considerably improve workability and ease of use in a wide variety of applications.

Spherical fillers like fly ash cenospheres also reduce shrinkage only because they allow lower binder contents but directly as a result of their shape. At high concentrations, the spheres are packed together and help maintain the volume of the original product. Fly ash cenospheres are therefore excellent fillers for crack and joint compounds, sealants, etc.

The free flowing nature of fly ash cenospheres means that they are easy to handle in a factory environment. They can be easily gravity fed without any blockage and can be pumped in dry form.

4.2 Particle Size Distribution

In their raw form, fly ash cenospheres have a continuous particle size distribution from a few microns to about 500 microns. These have been classified to particular sieve fractions of 250, 180, 106, 90, 75, 45 and below 45 microns. Hence, based on the data obtained it is seen that there exists a good distribution of particle sizes resulting in good packing factor and low porosity which are beneficial during product development.

4.3 Lightweight Character

The bulk density of fly ash cenospheres is in the range of 0.3 – 0.4 g/cc and the average true density is in the range of 0.4 – 0.7 g/cc. These varied densities depend on the size fractions obtained from various media. Each fraction was separated into various density fractions using the fly ash cenospheres flotation behavior in water, ethanol and n-hexane (0.32 – 0.45 g/cc). The average wall thicknesses of flyash cenospheres are in the range of 2 – 6 microns. When density counts, fly ash cenospheres can be the answer. The advantages of low density are in many cases quite obvious and clear. The automotive, marine and aerospace industries all demand the lowest possible weight for plastic parts, sealants, putties, sound dampening, etc., and the addition of hollow fly ash cenospheres are an ideal solution. Fly ash cenospheres are about 20 – 25% of the density of other mineral fillers but are also strong enough to withstand most mixing, compounding and processing additives. The building industry is also moving to more and more lightweight products. Low density results in ease of application and use, easier mixing, lower transport costs, low slump and sag, reduced worker fatigue, easier sanding, easier cutting, easier drilling and a considerably happier workforce.

4.4 Mineralogy

The high amorphous content of fly ash cenospheres makes it more reactive as compared to fly ash for pozzolanic applications, such as blended cements, concrete, etc. This amorphous character can also be effectively utilized for development of corrosion resistant paints, foam products and other composite materials.

4.5 Inertness

Fly ash cenospheres are inherently alumino-silicate spheres of very low reactivity. Their chemical composition makes them very resistant to acids and alkalis. They are neutral in pH after beneficiation and do not interfere in the chemistry or reaction of the products, they are used in. There is also certain amorphous character in this material which makes them pozzolanic and hence will react with the free lime liberated as cement hydrates and form stable phases.

4.6 Hardness

Fly ash cenospheres with Moh's hardness of 5 – 7 have a hard surface that provides excellent erosion and weather resistance. The glassy shell of the fly ash cenospheres is totally impermeable to liquids and gases.

4.7 Melting Point

Fly ash cenospheres have a high melting point of 1200 – 1500°C which is considerably higher than synthetic glass microspheres. They are therefore excellent for use in high temperature insulating refractory and fire resistant coatings and panels.

4.8 Water absorption

Fly ash cenospheres have virtually no water absorbing properties. The typical moisture content of processed fly ash cenospheres is 0.01 – 0.07%.

4.9 Thermally Insulating

Fly ash cenospheres have a low coefficient of thermal conductivity of 0.1 – 0.2 W/mK as a result of which they can find application in insulating refractory, oil pipe line insulation, geothermal cements, external wall insulation stuccos and may other applications where good thermal insulation is required.

4.10 Electrically Insulating

In lightweight insulation products, fly ash cenospheres have excellent electrically insulating properties and are used in potting compounds, electrical encapsulation, solenoids, buzz bars, etc. Properties are virtually unaffected at high frequencies and while there is some loss at power frequencies, these are considerably lower than that for dense silica fillers.

4.11 Lime Content

An interesting feature is the high lime content observed in fly ash cenospheres generated at Power Station A, which has been characterized as calcite (calcium carbonate). This could be an excellent raw material for scrubbing of flue gases generated in the thermal power plant, especially for the reduction of sulphur dioxide emission.

4.12 Oil Absorption

Fly ash cenospheres have a low oil absorption character. When it is considered that fly ash cenospheres are only 20 – 25 % of the density of most other commonly used fillers, they will have one of the lowest oil absorption levels of any available filler. This is due to the spherical, low surface area shape and the glassy, smooth, totally non-porous nature of fly ash cenospheres. Fly ash cenospheres are therefore an ideal choice when formulating low binder level without high viscosity increase.

4.13 Packing Factor

The ratio between bulk and true density for fly ash cenospheres is small resulting in a very high packing factor or 60 – 65%. This means that fly ash cenospheres occupy more volume per unit weight.

