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Fly Ash Cenosphere - Formation, Separation, and Applications in Diverse Fields

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ABSTRACT

Despite a global shift towards renewable energy sources, coal will remain a significant energy source in the near future. The by-products of burning coal, have already given rise to environmental issues and its associated pollution. The coal fly ash, bottom ash, and its disposal require large areas of land causing certain alarming issues related to thermal power plants. Separation techniques are available to isolate the valuable constituents from fly ash viz., magnetites, aluminosilicates, cenospheres, unburned carbon, etc. for its specialized applications. The fly ash cenosphere, a high-demand material, can be explored for many industrial applications due to its outstanding characteristics, including low bulk density, good heat resistance, chemical inertness, great workability, high strength, and spherical shape. An attempt has been made in this work to present a comprehensive description of fly ash cenosphere, its formation and separation, basic properties, and environmental issues; in addition, its applications in soil amelioration, ceramics, catalysis, oil well drilling, electronic components, and zeolite synthesis have been elaborated.

Keywords: Fly Ash; Fly ash cenosphere; Separation; Coatings; Applications.

1. INTRODUCTION

Energy resources are already heavily impacted and exploited due to increased population, materialistic advancements, and economic growth. Nearly 30 percent of primary energy consumption in the world comes from coal, the second-largest energy source and it will remain the primary means of generating power for the foreseeable future (Chávez, *et al.* 2011). Coal combustion can also produce toxic by-products that have become a global problem due to its increasing use and detrimental impacts on water, air, soil, and the environment (Yao *et al.* 2015). The Sustainable Development Goals (SDGs) aim for the production and consumption sustainably to achieve the efficient and suitable management of natural resources and reduce the generation of waste substantially through recycling methods and prevention techniques, to be achieved by 2030. The generated by-products from coal combustion need sustainable management techniques. Therefore, progress in this direction is crucial to achieving the SDGs (United Nations, 2015). Therefore, a variety of novel and creative recycling methods have emerged because of the awareness that industrial waste by-products can become resources for other applications.

During coal combustion, fly ash is generated as waste in huge quantities. An estimated 750 MT of fly ash gets generated per annum globally, with an increasing rate (Wang *et al.* 2008). The coal-fired power generation leads to by-products, mainly fly ash and bottom ash, and amounts to around 80 and 20 wt. % of the generation of fly ash. The use of fly ash merely for landfills becomes relatively hazardous and expensive; thus various high-end applications can be explored and suggested (Ahmaruzzaman, 2010).

Although there are various applications for the use of fly ash, its utilization is approximately 68% (China), 47% (Europe), 39% (US), 15% (Russia), 10% (Australia), and 25% worldwide (the overall). It implies that a significant amount of fly ash remains unused and currently is disposed of in landfills or ash lagoons. There are many separation techniques developed for the segregation and separation of the valuable components, viz. fly ash cenospheres, aluminosilicates, magnetites, and unburned carbon to better utilize fly ash for specific high-end applications (Blissett *et al.* 2012). Fly ash cenospheres are the most significant value-added substances separated and obtained from fly ash among all the above-mentioned components.

'Cenosphere' is constituted by two words in Greek: kenos means hollow and sphaira means sphere which describes its characteristics. Fly ash cenosphere particle has a spherical shape with a hollow interior (Cho *et al.* 2005; Nyale *et al.* 2014; Bhangare *et al.* 2014). The percentage of cenosphere in fly ash widely varies in the range of 0.01 to 4.75% (by wt.), although it is found mostly between 0.25 and 1.5% (by wt.). The formation of the cenosphere during combustion depends majorly on the grade of feed coal, its mineral constituents, and the process of combustion (Vassilev *et al.* 1996; Fomenko *et al.* 2013).

Cenosphere carries many exclusive and specific properties, e.g. very light in weight; excellent insulation; higher compressive strength; low water absorption; better flow characteristics; chemically inert, and superior thermal resistance. Such excellent and desired properties make it suitable for various specific purposes and industrial applications. Hence, the present paper focuses on the very exclusive characteristics of cenospheres, their process of formation, separation methods, characterizations, and prospective applications (Ahmaruzzaman, 2010; Fomenko *et al.* 2013).

The comprehensive discussion on cenosphere is significant given its unique properties, low cost, rapidly increasing market value and prospects of reducing the pollution load and its management in various industries (Vassilev *et al.* 1996; Sokol *et al.* 2000; Goodarzi *et al.* 2006; Anshits *et al.* 2010; Li *et al.* 2012; Ranjbar *et al.* 2017). Therefore the present article provides a comprehensive analysis of the cenosphere's composition, mechanism of formation, diverse influencing factors on cenosphere formation, industrial applications, and its utilization as a filler material in cement-based composites (Nyale *et al.* 2014). In conclusion, one can formulate conclusions regarding the merits and demerits of the applications, the method of utilization of fly ash, and potential avenues for research in the future. The paper aims to add a detailed understanding of the present utilization of fly ash, and cenosphere and to identify the promising applications (Ghosal *et al.* 1995; Vassilev *et al.* 2004; Shapiro *et al.* 2005; Hirajima *et al.* 2010; Kolay *et al.* 2014; Fomenko *et al.* 2015).

1.1 Properties of Fly Ash Cenosphere

During the burning of coal, fly ash cenospheres are formed at very high temperatures (about 1400 °C) in combination with mineral oxides; and can be subjected to a variety of high-end applications which rely mostly on its physical and chemical characteristics, viz. particle size, sphere thickness, phase composition, etc. The type of feed coal utilized and the combustion technique employed, provide an impact on cenosphere formation. Cenosphere is made of aluminosilicates and traces of Ti, P, Na, S, and other elements as well as extremely minute amounts of K, Ca, Mg, and Fe. Ranjbar and Kuenzel conducted a detailed analysis of the chemical compositions of the cenosphere as well as fly ash (Ranjbar *et al.* 2017).

The primary oxides found in fly ash cenospheres were observed using the ternary phase diagram. Cenospheres were found to be abundant in silica and the ferrosilicon group. For the internal gas to form inside the ash droplet that creates the cenosphere, there must be at least 5% iron oxide present. Consequently, it might be stated that except for the increased carbon in fly ash, the cenosphere's composition is comparable to that of fly ash. Al and Si are the major compositions in fly ash cenospheres (Ranjbar *et al.* 2017). Energy-dispersive X-ray (EDX) spectroscopy can be used to illustrate its composition in Fig. 1. The spectra show that fly ash cenosphere (FAC) has the highest concentration of aluminum and silicon oxides, along with evidence of iron oxides.

