Review

Pulp and Paper Mill Fly Ash: A Review

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Abstract: The continual growth of pulp and paper industry has led to the generation of tremendous volumes of fly ash as byproducts of biomass combustion processes. Commonly, a major part of it is landfilled; however, updated environmental regulations have tended to restrict the landfilling of fly ash due to rising disposal costs and the scarcity of suitable land. The pulp and paper industries are therefore urgently seeking energy-efficient mechanisms and management for the beneficial use of fly ash in an ecological and economical manner. This paper offers a comprehensive review of existing knowledge on the major physicochemical and toxicological properties of pulp and paper mill fly ash to assess its suitability for various bound and unbound applications. The current state of various methods used for the valorization of pulp and paper mill fly ash into more sustainable geomaterials is briefly discussed. This paper also presents promising and innovative applications for pulp and paper mill fly ash, with particular reference to agriculture and forestry, the construction and geotechnical industries, and the immobilization of contaminants. It was identified from a literature review that modified pulp and paper mill fly ash can be environmentally and economically advantageous over commercial coal-based fly ash in various sustainable applications.

Keywords: pulp and paper mill; fly ash; valorization; geopolymer; agriculture; construction; geotechnics; environment; sustainability

1. Introduction

The pulp and paper industry is one of the most important and profitable industries in Canada and is a growing portion of the global economy. Although there is worldwide shrinking in the graphic paper market due to digitization, there is overall continual growth in the pulp and paper industry because of the increasing market demand for several other applications, such as cardboard and packaging paper, tissue paper, pulp for personal hygiene products, and textile applications. Moreover, the generation rates of different types of wood ash, as byproducts of the biomass combustion process, have substantially increased [1]. Canada produces more than 1 million tons per year of wood ash, based on total contributions from pulp and paper mills and wood/forest biomass ashes [2]. Currently, pulp and paper mill fly ash (PPFA) is often treated as a nonhazardous commercial waste product and is landfilled at a cost to producers and to society at large. However, landfilling will tend to be reduced or banned in the future due to stringent environmental regulations, rising disposal costs, and the scarcity of landfill space [3–7].

With significantly increasing production rates of ash, the pulp and paper industries are intensely seeking energy-efficient mechanisms for ecological and economical ash management. A better alternative to landfilling could be recycling and reusing sludge and ash through composting. A stabilized compost has several advantages, such as reduced mass and odor, the degradation of toxic compounds, decreased nitrogen immobilization, and high nutrient contents for soil conditioning [3,8,9]. However, the costs for site preparation and equipment, lengthy treatment periods, targeting the final

use of compost products, etc., are drawbacks of composting [10]. Contaminant-free PPFA has great significance as a soil liming agent and fertilizer in agriculture and forestry [6,11]; however, its direct application requires safety precautions due to its undesirable handling and spreading characteristics and associated health risks [12,13]. Further, high pH and electrical conductivity values of pore water in wood ash might have perturbing effects on the microbial community [14]. In order to withstand extreme conditions, the bacteria may enter a dormant stage, thereby decreasing the microbial population and diversity and ultimately disturbing the ecological balance. PPFA and value-added materials also have multifunctional engineering applications, such as supplementary cementitious material (SCM) in concrete systems, aggregate in pavement construction, binder for soil stabilization, and adsorbent for the immobilization of toxic heavy metals [15–23]. Based on a statistical survey conducted on the management and utilization of boiler ashes generated at Canadian pulp and paper mills, it was reported that more than 50% of ash is landfilled, 20–25% is used as a soil amendment (direct application or compost), and less than 20% is used for other beneficial applications such as the construction of embankment fills, the stabilization of pavement layers, and the solidification of wastes. [1,2].

This paper reviews the existing knowledge on physicochemical and toxicological properties of PPFA in order to assess its suitability as a sustainable geomaterial for various bound and unbound applications. The bound applications of fly ash include its use as an ingredient for manufacturing concrete, blocks, bricks, glass ceramics, rammed earth, etc. Likewise, the unbound applications of fly ash refer to its use as fill material for embankment construction, as binder for the stabilization of pavement layers, and as a soil amendment in agricultural and forest land, etc. The current state of developing value-added geomaterial from PPFA and its prospective applications in various fields are briefly discussed. This paper also aims to specify beneficial areas that can significantly contribute to the maximum utilization of PPFA, such as agriculture and forestry, construction and geotechnical engineering, and the remediation of a contaminated environment. The findings of the study are expected to assist in the formulation of strategies for sustaining and improving the utilization of PPFA.