4.14 Product performance Improvement

Fly ash cenospheres can improve manufactured products by improving strength, durability, and by reducing weight. Fly ash cenospheres also provide added buoyancy, better insulating properties, and reduced shrinkage and warpage values. Their spherical shape provides improved product stability, and increased resistance to impact. During the production of insulating materials, fly ash cenospheres better control both sound and thermal conductivity. Many other benefits or advantages may be realized depending on the application.

They were first introduced as an extender for plastic compounds, as they are compatible with plastisols, thermoplastics, latex, polyesters, epoxies, phenolic resins, and urethanes. The compatibility of cenospheres with specialty cements and other building materials such as coatings and composites was also quickly identified. Since that time cenospheres have been used in a wide variety of other products, including sports equipment, insulations, automobile bodies, marine craft bodies, paints, and fire and heat protection devices.

Owing to favorable combination of the above physical and chemical characteristics, fly ash cenospheres can become a valuable industrial raw material. Certain modifications of cenospheres surfaces allow their positive properties to be intensified or impart new properties which govern imparting specific material characteristics for unique applications.

5.0 APPLICATIONS OF CENOSPHERES

5.1 Fly Ash Cenospheres for EMI Shielding Applications

With the widespread use of digital electronic devices in a myriad of consumer, industrial and commercial applications, and control of electromagnetic interference (EMI) from internal or "stray" signals has become increasingly important.

With the ever increasing speed of circuits and devices, crosstalk becomes a design problem. So does the ever more crowded communications spectrum both in bandwidth and proximity. EMI essentially consists of radio frequency (RF) electromagnetic energy interacting with the components of an electronic device. EMI can negatively affect the performance of consumer electronics equipment, such as televisions and stereos. This protection from RF energy can be provided by a surface that reflects the unwanted energy, shielding the sensitive internal electronic hardware.

The ideal particle for RF shielding is highly conductive and resistant to oxidation, leading to the use of metals for the majority of shielding applications. Choices include: gold, platinum, palladium, and the less expensive silver. Conductive coatings containing silver particles have been available for a long time and provide excellent shielding performance, but are still expensive and very heavy due to the large amount of silver metal required to produce a complete paint film.

From a shielding system, most of the RF energy is reflected by the surface of the metal particle, leaving the metal core essentially unused. This "skin effect" indicates that a hollow metal particle would provide as much shielding performance as a solid particle, resulting in weight and cost savings.

The ideal shape for this hollow particle is a sphere, which allows the particles to fill most volume while using the least surface area. The optimum particle size would be about 50 microns, which provides good coverage with thin films and can be sprayed from conventional spray gun orifices. The hollow ceramic by-product of fly ash cenospheres of coal-fired power plants provides an excellent substrate for the silver metal shell. The spherical shape allows for isostatic strength of 4,000 psi, and the silver metal strongly adheres to the ceramic, unlike other available substrate. This results in a strong, tough and highly conductive particle with a density around 0.7g/cc, compared to solid silver particles at 10.5g/cc.

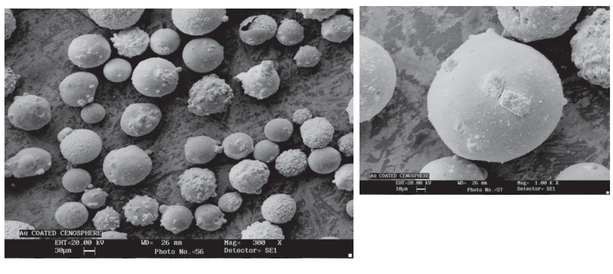
These hollow silver coated fly ash cenospheres or microspheres enable significant RF attenuation (reduction of RF interference) in much the same way as traditional solid silver particles, by developing chains of contacting particles into a vast network within the paint film. Solid silver particles rely on high loading and settling to obtain sufficient chaining. Another advantage of using cenospheres as the metal substrate is residual magnetic materials embedded in the ceramic sphere wall during formation. This magnetism helps pull the silver coated spheres together, forming chains without requiring high loadings. This lowers the cost even further, and eliminates spray problems such as sagging associated with solid particles.

Cenospheres or microspheres can also be incorporated into plastics, polymers, composites and rubber compounds during the forming or molding stage, thus providing excellent EMI shielding as an integral part of the finished product.

Gaohui Wu et al [7] and Xiaoli Huang et al [8] used fly ash cenospheres as a mixture in aluminum matrix composite by squeeze casting technique and studied the electromagnetic interfering shielding effectiveness (EMISE) at a frequency ranging from 0.03 MHz to 1.5 GHz. They have observed that the shielding effectiveness is higher than that of aluminium metal alone attributed to reflection and multiple reflections.

5.2 Coating of Metals on Cenospheres

Silver, copper and nickel were deposited on fly ash cenospheres particles using the electro-less plating technique from the respective chemical baths.