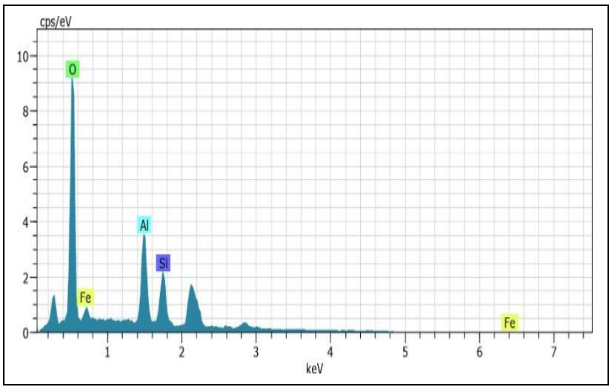

Fig. 1: Cenosphere particle SEM-EDX spectra exhibiting Al_2O_3 and SiO_2 peaks and Fe metal traces

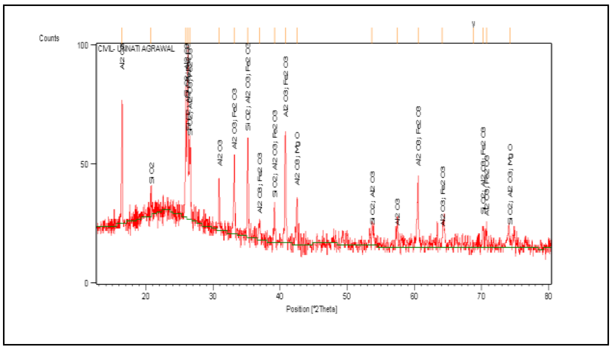

Fig. 2: XRD Characterization of fly ash cenosphere

According to XRD spectra in Fig. 2, the fly ash cenosphere's entire structure is made up of crystalline and amorphous phases. The needle-like design of the cenosphere's crystalline phase, including magnetic, mullite, acid plagioclases, lime, quartz, periclase, and K-feldspars, gives structural stability to the particle. The amorphous glass phase that makes up 90% of the cenosphere's structure provides a smooth shape to it. Acid treatment during engraving, drying, and storing of materials can dissolve the glass phase, leading to the exposure of additional minor phases on the surface of the cenosphere (Vassilev *et al.* 2004; Fomenko *et al.* 2015). The XRD spectra show that FAC is a primarily amorphous glass and a small amount of alumina-silicate crystal structure. Mullite and quartz are the two main crystalline phases.

Based on optical range, non-magnetic cenospheres can be roughly categorized as transparent, grey, and dark. Grey cenospheres possess a thicker, semi-transparent, and more porous layer in comparison to clear cenospheres. Due to the perforation on the surface and higher shell porosity, the black particles scatter the light totally (Kolay *et al.* 2014). The bulk of cenosphere particles range in size from 20-300 µm with a shell thickness of 1 to 18 µm, as shown in Fig. 3 and Fig. 4. Cenosphere particles range in diameter from 5 to 500 µm. The diameter of the cenosphere and its shell thickness are inversely correlated. The diameter-to-shell thickness ratio varies from 20-30 for finer particles and remains largely constant at 20 for bigger particles (Sokol *et al.* 2000; Anshits *et al.* 2005; Ngu *et al.* 2007; Fomenko *et al.* 2012). It has been attributed that the temperature of the furnace regulates the cenosphere's particle size. Coal minerals undergo melting during combustion, and at elevated temperatures, the molten droplets erupt into smaller drops. After the droplets solidify, the overall particle size is finally lower. Additionally, it can be postulated that the chemical makeup of molten droplets affects the size of the cenosphere particle (Li *et al.* 2012). The majority of researchers concluded that the SiO_2 content drops with cenosphere particle size. The composition of Al_2O_3 has been seen to decrease as the Al_2O_3/SiO_2 ratio increases. It can be concluded that the composition of Al_2O_3 increases with the cenosphere size. The viscosity of the molten droplet rises concurrently with the Al content and stabilizes the droplet as it expands by preventing it from shattering into smaller fragments (Vassilev *et al.* 2004; Li *et al.* 2012; Fomenko *et al.* 2015).

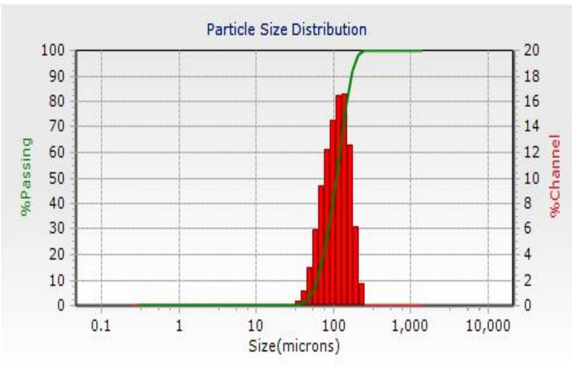

Fig. 3: Particle Size Analysis of fly ash cenosphere

The cenospheres have an apparent density ranging from 0.4 to 0.72 g/cm^3 and a bulk density between 0.25 and 0.7 g/cm^3. In contrast, alumino-silicate microspheres have a shell density of 2.65 g/cm^3, whereas Type IV fly ash has a density between 2 to 2.3 g/cm^3. In addition to its chemical composition, the hollow structure of FAC is the cause for its lower density (Hirajima *et al.* 2010; Ranjbar *et al.* 2017).

To reduce the amount of binder, polymer, and water required for making a composite material, an ideal filler for different polymeric composites should possess a lower surface area-to-volume ratio. The ability to impregnate the polymeric composites on the surface is provided by the cenosphere's spherical form. Nylon composites, syntactic foams, composites of polyurethane, and polyester composites are examples of materials that can utilize cenospheres as fillers in polymers.

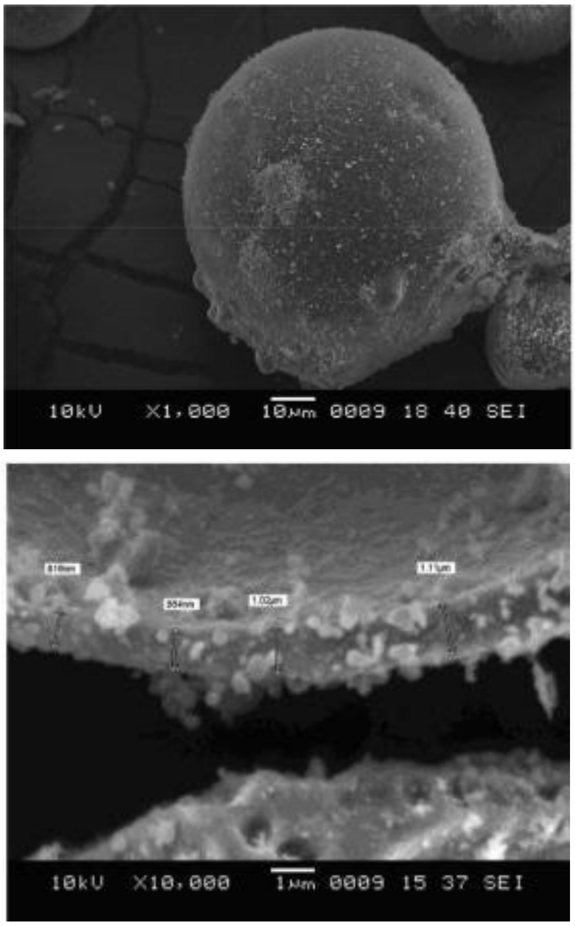

Fig. 4: SEM spectra of cenosphere with spherical shape and thickness of 1-18 µm.