2. Solid Waste Generation and Management in Pulp and Paper Mills

The production rates of solid wastes and sludge in pulp and paper mills as well as their properties are significantly influenced by pulp manufacturing processes and wastewater treatment technologies [24,25]. Commercial pulping operations are generally categorized as chemical and mechanical, among which the chemical process accounts for the maximum wood pulp production [25]. Kraft pulping is a lignocellulose process for pulp manufacturing, and it is dominant over other chemical pulping processes (viz. the soda process, the sulfite process) [26]. The main advantages of kraft pulp are superior strength, greater resistance to aging, and being easy to bleach: moreover, the kraft process can handle diverse softwood and hardwood species and has high chemical recovery efficiency [27]. Other than dedicated wood species, the biomass resources for the pulp and paper industry also include selected grass plants, sugar and oil crops, agricultural residues, residues from food and paper industries, municipal green wastes, sewage and de-inking sludge, organic wastes and residues, etc. [26]. Further, fluidized bed combustion (FBC) is the most recommended commercial combustion technology, and it works particularly well with wet sludge (produced by de-inking mills). This technology greatly improves the combustion process and also produces fewer sulfur dioxide and nitrous oxide emissions than conventional hog boilers do [28]. Although the boiler units have standard designs and operating conditions, variations in combustion conditions (viz. temperature and pressure) can occur for each boiler unit during operation.

The primary sludge (including dregs, grit, lime mud, and ash) is generated at different stages of the pulping process [26,28]. The ash components (viz. bottom ash and fly ash) are generated during high-temperature combustion of hog fuel in power boiler units. During the combustion process, the volatile matter and impurities in the wood burn off [29]. These fused particles are carried upwards along with the flue gas. As the flue gas approaches the low-temperature zones, the fused substances solidify to form fly ash, which is captured by bag filters, a flue gas desulphurization unit,

and electrostatic precipitators. The remaining combustion residue, which agglomerates and settles down at the bottom of the furnace, is called bottom ash (or boiler ash). The fly ash consists of fine particulates and precipitated volatiles, typically with a high specific surface area, whereas bottom ashes tend to be coarser in texture [25].

The digester uses white liquor (NaOH and Na_2S) to digest wood chips into pulp. The pulp (fibers) is separated from the black liquor (lignin and spent chemicals) by washing. The black liquor is evaporated and combusted in the recovery boiler to obtain smelt, a molten mix of different salts (enriched with NaCl and KCl) remaining after the decomposition of lignin [27]. The smelt is dissolved to generate green liquor (Na_2S and Na_2CO_3), which is passed through clarifiers/filters, the collection point of dregs. The grit is separated in a series of slakers/causticizing plants in which green liquor is mixed with lime to regenerate white liquor along with the production of lime mud. The white liquor is passed through filters and is reused in the digestion process for pulping. The lime mud is calcined in the lime kiln to regenerate quick lime to be used in the causticizing plants [28].

More than 35% of the wood chips entering a pulp mill becomes residue, mainly in the form of sludge and reject material [30]. The primary sludge generated in the pulp mills is commonly landfilled at the source point itself, while the dry sludge is sometimes reused to fuel the boilers [6]. The liquid waste undergoes primary treatment in sedimentation tanks to remove suspended solids. The secondary biological treatment mostly uses activated sludge and aerated lagoons to degrade the suspended solids using microbial activity [31]. After treatment, the water samples are tested in a laboratory to meet effluent permit regulations.

3. Major Properties of Pulp and Paper Mill Fly Ash

A better knowledge of the physicochemical, mineralogical, and leachate characteristics of PPFA and value-added geomaterials is essential for their eco-efficient utilization. These properties play a substantial role in accurately determining the quantity of the material required for achieving the desired or maximum improvement in the specific fields of application. The type of combusted fuel, the combustion technology used, combustion conditions, etc., have significant impact on the properties of PPFA and its further utilization [32,33]. The following subsections summarize the important properties of PPFA that have been reported in relevant literature.