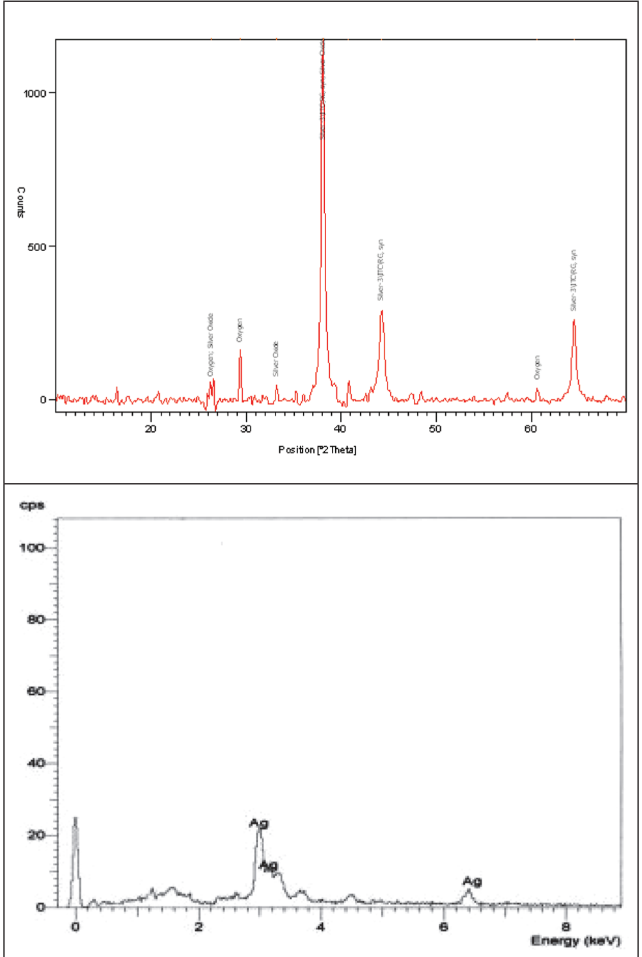


FIG. 4 SILVER COATED FLY ASH CENOSPHERES AND ITS XRD AND EDX PATTERN

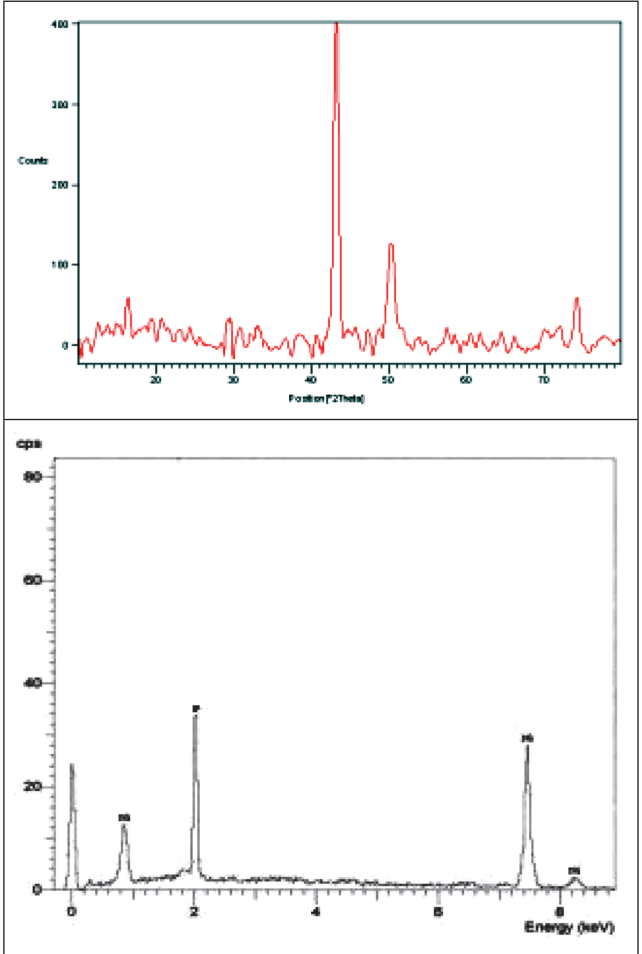
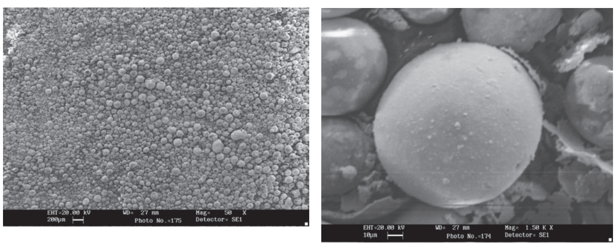


FIG. 5 NICKEL COATED FLY ASH CENOSPHERES WITH ITS XRD AND EDX PATTERN.

Zheng Xu et al [9] have also successfully attempted to coat metals on micro-powders including cenopsheres through Magnetron Sputtering.