Cenospheric materials can be used for a variety of applications, including high-temperature resistance, sound absorption, electromagnetic interference shielding, conductive filler, and insulator (Shukla *et al.* 2001; Chalivendra *et al.* 2003; Tiwari *et al.* 2015). It is clear from TGA analysis in Fig. 5 that the cenosphere experiences mass loss at temperatures around 300 °C because of the evaporation of carbon-based and volatile matter present in it. Additionally, no evidence of mass loss was observed until 1000 °C, proving the FAC's thermal durability at higher temperatures making it an appropriate filler for thermally robust composites. It is important to note that the cenosphere must be coated with metals or non-metals for the cenosphere's unique applications in the aforementioned domains.

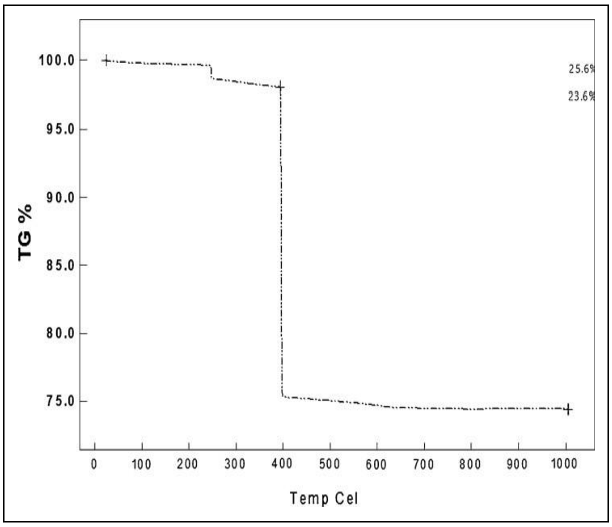

Fig. 5: TGA of cenosphere

2. SEPARATION OF CENOSPHERE FROM FLY ASH

The cenosphere and fly ash can be distinguished from each other by their different densities. Dry and wet separation methods are two categories into which the separation techniques can be divided.

2.1 Wet Separation

The most popular method for separating various components of coal fly ash is froth flotation, followed by gravity and magnetic separation. Cenospheric material can be separated using the hydraulic separation technique with water as a medium during gravity separation. The cenospheres are obtained by pond skimming and float on top of a fly ash solution (Yu *et al.* 2009; Wang *et al.* 2015). Owing to its simplicity and widespread accessibility, this strategy is often used; however, the efficiency of gravity separation techniques is determined by:

a) variations in the densities of the utilized liquid, buoyancy forces, and solid particles,
b) the feed particle concentration,
c) particle porosity and texture, (particles having smooth surfaces float more quickly to reduce surface-liquid interactions), and
d) Cycles of refinement.

The exerted buoyancy forces on a particular species of particle in the bi-disperse suspension are taken into account by the density difference term. A comprehensive list of liquids used in separation and their respective potential of removal can be obtained by utilizing liquids with varying densities for different density classification systems. For instance, a mixture of dibromomethane, di-iodomethane, and carbon tetrachloride, can be combined to create a separating media with a density of 2.2 g/cm^3. Acetone, distilled water, and lithium metatungstate with densities of 0.8, 1, and 1.5 g/cm^3, respectively, can likewise serve as separating liquid media (Shukla *et al.* 2002; Aixiang *et al.* 2005a; Zeng *et al.* 2012; Pang *et al.* 2012). Repeated stirring and settling can enhance the recovery of floaters.

Despite buoyancy forces, the extent of separation can be significantly delayed at lower concentrations of total solids and increased at sufficient solids concentrations. This phenomenon can be attributed to the formation of finger-like flow patterns aligned with the gravitational field. These structures are formed due to the lateral separation of heavier and lighter particles caused by the drag and the interactions of inter-particles; additionally, as the rough surface restricts motion inside the liquid medium, porosity, and particle texture affect the rate of sedimentation. In addition to settling-stirring, a centrifuge can be used to speed up the process of separation; however, it depends upon the overall effect of the amount of fly ash, the type of centrifuge, and its dilution (Aixiang *et al.* 2005a).

Another technique employs the use of the Boycott effect to enhance efficiency and speed up the wet separation that develops in inclined settings and is taken into account by the Inverted Reflux Classifier. A set of inclined parallel channels positioned beneath an inverted liquid fluidized bed serves as the foundation of this system (Fomenko *et al.* 2012). The overall effect of this approach depends on the concentration of the feed solids, the number of process stages, and the feed rate. As compared to a typical teetered (fluidized) bed separator, the inclined channels offer a significantly larger effective settling surface. To strengthen the process, it was seen that separation occurs exclusively due to density difference when employing the short channels to encourage laminar flow and high shear rates (Pang *et al.* 2012). This mechanism was assessed for both single and multi-stage processes. Since the total solid feed reduces in later stages, it limits the bulk streaming formation impact and the cenosphere recovery decreases with a multiple-stage system. The single-stage process can be used in the optimization of this method of solid concentration and a lower feed rate of roughly 38 wt. %, with 90 wt. % of the cenosphere recovered. The effectiveness of the separation system can be further improved by combining numerous techniques. To distinguish between non-magnetic and magnetic non-perforated cenospheres, techniques such as magnetic separation, classification of grain size assisted with a vibration device, and hydrodynamic gravitational separation can be used.

Fig. 6 demonstrates that the wet separation approach may effectively separate intact cenospheres from fractured ones by modifying the operating parameters. Owing to the disparity in vapor pressure between the interior and outside of particles, it is possible to boil a cenosphere/water suspension and extract 60% of the intact and non-porous particles. The cenosphere with or without pores and the fractured or intact particles behave similarly at room temperature and float on the surface.