3.1. Physical Properties

PPFA is the lightest component of solid residues generated during wood combustion, and its specific gravity ranges from 2.4 to 2.8 [34,35]. The bulk density ranges from 150 to 1300 kg/m^3, with an average value of 500 kg/m^3. The density decreases with increasing carbon content [34]. The particle size varies considerably and is largely dependent on the degree of biomass combustion. The average particle size is 150 to 250 μm, which closely matches high-calcium coal fly ash [35,36]. As shown in Figure 1, different PPFA samples have wide particle size distributions ranging from 1 to 10,000 μm [33,34,36,37]. The surface area is in the range of 4200 to 100,600 m^2/kg, which is more than 200 times that of class C coal fly ash [35,37,38]. The high surface area of PPFA is attributed to particle fineness, the high irregularity of particle shapes, and its more porous nature [39]. These properties also lead to increased adsorption properties as well as higher rates of leaching [35,39]. PPFA has a high moisture holding capacity due to its hydrophilic nature, and the particles also tend to agglomerate [16].
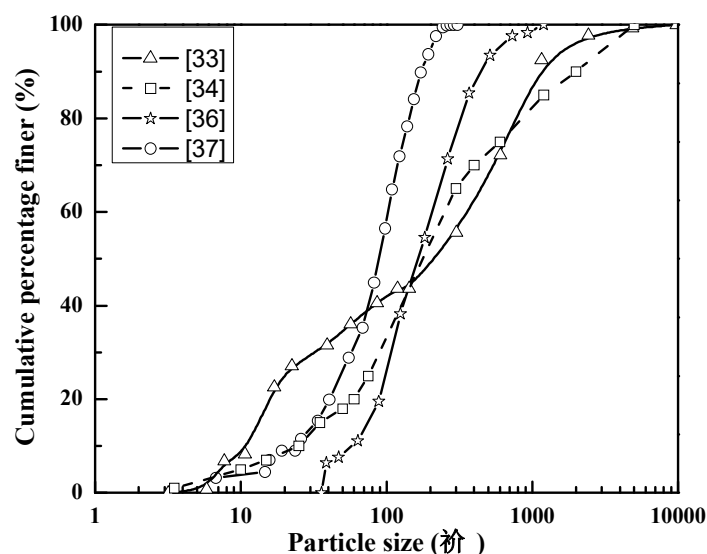
Figure 1. Particle size distribution of pulp and paper mill fly ash (PPFA).

3.2. Chemical Properties

The key determinants of PPFA chemistry are the wood species combusted, the nature of the combustion process, and the conditions at the application site [16]. The combustion temperature largely affects the chemical properties and quantity of ash produced. The amount of organic matter and heavy metal contents in the ash are also associated with the combustion temperature [6,15]. Due to the oxidation of carbon and nitrogen compounds during the combustion process, which form gaseous compounds, their quantity in PPFA is generally low [32]. The occasional presence of charcoal in PPFA can lead to the overestimation of organic carbon; however, it does not necessarily contribute to the nutrient contents [40,41]. The total carbon content of PPFA is associated with the combustion of inorganic carbonate species and free organic carbon, and it is generally indicated in terms of loss on ignition (LOI). LOI estimates the amount of carbon remaining in the ash; however, mass loss during ignition can also be contributed by sulfur, sodium, potassium, etc., to some extent [42]. The average LOI of PPFA is 20% to 30%, and the value ranges between 5% and 60% depending on the wood type and combustion conditions [33,43,44].

According to elemental composition analysis, PPFA predominantly consists of silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). Other metal oxides such as CaO, MgO, K_2O, Na_2O, TiO_2, and SO_3 are available in variable quantities. Scheepers and du Toit [6] stated that the amount of calcium in PPFA can significantly vary depending on the different source materials, and it can also be the most abundant element present. For instance, fly ash derived from coniferous trees has higher Si and Ca content compared to hardwood species and relatively low K and S content. Further, the concentrations of K, Na, and carbonate (CO_3^{2-}) decrease at higher combustion temperatures, whereas other metal ion concentrations increase or remain constant [15,16,45]. A determination of total elemental composition is essential, as it provides insight into the leaching characteristics of fly ash [33]. Table 1 presents the amount of different metal oxides detected in PPFA during X-ray fluorescence (XRF) analysis, as reported in relevant literature.