They have reported that Magnetron sputtering is capable of coating such metals as Ni, Cu, Co, Al, Ti and Ag on micropowder surfaces, producing even, smooth and continuous metal films tightly attached to the surfaces. The Cenospheres coated with metals which have been reported by Zheng Xu et al is shown in Figure 6.



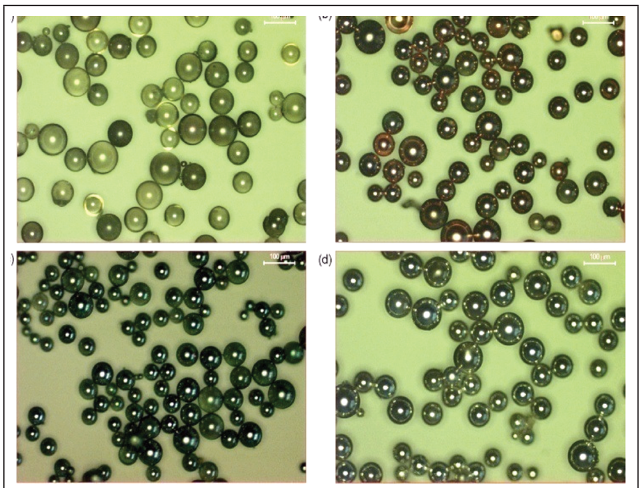


FIG. 6 CENOSPHERES AFTER COATING BY MAGNETRON SPUTTERING UNDER OPTICAL MICROSCOPE A) CU, LOW POWER; (B) CU, HIGH POWER; (C) NI; (D) AG.

Jing Zhan et al [10] have reviewed the R&D status and applications of fly ash cenospheres for microwave absorption. The cenospheres have been surface modified by chemical vapour deposition

(CVD) process and then the treated cenospheres have been made into an electromagnetic wave absorption material and then have evaluated for the performance.

Zeng Aixiang et al. [11] attempted to coat fly ash cenospheres with Ni-P using silver nitrate activator through electro-less route. They have reported that relative uniform coating has been obtained on the cenospheres coating. The low density Ni-P coated cenospheres particles may be utilized in the manufacturing of conducting polymers for EMI Shielding applications and as microwave absorbing materials.

5.3 Effect of Cenospheres reinforcement in metal matrix composites

Ananda Kumar et al [12]. have also studied the behavior of microwave sintered aluminum cenospheres metal matrix composite samples for their physical and mechanical properties and compared the results with the conventionally sintered ones. It is reported that the microwave sintered aluminum cenospheres metal matrix composite samples showed better physical and morphological properties when compared with the conventionally sintered ones. The microwave sintered samples showed decrease in apparent porosity by 44%, increase in hardness by 17%, and increase in bulk density by about 30% compared to the conventionally sintered samples.

Ananda Kumar et.al. [13] also have studied the Aluminum Metal Matrix Composites (AMC) comprising of aluminum powder and cenospheres in varying volume % fabricated through powder metallurgy (PM) route and the densification of the composites carried out in microwave sintering. The sintered composites have been measured for % porosity, thermal properties viz. co-efficient of thermal expansion (CTE) and thermal shock resistance (TSR) test. Compressive yield strength (MPa) was measured for the composites before and after thermal shock cycles. Microwave sintered aluminum cenospheres samples showed better properties compared to conventionally sintered ones. The microstructure of aluminum cenospheres metal matrix composite and the sample of the same are shown in Figure 7 and 8, respectively.

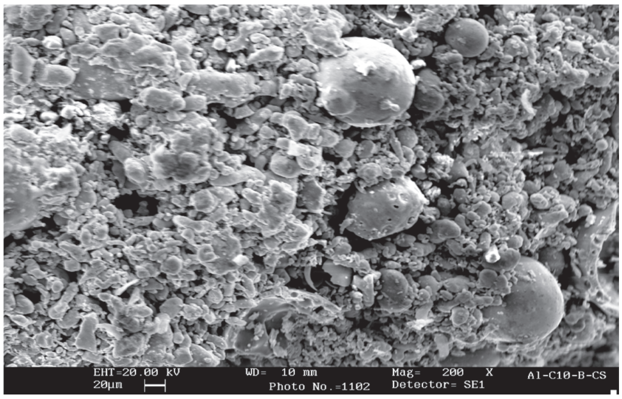


FIG. 7 MICROSTRUCTURE OF ALUMINUM CENOSPHERES METAL MATRIX COMPOSITE

FIG. 8 ALUMINUM CENOSPHERES COMPOSITE SAMPLE

Matsunaga et.al [2] also reported that fly ash cenospheres had low density, which is in the range 0.4-0.7 g cm^{-3}, compared with the densities of metal matrices, which is in the range of 1.6-11.0 g cm^{-3}.