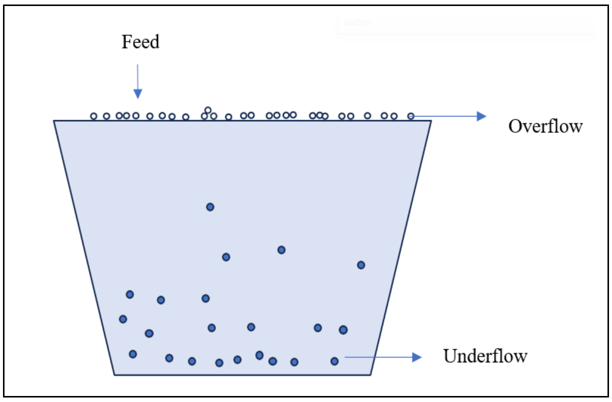

Fig. 6: Wet separation technique

When particles are boiling, inside pressure then rises, and if there are pores, gas escapes from the particle, water seeps in, and it becomes heavier - a way to differentiate broken cenospheres from intact cenospheres in fly ash. The amount of cenosphere present in the entire sample might be reduced by using this liquid by 78 wt. % during the first separation and another 58 wt. % during the second separation (Zeng *et al.* 2012). By triple-refining, the raw material in a laboratory setting, silicate globules could be extracted using water.

The raw cenosphere was subsequently divided into two fractions: uniform fraction made up of undamaged cenospheres (66% of the volume), and the sediments made up of cracked and fissured particles, coked and semi-coked coal particles impregnated with water, slag fragments, as well as the majority of magnetic cenospheres (34% of the volume). There are some significant drawbacks, even though numerous efforts have been made to improve the effectiveness of the wet separation method (Aixiang *et al.* 2005b). Firstly, a small portion of fly ash (0.2–5.0 wt.%) is susceptible to dissolving near water. Dissolution of its matrix and discrete phases, and coatings on the surface of the particles contribute to that fraction's leachability. Some of these dissolved substances provide a clear danger to humans; hence, it is important to take into account their minimal accumulation in water sources. In addition, the availability of land and water may make it difficult to implement wet-separation techniques in nations with a large population (Cao *et al.* 2015).

After the process of froth flotation, gravity, and magnetic separation are the most widely used processes for separating various components of coal fly ash from one another. Cenospheres may be extracted as part of the gravity separation procedure with a technique called hydraulic separation, which uses water as the medium. The method used to gather cenospheres, which are visible and floating on the top of a fly ash solution, is known as pond skimming. This method is widely used since it is simple to use and widely accessible (Pang *et al.* 2012). However, the following factors must be met for gravity separation techniques to be effective: the concentration of particles in feed, the texture and porosity of the particles, which are described as particles that have void space within them, the differences in the densities of solid particles and the liquid being employed, and the buoyancy forces.

The term "density differential" is included in the explanation of the buoyancy forces on a particle species when discussing a bi-disperse suspension. Various applications for classifying liquid densities include the use of different densities of liquids. For instance, creating a separation liquid with a density of 2.2 g/cm3 by mixing lithium metatungstate, carbon tetrachloride, and dibromomethane with distilled water of density of 1 g/cm^3, or acetone, which has a density of around 1.5 g/cm^3 (Shishkin *et al.* 2018).

The separation of floating particles can be improved by a procedure that comprises repeated stirring followed by settling. Even though buoyant forces are the main factor in determining the pace of separation, this rate is slightly slowed down when the total solids concentration is low and greatly accelerated when the total solids concentration is high enough. This phenomenon could be explained by the drag force's lateral segregation of light and heavy particles in the presence of interparticle interactions, which eventually produce fingering flow patterns that point in the gravitational field's direction (Shishkin *et al.* 2017). The rate of sedimentation is also impacted by the particles' porosity and roughness. This is due to the fact that particles find it more challenging to move through fluid environments when a surface is rough.

A centrifuge can be used in addition to stirring and settling to hasten the separation procedure. The kind of centrifuge, the quantity of dilution being used, and the volume of fly ash being separated; however, all affect how much spinning and how long a centrifuge is run for. Another strategy takes advantage of the Boycott effect to improve the performance of the wet separation process and speed it up when it takes place in an inclined environment, such as the one covered in the Inverted Reflux Classifier (Meng *et al.* 2010). Several parallel inclined pipes that are placed directly beneath an inverted fluidized bed of liquid form the system's framework. The effectiveness of the strategy depends on the feed's solid concentration, feed rate, and the process's number of phases. The inclined channels give a substantially larger settling region than a traditional teetered bed (fluidized) separator.

It was discovered that the recovery is mostly dependent on the difference in density between the two fluids when tiny channels are used to create laminar flow and high shear rates. This was done to make the mechanism better. Using this method, single-stage and multi-stage processes were both looked at and analyzed. A system with multiple stages has a lower chance of cenosphere recovery than one with a single step because later stages' total solid input is reduced, limiting the impact of bulk streaming formation. In this method, 90% of the cenospheres were recovered while the optimal value of solid concentration was achieved by a single-stage process with a low feed rate of roughly 38%. The already excellent level of productivity of the separation process has the potential to be greatly increased by integrating many methodologies into a single workflow. For example, hydrodynamic gravitational separation, grain-size classification by vibration device, and magnetic separation have all been used to separate magnetic and non-magnetic non-perforated cenospheres (Aixiang *et al.* 2005a; Pang *et al.* 2012; Shishkin *et al.* 2017).

One of the many advantages of the wet separation technique is shown in Fig. 6, where the process characteristics can be changed to separate intact cenospheres from fragmented cenospheres. By boiling a cenosphere/water solution, it is possible to remove 60% by weight of the unbroken and those without porous particles due to the difference in vapor pressure between the interior and exterior of particles. Cenospheres behave uniformly at room temperature and float on top whether they contain pores or not, along with the whole and broken particles. When the water boils, the pressure within the particles rises. If the particles have holes, the gas escapes, water enters, the particles get denser, and the particles sink to the bottom of the jar. Another method for isolating broken cenospheres from intact cenospheres that are contained in fly ash is to use acetone that contains 1% by weight of triethanol amine lauryl sulfate (TEALS) (Aixiang *et al.* 2005a). Using this liquid during the first separation allowed for the removal of 78 wt. % of the total amount of cenosphere that was present in the assay, and using it during the second mixing allowed for the removal of an additional 58 wt. %. The triple refinement of the raw material on a laboratory scale allowed for the extraction of additional silicate globules using water.