The average pH value of PPFA is reported to be 11, and the range spans between 8 and 13 in the majority of the literature [32,46,47]. Ash containing high calcium oxide in it shows high pH values of 12 and above. The high alkalinity primarily arises from the addition of lime as a causticizing material in the pulping process [47]. However, the presence of sulfates in PPFA can sometimes cause an initial acidic pH, also called a masking effect [48]. It also exhibits a high pH buffering (acid neutralizing) capacity and hence induces a liming effect [15,32].

Table 1. Summary of the typical oxide compositions of PPFA.

Reference	Composition of Major and Minor Oxides (%)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	MnO	P_2O_5
Muse and Mitchell [11]	N/P	1.25	0.63	12.0	0.77	0.14	1.33	N/P	N/P	N/P	N/P
Pitman [16]	N/P	9.1	5.1	1.66	0.11	0.01	0.26	N/P	20	N/P	N/P
Naik et al. [33]	26.5	9.0	5.4	16.0	3.0	1.7	5.0	0.51	4.8	N/P	N/P
Vassilev et al. [42]	31.6	13.2	5.12	28.9	5.4	1.42	13.2	N/P	2.67	2.77	2.64
Serafimova et al. [44]	N/P	N/P	N/P	52	1.32	N/P	2.39	N/P	N/P	N/P	0.72
Ohno and Eric [49]	N/P	8.21	1.43	9.49	0.65	0.67	1.03	N/P	N/P	N/P	N/P
Abdullahi [50]	31.8	28	2.34	10.53	9.32	6.5	10.38	N/P	N/P	N/P	N/P
Chowdhury et al. [51]	50.7	8.2	2.1	19.6	6.5	2.1	2.8	N/P	N/P	N/P	N/P
Johakimu et al. [52]	0.68–52.78	0.12–28.3	0.37–3.69	1.59–4.88	0.35–83.58	N/P	0.43–1.97	0.01–1.68	4.23–62.62	N/P	N/P

N/P, not provided.

3.3. Morphological and Mineralogical Properties

PPFA has a heterogeneous mixture of particles of varying sizes and shapes [33,34,53]. Figure 2 depicts the scanning electron microscope (SEM) images of a PPFA sample procured from a pulp mill based in British Columbia, Canada. The images, which were captured using a Tescan Mira 3 XMU SEM, reveal irregular and angularly shaped inorganic particles with thin layers of crystalline structures. These irregular particles are essentially hydrophilic in nature and absorb water into their pores through capillary action simultaneous to the hydration of oxides [15,34,36]. There are many agglomerated particles and a few spherical particles as well. Some particles have a porous cellular form: they are the remains of unburned or partially burned wood [33].
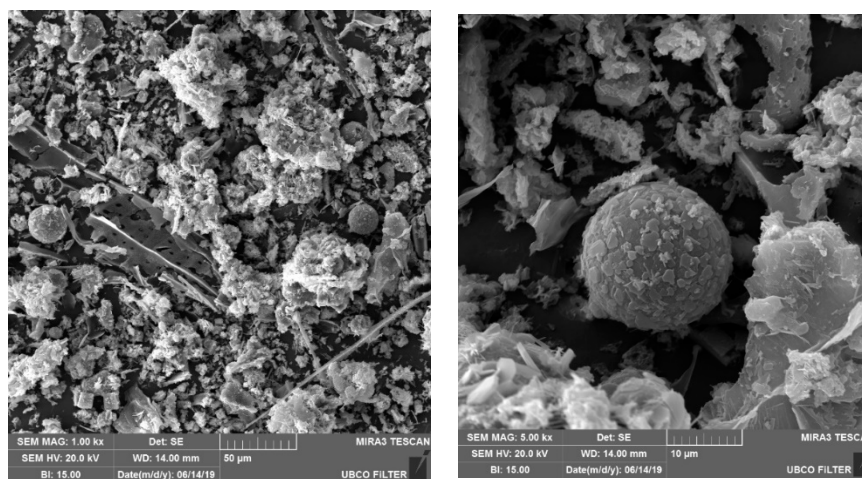
Figure 2. PPFA particles observed with SEM at 50 μm and 10 μm.

PPFA constitutes amorphous glassy material composed predominantly of silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3). The several crystalline phases, including quartz (SiO_2), calcite ($CaCO_3$), lime (CaO), portlandite ($Ca(OH)_2$), tricalcium silicate (Ca_3SiO_5), and tricalcium aluminate ($Ca_3Al_2O_6$), might be present in varying amounts [16,33,44]. The amorphous components (SiO_2, Al_2O_3, and Fe_2O_3), crystalline calcium oxide, and sulfates are major contributors to the mechanical and cementation properties of PPFA. Hence, high calcite and aluminosilicate contents make it suitable as a cement replacement material in the construction industry and as an aggregate or binder in road construction. However, a high sulfate content is undesirable for concrete applications, as it can lead to the formation of ettringite crystals, resulting in expansion cracking [16,54].