Sudarshan et al [14] studied the fly ash particle reinforced A356 Al composites and their characterization. It is concluded that the cenospheres present in the fly ash showed good interfacial bonding between the Al and cenospheres reinforcement than fly ash in the matrix. It was observed that though the compressive strength of the composite was low with cenospheres reinforcement, the fly ash reinforced composite showed an increase of about 0.2 % proof stress in compression than in tension. The superior damping characteristics were exhibited by the composites when volume fraction of the fly ash was increased in the composite.

Wu G. H et.al [15] also studied similar damping characteristics in aluminum cenospheres composites with about 40 vol.% porosities, by using the forced vibration mode and the bending vibration mode. They have observed that the damping capacity of the fly ash cenospheres / 6061 Al composites reached $3.2x10^{-2}$ which is the high damping capacity level. They have also done similar study on the squeeze cast composites and have reported the relationship between the relative wall thickness of the cenospheres and the compression strength of such foams. The quasi static compression tests have indicated that annealed cenospheres- aluminum syntactic foams can deform plastically at a relatively higher stress ~45-75MPa and their energy absorbing capacity can reach ~20-35MJm-^{3}

Guo R.Q et.al [16] studied the differential thermal analysis to establish the stability of the aluminum fly ash cenospheres composites during synthesis and reheating. They have observed that with 40 vol.% of fly ash cenospheres in the aluminum matrix when held at 850^{0}C showed considerable reaction between fly ash cenospheres resulting in increase of silicon and iron content at the aluminum side owing to the solute enrichment due to dissolution and reduction of the silicon and iron oxides in the fly ash. The liquidus temperature was also seen to decrease from 655 to 644^{0}C. The silica, iron and aluminum had formed an Al-Si eutectic and Al5FeSi precipitate phases during solidification of the melt.

Dou Z.Y. et al. [17] have studied and reported that mechanical behaviors and energy absorption properties of a particular class o foam structure, syntactic foams, consisting of cenospheres embedded matrix of aluminium. The composite possessed higher energy absorption capacity, specific stiffness and strength compared to usual aluminium alone. The composite have been studied and compared for the high strain rate compression behavior with the results from the quasi static loading conditions. The foams exhibited distinct strain rate sensitivity and the peak strengths increased from ~45-75 to ~65-120 MPa and the energy absorption capacity also increased by ~50-70%.

Rohatgi et.al [18] have studied the thermal co-efficient expansion (CTE) of aluminum-cenospheres MMCs synthesized through pressure infiltration technique at various applied pressures and infiltration times. The study has indicated that CTE to be in the range of 13.1 x 10-6-11x$10^{-6}/^{o}$C which is lower than that of pure aluminum which is having a CTE of 25.3 x $10^{-6}/^{o}$C. The CTE of cenospheres is estimated to be 6.1 x $10^{-6}/^{o}$C.

5.4 Cenospheres in thermal insulation refractory

Fly ash cenospheres based thermal insulation refractory product has been developed and the measured thermal properties of the product show low co-efficient of thermal expansion in the range of 4.0 to 6.0 μm/m^{o}C. The thermal conductivity is in the range of 0.15 to 0.25 W/mK. The refractoriness of the fly ash cenospheres insulation refractory is about 1325^{o}C.It is also observed that the cold crushing strength is about 30 to 35 kg / cm2 and the modulus of rupture is around 28- 30 kg / cm2 which is better than that of the conventional refractory materials in use for such applications. The bulk density- 0.56 to 0.63 g/cc and the fired shrinkage of< 0.05% are added features of the product. The water absorption is in the range of 52 to 65% and the measured apparent porosity is around 65%. The product also has good corrosion resistance.

FIG. 9 THERMAL INSULATION REFRACTORY FROM FLY ASH CENOSPHERES

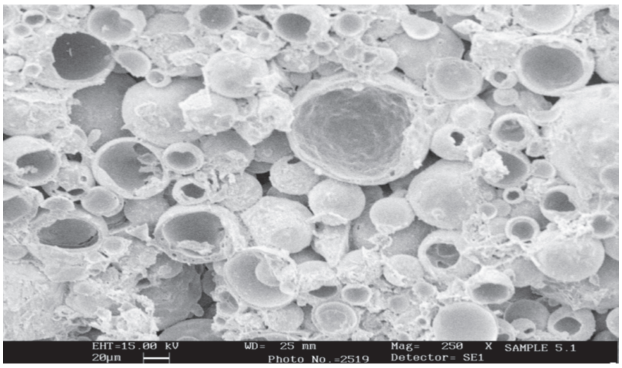


FIG. 10 MICROSTRUCTURE OF CENOSPHERES THERMAL INSULATION REFRACTORY

The Figure 9 depicts the fly ash cenospheres thermal insulation refractory developed and Figure 10 depicts the microstructure of the insulation refractory product.