The dense build-up of solid fly ash particles on the surface of buoyant fly ash, which prevents the sinking of solid particles in Class C and Class F fly ash and increases the impurity of the cenosphere product, can be another disadvantage. When buoyant materials are exposed to high temperatures, this can happen. Additionally, there is a chance that $Ca(OH)_2$ crystals will form on the cenospheres' surface if the fly ash has a high calcium content. When the cenospheres are left to dry, these crystals grow more fragile, thus limiting their usefulness. As a result, the utilization of this fraction in the cement industry is constrained because the removal of calcium from fly ash reduces the interactions of this additive with cement. Fly ash and cenospheres must be dried first, which requires energy, raising the price of these raw materials; this is another negative aspect of this practice. As a result, it is required to come up with a different strategy to overcome these obstacles. The buoyancy of the fly ash particles on the surface prevents the solid fly ash particles in classes C and F from sinking, increasing the impurity of the cenosphere product; additionally, cenosphere surfaces can develop $Ca(OH)_2$ crystals when fly ash contains a high calcium content. These crystals solidify when the cenospheres dry, limiting their ability to be used in other applications. Then, the interaction of fly ash with cement is reduced when the calcium is removed, which restricts the usage of this fraction in the cement industry. Another disadvantage is that fly ash and cenospheres must first be dried before being used, which takes energy and raises the cost of these raw materials. Hence, a different approach is needed to overcome these problems (Li *et al.* 2010).

2.2 Dry Separation

In recent years, dry separation has been employed as an alternative technique to address the shortcomings of wet separation.

The benefits of this process include maintaining the chemical composition, minimizing drying-related water pollution and energy use, and requiring less room for the technical equipment than wet separation. One suitable technology is the air classifier, which separates solid particles by particle geometry or aerodynamic/ hydrodynamic equivalent diameter (Pang *et al.* 2012)

Air classifiers come in five different varieties: gravity, fluidized bed, cascade, centrifugal, and inertial. Only the centrifugal and inertial air classifiers are made to sort particles smaller than a micrometer; the others can be used for millimeter-sized particles. The separation principle is based on the idea that particles floating in a flowing gas under the influence of drag and gravity would separate from one another (Pang *et al.* 2012; Ranjbar, 2017).

The top of the column is reached by light particles whose terminal settling velocity is smaller than the velocity of air, while heavy particles whose terminal settling velocity is bigger than the velocity of airflow downward against the air stream. A micron separator is a centrifugal air classifier with a feed rate of around 160–180 kg/h, a cutting size of 20–100 m, and a coarse product recovery of 70–80 wt. %. It is also possible to use a closed-type pneumatic separator, which enables adjusting the fan speed between 1.2 and 3.7 m/s in order to manage various yields (Shishkin *et al.* 2017). The closed-type pneumatic, which has an efficiency of "only"

63 wt. % is somewhat less efficient than the micron separator, which has a little over 66 wt. %. At increased overflow product output, a closed-type pneumatic separator re-concentrates fly ash particles in the underflow product, changing fly ash and cenosphere concentrations and decreasing Newton's efficiency. This is the cause of the slightly better performance of a micron separator. These findings have led to the suggestion that the dry separation process functions like the wet separation procedure. However, compared to wet processing, this separation method's primary disadvantage is the complexity of the initial setup and its operations.

2.3 Synthesis

Fly ash contains extremely little cenosphere volume, hence there are situations when synthesizing cenospheres is more efficient than using separation techniques where the raw materials are a few. In this line, fly ash and blast furnace slag were converted into smooth cenospheres and glass microspheres, respectively, using the thermal flame projection process.

3. VARIOUS COATING TECHNIQUES

The different coating techniques and their corresponding applications for metal-coated cenosphere are detailed below. In contrast to the majority of methods, which necessitate conventional activation and sensitization stages involving expensive and hazardous chemicals such as Pd and Sn (Shukla *et al.* 2001), certain methods demand a custom-designed apparatus for coatings (Yu *et al.* 2009). Consequently, this concern must be adequately resolved before commercialization.

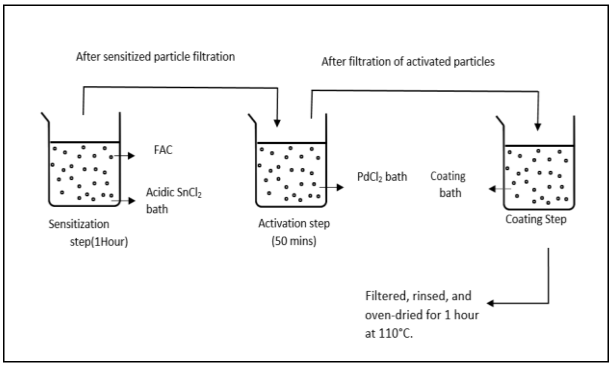

Fig. 7: General Steps of Electroless Coating Process

3.1 Electroless Coating Method

The electroless method (Shukla *et al.* 2001) presented the initial documentation of a method to deposit copper metal onto FAC without increasing external power consumption. The method was implemented by Shukla *et al.* (2001) in order to encapsulate copper on the surface of the cenosphere. Due to the non-catalytic nature of the FAC surface, two stages are necessary to modify it. In general, the electroless coating process consists of two consecutive steps: activation and sensitization of the outer surface of FAC, as demonstrated in Reaction 1. As a sensitizer, an acidic $SnCl_2$ solution is employed, while an acidic $PdCl_2$ solution functions as an activator. The FAC particles are sequentially deposited into the activation and sensitization baths. Following filtration and deionized water washing, the particulates are conveyed to the coating bath (Reactions 2 and 3) in preparation for the final deposition of copper. The electroless process is illustrated in Fig. 7. These chemical reactions contribute to the copper coating that cenosphere particles acquire.

Activation and sensitization stage:

$$Sn^{2+} + Pd^{2+} \rightarrow Sn4+ + Pd^0 \quad (1)$$

Coating stage:

$$HCHO + OH^- \rightarrow H_2 + HCOO^- \quad (2)$$

$$Cu^{2+} + 2HCOO^- + 3H_2 \rightarrow Cu + 2HCHO + 2H_2O \quad (3)$$

Overall reaction:

$$Cu^{2+} + H_2 + 2OH^- \rightarrow Cu + 2H_2O \quad (4)$$

The study was aimed to find a more affordable alternative to the expensive activator Palladium chloride. To do this, the researchers conducted the same experiment using cost-effective chemical activators such as $AgNO_3$. The results showed that the deposition characteristics were not affected by the use of these alternative activators (Shukla *et al.* 2002). The utilization of hazardous compounds such as Sn and valuable metals such as Pd, as well as the excessive number of stages required in the coating procedure, continue to pose significant challenges in the process of commercialization. Subsequent research has concentrated on employing just the activation process using $[Ag(NH_3)_2]^+$ as an activator, without the inclusion of any traditional sensitization processes. The electroless approach was used to change the Ni-Co-P coating of cenosphere particles (Aixiang *et al.* 2005a), whereas Ni-P coating was achieved by coating Ni-P on FAC particles (Aixiang *et al.* 2005b). The cenosphere is coated with electroless Ni-Fe-P alloy films using a cost-effective two-step technique. This process involves the use of γ-amino propyltriethoxy silane (APS) as a coupling agent and $AgNO_3$ as an activator (Pang *et al.* 2012). The use of $AgNO_3$ leads to an increase in manufacturing costs. Therefore, $CuSO_4$ was initially described as an activator to apply a coating of Ni-P on cenosphere particles using the electroless technique (Zeng *et al.* 2012). Copper-coated ferrite-activated carbon (FAC) and nickel-phosphorus-coated FAC may be used as low-density fillers in the metal matrix. These fillers can function as conducting polymers for radar-absorbing material, electromagnetic interference (EMI) shielding, and microwave absorption (Aixiang *et al.* 2005a; Cao *et al.* 2015).