3.4. Leachate Characteristics

A determination of the toxicity of PPFA in terms of leachate characteristics is important for assessing the possible environmental impacts associated with its utilization. The environmental protection agency recommends regularly testing the environmental compatibility of fly ash when it is used as a geomaterial in real-life applications such as construction and geotechnical projects. In the past, several studies have been carried out to evaluate the leachate characteristics of a wide variety of fly ashes from different sources [15,23,39,55–60].

3.4.1. Trace Metal Concentrations

The trigger concentrations of trace metals in contaminated soils have been the guide to acceptable threshold levels of PPFA for various applications. They are categorized as cytotoxic or hazardous to human health (such as As, Cd, Cr, Pb, Hg, and Se) or phytotoxic or hazardous to plant growth (such as B, Cu, Ni, and Zn) [16]. The variability of Zn, Ni, and Cu in PPFA can pose a risk of exceeding permissible levels if it is applied in large quantities in forestry and agriculture.

Table 2 provides a summary of the leachate characteristics pertaining to wood-based ashes from different sources, as reported in the literature [11,34,44,49,56,59,60]. Wood ash is generally considered to be nonhazardous material, since heavy metal concentrations are below the permissible limits of environmental standards from, e.g., the United States Environmental Protection Agency (USEPA) [59]. Since the major and trace metals in PPFA are mainly held in the amorphous aluminosilicate matrix, they are not easily leachable [60,61]. Further, the high alkalinity of pulp mill ash also aids in the retention of metals [48]. Leaching can be further reduced by altering the physical form of PPFA through granulation or pelleting [58]. However, the leachability of different elements also depends on leaching procedures and the mobility of ions [56]. Cadmium (Cd) is the most mobile and potentially toxic metal in PPFA, followed by copper (Cu), zinc (Zn), nickel (Ni), lead (Pb), and chromium (Cr) [39].

Table 2. Summary of the typical oxide compositions of PPFA.

Reference	Concentration of Trace Elements (mg/kg)												
	As	**Ba**	**Bo**	**Cd**	**Co**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Se**	**V**	**Zn**
USEPA [59]	75	N/P	N/P	85	N/P	3000	4300	57	75	420	100	N/P	7500
Muse and Mitchell [11]	N/P	588	95	<2	14	75	67	15	16	72	N/P	N/P	183
Grau et al. [34]	N/D	N/D	0.47	N/D	N/D	0.03	N/D	N/D	N/D	N/D	N/D	N/D	N/D
Serafimova et al. [44]	11.3	N/P	N/P	1.11	N/P	23	N/P	N/P	16.1	99.7	N/P	N/P	133
Ohno and Eric [49]	N/D	549	N/D	N/D	N/D	1036	151	61	65	32	N/D	N/D	423
Zhou et al. [56]	N/D	0.13	1.41	N/D	N/P	0.05	N/P	N/D	N/D	N/D	0.03	N/P	0.67
Poykio et al. [60]	13	745	N/P	2.9	6.6	66.9	N/P	3.8	32.4	28.7	3.3	92.7	295.3

USEPA, United States Environmental Protection Agency; N/P, not provided; N/D, not detected.

3.4.2. Inorganic and Organic Compounds

The inorganic composition of PPFA is dependent on the minerals present in the fuel wood, whereas organic compounds are primarily influenced by the effectiveness of combustion and cooling [48]. Since the temperature inside the boiler during the combustion process is very high, it will break down most of the organic compounds, leaving behind a small amount of elemental carbon. As a result, the biodegradation of the pulp mill ash does not evolve any volatile phases. However, the pulp mill ash might constitute some deleterious organic compounds, such as polycyclic aromatic hydrocarbons (PAHs), resulting from the incomplete combustion of wood [1,16,48]. However, PAHs are strongly bound by ash particles and are sparingly soluble in water. As a result, the total concentration of PAHs in PPFA leachate is significantly lower than the permissible limit [48]. Similarly, phenols are another family of organic compounds present in PPFA, but mostly in very low levels below the detection limit. Phenols have a considerably shorter half-life than PAHs do, and hence they will be retained in the ash, will be released very slowly, and will be degraded in the environment [16].