Suresh et al. [19] have studied Aluminium metal matrix composites reinforced with cenospheres(from1% to10%) particulates through stir casting route. In the investigation, composites were produced with cenospheres as a reinforcement and eutectic Al–Si alloy as a matrix. The results indicate that with increase in the content of cenospheres, hardness and ultimate tensile strength increased by 34.7% and 44.3% respectively, while the density decreases by13.2%. The wear loss decreases by 33% at the highest sliding distance.

Yingna Zhao et al. [20] prepared and studied the porous lightweight ceramics using cenospheres as the raw material and as matrix. Using the microwave selective heating process, designing the interlayer composition in the matrix and ceramic bonding of the material has been achieved using microwave. The study was conducted to design the join of porous cenospheres ceramic material with 3D silica fiber reinforcement has been achieved using microwave sintering. It is reported that the higher flexural strength in the order of 23MPa was achieved which was higher than the porous ceramic material.

Richard A Kruger et al [21] have reported that cenospheres have physical and chemical properties that are inherently beneficial for the manufacture of insulating refractory. Their use imparts excellent flow properties to the product, thus enhancing the place ability of monolithic linings. This phenomenon has been ascribed to the lubricating (ball-bearing) effect of the spherical particles. Insulating refractory based on fly ash, exhibit remarkable strength to density ratios, excellent thermal shock resistance and an improved ratio of thermal conductivity to bulk density. Most importantly, they are far more cost effective than competitive products.

Parvati et al [22] studied the applications of cenospheres in thermal barrier coating deposited on metallic substrates through plasma spray technique. The SEM micrograph of the cross section of cenospheres plasma spray coated component is depicted in Figure 9. The cenospheres based TBC's have shown better performance in terms of energy saving applications by reduced heat transfers from the surface thereby contributing to energy savings.

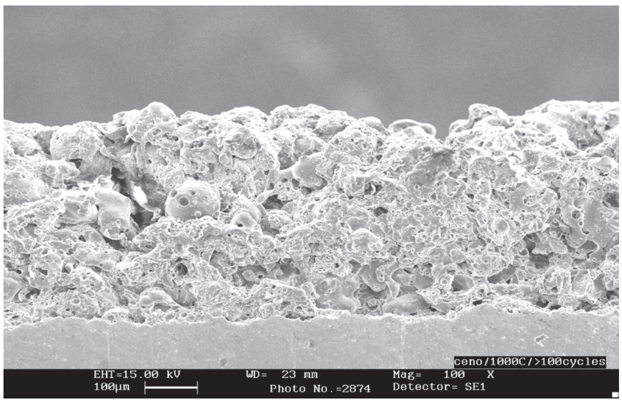


FIG. 11 SEM MICROGRAPH OF CROSS SECTION OF CENOSPHERES PLASMA SPRAY COATED COMPONENT

5.5 Cenospheres application in geo-technical applications

Asokan et al [23] have reported that the particle size and density relation is an important aspect to predict the Fe_2O_3 distribution and the amount of cenospheres in the fly ash. The crystalline to amorphous ratio in cenospheres varies with the particle size, whereas the crystallinity decreases as the particle size increased. The specific gravity of the cenospheres plays an important role in geotechnical applications and it is reported that the cenospheres specific gravity is less than that of soil owing to the variation in particle size, shape, mineralogy and composition.

The Young's modulus of cenospheres particles have been reported as 13-17 GPa and hardness values as 160-400 kg mm^{-1}for coarser size of 120µm size and 250-270kg mm^{-1}for finer size of 20µm. The co-efficient of permeability is found to be 10^{-4}mm/s to 10^{-3} mm/s. The higher lime content in the dry cenospheres contributed to increase in compressive strength with curing time due to pozzolanic reactivity and the lime reactivity of the cenospheres very much depend on the SiO_2 content. Compacted fly-ash cenospheres have requisite properties to be used in load bearing fills and highway sub bases and hence appears to be a useful material for the geotechnical applications.

Vikrant Tiwari et al. [24] have used cenospheres as reinforcement in cement matrix and asphalt concrete to study the acoustic properties of the mix and to develop a sound absorbing light weight structural materials. It is reported that the 40 volume % addition of cenospheres in the cement matrix increased the noise reduction coefficient by 100% of concrete mix when tested over frequencies range of 0 - 4000 Hz, whereas the sound absorption coefficient of asphalt concrete decreased with an increase of cenospheres volume fraction.

5.6 Fly Ash Cenospheres as reinforcement in polymer matrix composites

Use of inorganic fillers in polymer composites is increasing. Fillers not only reduce the cost of composites, but also frequently impart performance improvements that might not otherwise be achieved by the reinforcement and resin ingredients alone. Fillers can improve mechanical properties including fire and smoke performance by reducing organic content in composite laminates. Also, filled resins shrink less than unfilled resins, thereby improving the dimensional control of molded parts. Important properties include water resistance, weathering, surface smoothness, stiffness, dimensional stability and temperature resistance.