3.2 Magnetron Sputtering Method

The procedure necessitates the use of custom-made equipment that includes the capability of ultrasonication. Physical vapor deposition is a process, sometimes called vacuum coating technology that enables the deposition of various substrates, which include ceramics and metals, utilizing a magnetic field supplied to a diode sputtering target (Yu *et al.* 2009). The metal precursor is subjected to ion bombardment using inert gasses to induce firing. The collision of these highly charged ions with the metal precursor causes the expulsion of metal atoms into outer space. Ultimately, the expelled metal atoms settle into the substrate material, creating a thin coating on the surface of fly ash cenosphere (Shishkin *et al.* 2018). Researchers have examined the application of the pulse and spark magnetron sputtering technique to produce TiO_2, copper, and nickel coatings on FAC particles (Yu *et al.* 2009; Shishkin *et al.* 2018). The deposition rate is higher at reduced pressures in comparison to other approaches; however, the utilization of a specifically constructed apparatus increases the expense of the process in comparison to alternative methods (Aixiang *et al.* 2005a).

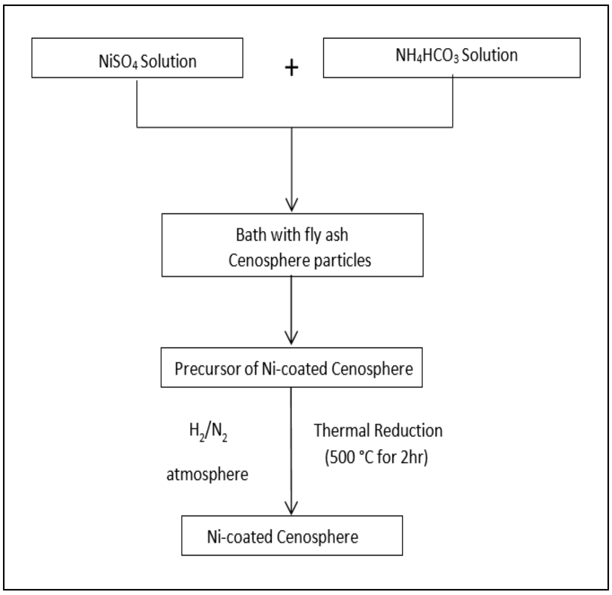

Fig. 8: Process for Heterogeneous Nickel coating on cenosphere

3.3 Heterogeneous Precipitation Method

To create a metal coating on an FAC, a metal precursor can be utilized together with a chemical that enhances the formation of precipitates. Meng *et al.* (2010) conducted the first experiment to apply a nickel-metal coating on the surface of cenospheres using the heterogeneous precipitation approach (Meng *et al.* 2010). Fig. 8 provides a concise summary of the procedure for depositing metal onto cenospheres. The chemical reaction occurring on the surface of the cenosphere is denoted as reaction (5):

$$3Ni(NO_3)_2 + 6NH_4HCO_3 + H_2O \rightarrow NiCO_3.2Ni(OH)_2.2H_2O \downarrow + 6NH_4NO_3 + 5CO_2 \uparrow \quad (5)$$

The process involved coating nickel metal onto FAC particles, followed by coating binary alloys of metals (Fe-Ni, Fe-Co, γ-Fe-Ni, Ni-Co) using a heterogeneous precipitation approach. This was then followed by thermal reduction at certain pressures and temperature (Meng *et al.* 2010; Li *et al.* 2010).

3.4 Sol-Gel Method

The sol-gel method is a wet chemical procedure that is commonly utilized in the fabrication of glass and ceramic materials. To generate a gel network with distinct particles, monomers must be transformed into a solution known as a precursor solution. In particular, the sol-gel technique is used to treat the oxides of SiO_2 and TiO_2. Surolia *et al.* (2010) created a TiO_2-coated cenosphere as a photocatalyst for the photocatalytic degradation of methylene blue dye (Surolia *et al.* 2010). Titanium tetra isopropoxide, or metal oxide, was selected as the source of titanium for the investigation and dissolved in ethanol to produce the solution precursor mentioned previously. To create a colloid, the proper amount of cenosphere was added and hydrolyzed under carefully regulated circumstances. These colloids are strong enough to generate significant flocculation and aggregation before they expand when acid is present (Lu *et al.* 2013). Subsequently, the solvent was evaporated, dried, and then calcined to produce fine particles coated with TiO_2-cenosphere.

TiO_2 has a higher photocatalytic activity, although it usually suspends or sinks in the solution, reducing the pace at which it uses light. The low-density fly ash cenosphere's special hollow structure allows it to float on the water's surface, where it is used as a carrier and support to create a floating photocatalyst. TiO_2-covered cenospheres are therefore extensively researched in visible light. The literature reports using catalyst sensitizers such as cobalt sulfophthalocyanine, and H_2O_2 to further improve their activity (Huo *et al.* 2009; Huo *et al.* 2010). An inexpensive, low-temperature sol-gel process is used to produce TiO_2 coatings on FAC.

3.5 Plasma Spray Method

The plasma spray technique is a high-temperature method that involves spraying powdered material that has been melted or heated quickly at a high speed onto the substrate surface that has to be coated. The substrate material is strongly impacted by the hot substance, which quickly cools to produce a coating layer. A similar procedure was used in a research study to investigate the deposition of Cr_3C_2-NiCr on MDN 321 steel with and without cenosphere coatings (Mathapati *et al.* 2018). Table 1 displays the characteristics of the plasma spray technique.