PPFA might have small traces of several dioxins associated with the incomplete combustion of material containing chlorine [1,62]. It is formed due to the low chlorine content of wood combined with high combustion temperatures in boilers [6,16]. PPFA often contains higher levels of dioxins and heavy metal concentrations than bottom ash does, since the vaporized metals in the combustion process cool away from the heating zone [16].

3.5. Radioactivity

PPFA might rarely cause radiation from the concentration of natural minerals (viz. uranium, thorium, and potassium) present in wood sources. However, the literature has indicated that pulp manufacturing processes do not cause any significant increase in the radioactive composition of PPFA [1,6,16,62]. Moreover, radioactive content in PPFA has been determined to be below levels of significance. Even though it has been proven over the decades that PPFA does not represent any significant environmental risk, it is very essential to examine leachate and radioactive emissions from PPFA-based construction and materials.

4. Valorization of Pulp and Paper Mill Fly Ash

The valorization of fly ash mainly aims at transforming potentially hazardous ash into inert geomaterials with enhanced pozzolanic characteristics, fineness, and various other properties suitable for specialized applications. Geopolymerization is an established fly ash valorization technique that leads to the formation of amorphous three-dimensional aluminosilicate materials that are termed geopolymers [63,64]. The polymerized fly ash material is usually obtained through alkaline activation, treatment with certain highly alkaline solutions such as NaOH or KOH in combination with silicate compounds such as Na_2SiO_3 or K_2SiO_3 [65]. During treatment, the high hydroxyl (OH^-) concentration in the medium breaks down silica and alumina bonds, leading to the dissolution of free Si and Al. These ions react with alkaline cations (viz. Na^+ and K^+) to form intermediate products that precipitate and reorganize into more stable and ordered aluminosilicate structures. These polymeric compounds are characterized by higher particle sizes, reduced exposed surfaces, and better reactivity [66,67]. The structure and composition of geopolymers is governed by various factors such as activator concentration, synthesis temperature, curing time, and the pH of the mixture [63,68].

The high strength as well as the low energy consumption and carbon footprint of activated fly ash offer better replacement for cement in eco-efficient construction and geotechnical applications [69–72]. The fly ash can be valorized into heat-resistant geopolymers, which in turn can be used for metal surface protection in high-temperature furnaces and kilns [52]. It can also be applied in environmental technology as an immobilizer of organic and inorganic pollutants [73,74]. Fly ash-based geopolymers are used in concrete systems, as they possess excellent mechanical properties and durability in aggressive environments [75,76]. Leong et al. [68] demonstrated that soil fly ash geopolymers exhibited high compressive strength and hence could be a potential alternative to traditional clay-fired bricks. However, one major limitation of using fly ash geopolymers as ingredients in concrete is their high sensitivity to casting and curing conditions. For instance, they require high-temperature curing to achieve better strength and durability: therefore, their application can yield the best performance in precast units/elements in the construction and geotechnical industry.

The stabilization of soft and expansive subgrade soils using activated fly ash has shown significant improvement in reaction kinetics and strength gain [22,64,71,77]. The effectiveness of geopolymerized fly ash in terms of the durability properties of rammed earth was also evaluated in some recent research [65,78–81]. However, not many studies have considered developing geopolymers using PPFA as a precursor or have evaluated their suitability for various promising applications. At present, the key challenge in utilizing PPFA geopolymers as alternative binders is attaining desirable improvement in ambient curing conditions with low activator dosages. An important effort is required to develop more economically and ecologically favorable chemical catalysts for PPFA geopolymerization, considering the huge cost of activators (such as sodium silicate, Na_2SiO_3) and the hazardous nature of the

alkalis (such as sodium hydroxide, NaOH) that are commonly used. Further, a more comprehensive study is required to elucidate the chemicomineralogical and morphological evolution of geopolymer materials and treated systems during curing and thereby gain a better understanding of the key stabilization mechanisms.