Fly ash cenospheres are one of those specialty materials, which can effective meet these requirements and serve as excellent filler materials for the manufacture of thermo-set and thermoplastic products. The development of polymer composite products using cenospheres as filler material with various thermoplastic matrix materials for domestic applications is depicted in Figure 12.

FIG. 12 FLY ASH CENOSPHERES BASED POLYMER MATRIX COMPOSITE PRODUCTS.

Deepthi et al. [25] have reported that fly ash cenospheres was used as reinforcing filler in HDPE to develop lightweight composites. Cenospheres are compatible with plastisols thermoplastics, latex, polyesters, epoxies, phenolicresins and urethanes. The advantages include reduced weight, increased filler loadings, better flow characteristics, less shrinkage and warping and reduced water absorption. In order to improve the interaction between the inorganic filler and the organic matrix, the Cenospheres were surface treated with silane coupling agent and HDPE-g-dibutylmaleate was used as compatibilizer. The tensile and thermal properties of the composites were measured as per ASTM methods. The results reveal that, both surface modifications of cenospheres accompanied by compatibilization led to the substantial improvement in mechanical properties and thermal stability of the composites.

Baljeev Kumar at al. [26] has also reviewed the effect of fly ash as filler on various properties of HDPE/ fly ash polymer composites and has found that there is an excellent compatibility between fly ash and polymers. It is opined that modification of fly ash cenospheres accompanied by compatibilization leads to the substantial improvement properties of the composites.

Dadkar et al [27] have studied cenospheres-filled and aramid fibre reinforced phenolic based hybrid polymer matrix composites (PMC) fabricated and characterized for tribo-evaluation. The friction-fade and friction-recovery behavior has been rigorously evaluated as a function of in situ braking induced temperature rise in the disc at the braking interface on a Krauss friction testing machine as per the ECE regulations. They have observed that the frictional fluctuations have been observed to decrease with the increase in cenospheres content.

Raghu Panduranga et al. [28] have developed Eco-Core a fire resistant sandwich core material that using a low binder content syntactic process using cenospheres and high char yield binder. Eco-Core is modified by adding different commercially available short fibers of various lengths. The study was undertaken to examine the effect of fiber content and fiber length on fracture, flexure and shear properties of Eco-Core. Fibers of 1.6, 3.2, 4, 6.3 and 12.7 mm were chosen and mixed with the Eco-Core compound in weight percent varying from 2.5 to 10 % of total compound. The results obtained in the study were compared with the baseline Eco-Core. Fracture toughness expressed in terms of critical stress intensity factor (KIC) can be increased by 1/3 over the baseline value by adding 4.5 % weight of 6.3 mm long JM3 fiber glass. The work has demonstrated the usefulness of fiber reinforcement approach to achieve desired properties for Eco-Core such as low weight, high stiffness, high shear and high toughness.

6.0 CONCLUSIONS

The fly ash based cenospheres efficiently harvested from the ash pond of coal fired thermal power stations on comprehensive characterization reveals properties par excellence and therefore is a highly resourceful material for effective use in high value products for various engineering applications like lightweight polymer composites, special concretes, metal matrix composites, high temperature refractories both for thermal insulation as well as bulk refractories for castables, etc.

The unique structure of the cenospheres and its associated properties such as physical structure, chemical and morphological properties have enabled cenospheres to be used in various products that are tailor made to suit the engineering application requirements.

The products that are made of fly ash cenospheres show good physical, chemical and mechanical properties.

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REFERENCES

[1] Central Electricity Authority, Government of India, Power Generation Report, December 2013.

[2] Matsunaga T, J K Kim, S Hardcastle, P K Rohatgi, Crystallinity and selected properties of fly ash particles, Materials Science & Engineering, A 325, pp 333-343, 2002.

[3] Fenelonov V B, M S Mel'gunov, V N Parmon, The Properties of Cenospheres and and the Mechanism of their formation during High Temperature Coal Combustion an Thermal Power Plants, Kona Powder and Particle Journal No.28, PP 189-2083, 2010.

[4] Tapiwa Z, Gurupira, L Charles Jones and M John Stencel, Cenospheres Separation from fly ash Using Pneumatic Transport, Tribo-electric Processing, Center for Applied Energy Research, University of Kentucky 2540 Research Park Drive, Lexington, KY 40511-8410.

[5] www.apitco.com, Cenospheres from fly ash, pdf file.

[6] Joseph J Biernacki, K Anil Vazrala, H Wayne Leimer, Sintering of a class F fly ash, Fuel 87, pp. 782-792, 2008.

[7] Gaohui Wu, Xiaoli Huang, Zuoyong Dou, Su Chen, Longtao Jiang, Electromagnetic interfering shielding of aluminum alloy-cenosphere composite, Mater Sci, 42: 2633 2636, 2007.

[8] Xiaoli Huang, Gaohui Wu, Effect of hollow structure on the Electromagnetic Interference (EMI) shielding of Aluminum-Cenosphere composition, Advanced Materials Research, Vols.97-101, pp 1760-1763, 2010.