Table 1. Process parameters for plasma spray method

Operating Parameter	Value
Plasma gas (Ar + H_2)	0.75 MPa pressure, 40 lpm flow rate
Current	490 A
Powder carrier gas (Ar)	0.35 MPa pressure, 7 lpm flow rate
Powder feed rate	60 gm/min
Voltage	60 V
Stand of distance	100-125 mm

3.6 Fluidized Bed Reactor Process

The production of copper-coated cenospheres involves the following consecutive procedures. Initially, cenospheres undergo a process of washing with distilled water and are subsequently dried in a temperature-controlled oven at 110 °C for 24 h. This procedure effectively eliminates any volatile substances and contaminants present. The cenosphere possesses a porous structure created by the inclusion of gas in it and is coated with a nanoscale film made of glass-crystalline material. Perforated cenospheres with minuscule holes that penetrate through the shell can be created by eliminating the thin layer. Therefore, the subsequent action involves perforating cenospheres by introducing a certain quantity of hydrofluoric acid to the mixture of distilled water and cenosphere, and then adding a solution of metal sulfate (such as $CuSO_4$) while gradually pouring in an ammonia solution. Ammonia facilitates the formation of a precipitate consisting of copper hydroxide, a metal hydroxide. The precipitate can be separated by filtration, rinsed with distilled water, and dehydrated in a vacuum oven to produce the copper oxide-fly ash cenosphere precursor (CuO-FAC). The copper-coated cenosphere can be obtained by reducing oxide-coated particles using nitrogen and hydrogen in a fluidized bed reactor (Wadatkar *et al.* 2020). The following chemical reactions are provided to facilitate comprehension of the process:

Oxidation:

$$CuSO4 + NH_4OH \rightarrow Cu(OH)_2 \downarrow + (NH_4)_2SO_4 \quad (6)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \quad (7)$$

Reduction:

$$CuO + H_2 \rightarrow Cu + H_2O \quad (8)$$

Fluidized bed reactors can be used to deposit metals such as copper, iron, and nickel on particles of the cenosphere in H_2/N_2 atmosphere and controlled conditions.

4. APPLICATIONS OF FLY ASH CENOSPHERE

Cenospheric materials are frequently included into concrete to create lightweight composites, which is one of their principal uses. A large amount of cenosphere can lead to a major reduction in the density of the concrete. However, it can also increase the viscosity of the mixture, reduce the mechanical properties, and constrain the permeability of solid composites (Huo *et al.* 2010; Meng *et al.* 2012; Cao *et al.* 2015). Unlike regular concrete, the reduction in mechanical properties affects failure modes and modifies the overall performance of the material. Thus, it is crucial to consider this carefully (Jha *et al.* 2011).

Since cenospheres are employed as a nearly inert material, improving the mechanical performance of the composite depends on the strength of the cenosphere particles themselves as well as the interfacial bonding and binder strength of the binder/cenosphere surface.

To enhance the total mechanical performance of the composite, it is necessary to enhance the strength of the binder, which will help minimize internal stresses. The favorable aspect of cenospheres lies in their spherical form, which leads to minimal surface area-to-volume ratios. Consequently, this reduces the amount of water required to wet the surface and enhances workability. Consequently, reducing the water/cement ratio leads to an increase in the durability of the binder (Lu *et al.* 2013).

However, the incorporation of cenospheres into a cement matrix results in the formation of a hollow spherical structure. Consequently, the application of a compressive force to this composite generates axial splitting microcracks that align with the direction of the compression. As a result of the intense deviatoric stress, the primary factor is the expansion of volume due to inelastic dilatancy (Fu *et al.* 2007). Due to the smaller cross-section of the hollow sphere, this results in a transverse tensile stress that grows microcracks in the direction of the compression force, which in turn generates local fractures (Surolia *et al.* 2010). In addition, it is known that for cementitious materials, once exposed to a bending stress, Mode I fractures are lesser than Modes II or III fractures. The incorporation of cenospheres in the composite specimen reduces its effective cross-section and leads to the concentration of stress at the binder region, hence worsening this weakness. Consequently, the composite material fails if the binder fractures due to the external force being applied (Lu *et al.* 2013). The poor connection between the binder and cenospheres, along with the low roughness of the cenospheres, leads to an almost hydrophobic surface and reduces binder adhesion.

Several pre-treatment procedures have been devised to enhance the surface reactivity of cenospheres. Enhancing the chemical interaction between Ca^{2+} and

Mg2+ cations from Portland cement was achievable by applying a layer of reactive silanol groups on the surface through ion exchange processes. Cenospheric mixtures with hot, diluted HCl is another pre-treatment technique. Comparing this method to non-treated systems, it was possible to enhance the composite's compressive strength by up to 2.4. The interfacial strength that exists between the binder and the cenospheres can be enhanced by using surface modifiers such as silica fume and silane. A cenosphere concrete's compressive strength could be raised to 80% by simply adding silica fume, while its tensile strength, flexural strength, and fracture toughness could all be increased by 35%, 60%, and 41%, respectively, by simply adding silica fume. Similarly, it has been noted that including nano silica into a cement matrix for cenospheres enhances the interaction between the cenosphere shell and the binder, despite the ultimate closure of pores due to hydration products (Huo *et al.* 2009; Li *et al.* 2010). The impact of curing temperature on cement/ cenospheric mixtures has also been the subject of recent research (Wang *et al.* 2015). The study has shown that raising the curing temperature from ambient temperature to 75 °C accelerates the chemical interaction between cenospheres and portlandite, leading to an increase in hydration products and enhanced interfacial contacts.

4.1 Applications in Electromagnetic Interference Shielding

Electromagnetic interference, caused by radiofrequency and microwaves from electronic devices, can be reduced through shaping loading, distributed loading, active loading, and passive loading. Microwave absorbing materials, such as epoxy, polyurethane, foams, polyaniline, and polyethylene terephthalate, rubbers have been developed to improve electromagnetic shielding. These materials should have a wide bandwidth, be lightweight, and be economical. Hollow microsphere and core-building cenosphere-based frameworks are attractive for lightweight broadband microwave retention. Flexible Microwave Absorbing Materials (MAMs) can be used as sandwich layers or blended with paint to reduce RCS (Xu *et al.* 2011).

PVB (Polyvinyl butyral) is used in many interesting practical applications, such as organic hardware, because of its straightforward wettability and resemblance to several other polymer groups, such as phenolics, isocyanates, and epoxies. When combined with the proper fillers for microwave retaining applications, it may also be used as a follower coating on metal surfaces. For a variety of uses, the fly ash cenosphere (FAC) is an enticing filler (Vassilev *et al.* 2004; Fomenko *et al.* 2015). FAC is an empty microsphere that weighs between 0.6 and 0.8 g/cc and is mostly composed of silica and alumina (Anshits *et al.* 2005). Because of its unique combination of characteristics, such as its low explicit gravity, excellent thermal durability, circular form, acoustical insulation, high pressure, and inactivity toward soluble bases and acids, FAC is used in a variety of industrial applications. Because of its appealing qualities, FAC is a great option for producing lightweight and practical composites (Vassilev *et al.* 2004; Ngu *et al.* 2007). Studies indicate that FAC containing PVB is beneficial for dielectrics and device epitome applications (especially natural hardware) (Chalivendra *et al.* 2003; Tiwari *et al.* 2015).