5. Existing and Prospective Applications of Pulp and Paper Mill Fly Ash and Value-Added Geomaterials

As mentioned above, compounding environmental concerns and strict regulations on landfill management have driven the pulp and paper industries to pursue better alternatives for recycling and reusing the generated fly ash. A continued emphasis on sustainable development has further increased the focus on the utilization of PPFA and value-added geomaterials as cost-effective substitutes for natural components in construction and geotechnical engineering projects. The potential applications of PPFA include as geomaterial components in concrete and rammed earth construction, as soil amendments in agriculture and forestry, in the construction and stabilization of roads, in the construction of embankments and flowable fills, in material manufacturing (glass ceramics, bricks), etc. [82]. The following subsections present a brief summary of up-to-date research and prospective methods of utilizing PPFA and its value-added geomaterials in various beneficial applications.

5.1. Soil Amendments in Agriculture and Forestry

The amendment of forest soils is one of the major applications of PPFA, as it can replenish the nutrients removed during timber and biomass harvesting, counteract the effects of atmospheric deposition on soil acidity, and increase soil fertility and forest productivity [83]. Short-rotation forestry practices and whole-tree harvest systems can induce periodic or persisting nutrient deficiencies and acidify the soil. This may affect the ability of a site to sustain adequate nutrient levels over successive rotations. PPFA can be a potential forest fertilizer, as it can offset or correct some nutrient deficiencies and imbalances induced by intensively managed plantation forests [6,15,16]. Further, PPFA has highly beneficial effects in soil liming due to its pH buffering properties [1]. This is attributed to a high concentration of carbonates, hydroxides, and other calcium-containing minerals present within it [6]. However, the soil-specific (pH and buffer capacity) and ash-specific characteristics (toxic levels of leachate) should govern decisions on the application rates of PPFA [16].

The high moisture-holding capacity, nutrition value, and cementation properties of PPFA could enable its successful application in the postfire stabilization of forest soils. The PPFA treatment of burnt soils can lead to carbon and nitrogen remineralization [84]. It contains high nutrient concentrations that are released rapidly following application due to its high calcium content and pH [6]. PPFA can also reduce runoff rates, since the hydrophilic ash particles can absorb rainwater and improve the infiltration rate. It can also provide better erosion control by strongly binding and cementing soil particles, thereby improving soil aggregate stability. Physical treatment methods such as seeding and mulching can be used in combination with PPFA applications in order to obtain better results [85,86]. Chemical treatments are more effective in erosion control, whereas physical treatments provide better nutrient replenishment [87,88].

5.2. Supplementary Cementitious Material in Construction Industry

Due to the presence of reactive silicates and calcium carbonate in PPFA, it can be substituted as a supplementary cementitious material for more environmentally friendly cement/clinker manufacturing [89]. Moreover, it is useful as a partial replacement for cement and small aggregates in building concrete [90–94]. The development of alternative value-added geomaterials from PPFA for mortar/concrete manufacturing demands a comprehensive study of rheological properties and the mechanical performance of the new composite material [91]. Further, PPFA can be agglomerated through a pelletization technique and postprocessed (by sintering, autoclaving, and cold-bonding) in order to attain a desired strength for use as a light-weight aggregate for various applications in the

construction industry [18]. These aggregates can be considered for various applications such as wall panels, masonry blocks, roof insulation material, structural load-bearing elements, and permeable reactive barriers based on their obtained properties.

In recent years, rammed earth construction has become popular among environmentally conscious engineers due to its energy-efficient, eco-friendly, and sustainable approach [95–97]. Previous studies have shown that inserting fly ash into a soil blend increases the amount of amorphous material available, which enhances cementitious reactions in the presence of lime and water [98]. As a result, the inclusion of PPFA in compressed earth blocks can provide high compressive strength and water absorption properties due to the time-dependent growth and deposition of new cementitious phases [99].

5.3. Binder Components for Geotechnical Engineering Applications

Fly ash is very effective as a stabilizer for improving the engineering performance of expansive foundation soils, road subgrades and subbase layers, hydraulic layers, etc. [64,100–102]. Past studies have conducted both laboratory and field experiments to assess the performance of PPFA-stabilized roads based on technical, environmental, and economic considerations [56,103,104]. Field monitoring showed significant increases in stiffness and decreases in permeability over time, which were attributed to the hydration of ash. The self-cementitious property of PPFA arising from its high calcium and aluminosilicate contents can result in substantial improvements in the strength and volume change properties of expansive subgrades and foundation soils [20–22,105]. Due to very low permeability, PPFA-based geopolymers can also be successfully employed as hydraulic barriers, including for cover for landfills [106,107]. Further, PPFA could be used as a drainage material in a covering layer of landfills, substituting for conventionally used materials [70,101].