[9] Zheng Xu, Xiaozheng Yu , Zhigang Shen, Coating metals on micro powders by magnetron sputtering, Science Direct, China Particuology 5, pp 345-350, 2007.

[10] Jing Zhan, Jianglong Yu, Pingyang Wang, Huan Zhao, A review on R&D status and applications of fly ash cenospheres in Microwave absorption, Advanced Materials Research, Vols. 634-638, pp 1886-1889, 2013.

[11] Zeng Aixiang, Xiong Weihao, XuJian, Electorless Ni-P coating of Cenospheres using silver nitrate activator, Science Direct, Surface & Coatings Technology 197, pp 142-147, 2005.

[12] M G Ananda Kumar, S Seetharamu, Jagannath Nayak, A Study on the Physical and Morphological Characteristics of Aluminum Cenosphere Composite Sintered at High Temperature in Microwave, The Journal of CPRI Vol. 10, No. 2, June, 2014.

[13] M G Ananda Kumar, S Seetharamu, Jagannath Nayak, L N Satapathy, A Study on Thermal Behavior of Aluminum Cenosphere Powder Metallurgy Composites Sintered in Microwave, Elsevier, Science Direct, Procedia Materials Science 5, pp. 1066 – 1074, 2014.

[14] Sudharshan, M K Surappa, Synthesis of fly ash particle reinforced A356 Al composites and their characterization, Materials Science & Engineering A 480, pp. 117-124, 2008.

[15] G H Wu, Z Y Dou , L T Jian, J H Cao, Damping properties of aluminium matrix-fly ash composites, Materials Letters 60, pp. 2945-2948, 2006.

[16] R Q Guo, D Venugopalan, P K Rohatgi, Differential thermal analysis to establish the stability of aluminium- fly ash composites during synthesis and reheating, Materials Science & Engineering A 241, pp. 184-190, 1998.

[17] Z Y Dou, L T Jiang, G H Wu, G H Zhang Q, Z Y Xiu, G Q Chen, High strain rate compression of cenospheres-pure aluminum syntactic foams, Scripta Materialia, 57, pp. 945-948, 2007.

[18] P K Rohatgi, N Gupta, Simon Alaraj, Thermal Expansion of Aluminum- Fly ash Cenosphere Composites Synthesized by Pressure Infiltration Technique, Journal of Composite Materials, Volume 40, No.13, pp. 1163- 1172, 2006.

[19] N Suresh, S Venkateswaran, S Seetharamu, Influence of cenospheres of fly ash on the mechanical properties and wear of permanent moulded eutectic Al–Si alloy, Materials Science-Poland, Vol. 28, No.1, 2010.

[20] Yingna Zhao, Caifer Wang, HaiXu, Yiachen Liu, Preparation of porous lightweight ceramics and Fibre joining Materials, Advanced Materials Research, Vol. 415-417, pp. 1038-1041, 2012.

[21] A Richard Kruger, Ash Resources (Pty) Ltd., ‘Energia’-pdf CAER University of Kentucky, Center for Applied Energy Research, Vol. 7, No. 4. 1996.

[22] Parvati Ramaswamy, S Vynatheya and S Seetharamu, Studies on cenospheres based thermal barrier coatings on metallic substrates, Paper presented in Conference on Thermal Spray Coatings, PESIT, Bangalore-17, 2008.

[23] P Asokan, Mohini Saxena, R Shyam Aslokar, Coal combustion residues-environmental implications and recycling potentials, Resources Conservation & Recycling, 43, pp. 239-262, 2005.

[24] Vikram Tiwari, Arun Shukla and Arjit Bose, Acoustic properties of cenosphere reinforced cement and asphalt concrete, Applied Acoustics 65, pp. 263-27, 2004.

[25] M V Deepthi, Sharma Madan and R R N Sailaja, Mechanical and thermal characteristics of high density polyethylene–fly ash Cenospheres composites, Materials & Design, Design of Nanomaterials and Nanostructure, 31(4), pp. 2051–2060, 2010.

[26] Baljeev Kumar, Rajeev Garg and Upinderpal Singh, Utilization of Fly ash as Filler in HDPE/Fly ash Polymer Composites: A Review, International Journal of Applied Engineering Research, ISSN 0973, 4562 Vol.7 No.1, 2012.

[27] N Dadkar, B Tomar Sand, B K Satapathy, Evaluation of fly ash filled and aramid fibre reinforced hybrid polymer matrix composites (PMC) for friction braking applications, Mater Des, 30, pp. 43-69,2009.

[28] Raghu Panduranga, Matthew Sharpe and N Kunigal Shivakumar, Fiber Reinforced Fire Resistant Syntactic Foam and Fracture Toughness Characterization, 50th Structures, Structural Dynamics, and Materials Conference 17th AIAA 2009-2685, 4-7, Palm Springs, California, 2009.