Coatings are often used to supply center shell-type composites since FAC is inactive (Meng *et al.* 2010). Meng *et al.* (2010) conducted a study to examine the impact of Ni coatings on hollow glass microspheres. The study focused on microspheres with different volume proportions and coating thicknesses ranging from 100 to 250 nm. Upon analysis, it was discovered that when the barrier had a transmission capacity of 2 GHz and a thickness of 2 mm, it experienced a reflection loss of 35 dB. Kim *et al.* (2019) applied a coating of Ni, Co, and Ni-Fe over fly ash cenospheres with a diameter of 50 µm. Their findings suggest that under comparable test settings, the Ni-Fe coated cenosphere exhibits preferential impedance coordination over the Ni and Co coated ones, where the Ni thickness was in the range of a few microns (Xu *et al.* 2013; Kim *et al.* 2019).

4.2 Applications in Dye Removal

Industrial wastewater including a wide range of colors and dyes is one of the biggest global issues. Because color pollutants can induce cancer and mutate human DNA, disposing of wastewater in natural water bodies is extremely harmful to amphibians, the environment, and human health in particular. The utilization of FAC has demonstrated its efficacy as an efficient adsorbent for the elimination of dyes from industrial wastewater, as well as its potential as a precursor for the synthesis of mesoporous and nano-sized adsorbents. A few researches demonstrate the potential use of fly ash cenospheres for the surface-adsorption mechanism-based removal of artificially produced colors and toxic mixtures from aqueous solutions.

To remove dyes and colors from the wastewater, researchers looked at the adsorbent productivity of coagulants (ferrous sulfate, alum, and ferric chloride) combined with fly ash. The degradation efficiencies of ferrous sulfate, alum, ferric chloride, and fly ash cenosphere were, respectively, 57%, 20%, 63%, and 58%; however, the cross-breed cycle degradation limit of alum-FAC, ferrous sulfate-FAC, and ferric chloride-cenosphere had also significantly expanded, eliminating the toxins up to 73%, 60%, and 68%, separately (Tiwari *et al.* 2015). Lu *et al.* (2013) produced mesoporous Al-MCM-41 by using FAC as a support, and then used it to remove Methylene Blue (MB) from aqueous solutions (Lu *et al.* 2013). The maximum adsorbent uptake at pH 10 was achieved in 2 h at 277.78 mg/g. The pseudosecond-order kinetic and Langmuir isotherm models provided a good match to the trial experimental data, demonstrating a monolayer chemisorption.

Furthermore, thermodynamic studies confirmed the unrestricted and exothermic entropy-decrease characteristics of MB adsorption. A distinct type of FAC-based nano-zeolite photocatalyst (Fe_2O_3-Na-X) was responsible for the photocatalytic destruction of MB. For MB at pH 6.9, the Fe_2O_3-Na-X photocatalyst demonstrated a 90.53% degrading efficiency in under three hours (Kolay *et al.* 2014). A consistent Ag-doped ZnO/CFA nanocomposite was used to achieve the amazing photocatalytic destruction of MB (around 98%) (Kim *et al.* 2019). According to Song *et al.* (2017) assessment, the depolarization of MB using the CeO_2/FACs photocatalyst obtained 60% degradation efficiency in 5 h (Song *et al.* 2017). Fe_2O_3-TiO_2/FAC composite was used in a different experiment to photocatalytically oxidize MB. In one hour in visible light, the highest efficiency was recorded at 86.81%. Wang *et al.* (2015) also used FAC/TiO_2 nanofiber to conduct the MB decay. After a duration of two hours, it could be observed that the photocatalyst that had been created successfully eliminated all traces of MB from the aqueous solutions. Two kinds of CFA composites, hydrous zirconia/zeolite, and hydrous iron oxide/zeolite, were used for MB adsorption. At pH 7, the two composites demonstrated an amazing adsorption productivity of around 100%. The hydrothermally modified FAC effectively removed MB from watery arrangements with 90% adsorption productivity (Visa and Chelaru, 2014). An analogous analysis was conducted with hydroxy sodalite that was blended from CFA. The highest adsorption effectiveness for MB, reaching 94%, was found at a pH of 5 (Mushtaq *et al.* 2019).

4.3 Applications in Ceramic Industry

Calculable amounts of SiO_2, Al_2O_3, CaO, and Fe_2O_3 are present in the fly ash cenosphere, among other oxides. These oxides are frequently thought of as an inexpensive resource for the clay industry. Moreover, the small particle size of the powder structure allows for easy consolidation into ceramic pastes with minimum preparation, making it highly appropriate for direct incorporation (Lu *et al.* 2013). Recent studies have focused on the creation of glass ceramic, sintered materials, and glass using coal fly ash cenosphere. The basic idea behind manufacturing is that the fly ash is heated to varying degrees, and co-reagents control how the glass or ceramic turns out in the end. Li_2O–Al_2O_3–SiO_2 ternary glass-ceramic materials have important industrial applications owing to their low or negative coefficient of thermal expansion (CTE); however, since these materials are often made using premium chemicals, the finished product is expensive. $Li_2Al_2Si_3O_{10}$ was arranged by using FAC as the raw material; comparing the calculated CTE value to commercial lithium glass ceramics, it was around 18% lower. $Li_2Al_2Si_3O_{10}$ was also produced in the subsequent investigation using FAC as a precursor.

The final product had tiny grains and was well-crystallized (Pang *et al.* 2012; Shishkin *et al.* 2018). The utilization of FAC and fly ash in asphalt and highway construction applications has demonstrated significant advantages. When used for base course and subgrade correction, the solidity was on par with or more pronounced than lime rock. In addition to joining in solid development, geotechnical applications also use FAC. A study conducted and examined the potential of pozzolanic FAC as a pressure-driven barrier in landfills. This investigation demonstrated that FAC did not split because of its minimal shrinkage. The volume of compacted fly detritus barely changed. Moreover, Yilmaz (2004) said that the addition of bentonite and elastic to FAC showed assurance for the creation of liners (Mushtaq *et al.* 2019).

5. CONCLUSION

One notable component of fly ash waste that ought to be separated rather than dumped in a landfill is the cenosphere. Due to their unique attributes, including their low bulk density, chemical inertness, high mechanical strength, high insulation, synthetic latency, and hollow nature, fly ash cenospheres are widely utilized in many different sectors, including the medical field, oil dwelling, composites, and dye degradation. Thus, fly ash cenosphere may be used in both field and lab studies. Fly ash cenosphere is the subject of investigation, which combines it with various inorganic and organic amendments to improve soil and develop biosensor applications; better techniques and methodologies need to be developed to segregate the cenosphere from fly ash, as fly ash generation is increasing exponentially.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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