5.4. Raw Materials for the Material Manufacturing Industry

PPFA, which is predominantly an aluminosilicate material, can become an excellent eco-product for glass ceramics applications [108]. Fly ash is subjected to heat treatment and controlled crystallization to form phase-transformed material with superior physical and mechanical properties suitable for producing glass as a building eco-material [109,110]. Likewise, using fly ash as a raw material to produce anorthite-based ceramics is a feasible approach to reusing such waste [19]. The use of pulp mill sludge in fired bricks develops desirable compressive strength and hence can be a potential pathway to sustainable construction [111]. The high calcium carbonate and aluminosilicate content, high fineness, spherical particle shape, and high tensile strength of PPFA makes it a suitable substitute for commercial fillers used in plastic products and polymer composites [112–115]. However, the ash from large commercial sources such as pulp and paper industries as well as wood-burning power plants needs to be preprocessed and tested to meet product specifications and industry standards for its commercialization as a plastic filler [115].

5.5. Adsorbent for Remediation of Contaminated Environments

PPFA is a natural adsorbent of heavy metals, and hence it can be used as a low-cost material for heavy metal removal from municipal and industrial effluents, acid mine drainage, etc. [116–118]. The various metal oxides present in PPFA form metal hydroxides in highly alkaline conditions. These hydroxides are good adsorbents of suspended and dissolved organic pollutants such as domestic laundry wastewater [117,118]. The adsorption capacity of PPFA increases with carbon content and makes it more suitable for removing hazardous metal concentrations [118–120]. Further, fineness, surface area, porosity, and ion exchange capacity are intrinsic properties of PPFA that play a key role [74,119]. The other important parameters that affect efficiency are pH, temperature, adsorbent dosage, and contact time [121]. Ash can be pretreated by heating to high temperature (termed as calcination), to prepare a highly porous material with improved contaminant removal ability [122].

For the various aforementioned field applications, the small particle size and fine texture of PPFA pose difficulties in transportation and spreading. The direct use of PPFA in a powder form might

have the potential for health risks to operators and deleterious effects on ground vegetation, such as the risk of overliming [123]. To overcome these problems and use PPFA more effectively, granulation methods have been followed [13,124]. The granulated form also has a slower release of chemical elements, which reduces the risk of high-magnitude alkaline substances being flushed into the natural environment. Further, the geopolymerization of PPFA also minimizes handling issues to a great extent, as it forms more environmentally safe and stable compounds [67].

6. Summary

The worldwide demand for graphic paper has been declining over the past several years due to the digital transformation of society. Nonetheless, the pulp and paper industry as a whole is steadily growing at a slower pace due to increasing demand for cardboard and packaging paper, tissue paper, etc., as well as for pulp for hygiene products and textile applications. The pulping process generates large quantities of fly ash every year, and a major fraction of it still remains unutilized. Hence, it is essential to identify promising opportunities to further increase the utilization of these ashes. This paper presented a comprehensive review of up-to-date knowledge on PPFA, which will aid in formulating effective strategies for improving its application as an eco-efficient, environmentally friendly, and economic geomaterial. The favorable physicochemical, microstructural, and toxicological properties of PPFA indicate the feasibility of its valuable application for sustainable development. The valorization of PPFA by alkaline activation further enhances its engineering properties and immobilizes toxic contents. Hence, value-added PPFA can be preferable in beneficial applications in order to minimize deleterious impacts on the environment.

The high aluminosilicate and calcium concentrations in PPFA provide self-cementation properties that offer many promising applications, such as in building materials in the construction industry or as chemical binders for soil stabilization. PPFA has high acid-neutralizing properties and fast nutrient-releasing capacity, and due to this it can potentially act as a soil conditioner in agriculture and forestry applications. Due to the high sorption capacity of PPFA (attributed to its high fineness, specific surface area, and porosity characteristics), it can be used as an adsorbent for the immobilization of hazardous organic and inorganic compounds from contaminated environments. However, none of the above-discussed practical applications of this ash have been successfully commercialized, probably due to a lack of technical standards and specifications. The present study concludes that the effective implementation of PPFA enables the conservation of natural resources by reducing energy demand. It further helps to reduce carbon footprints, which result from manufacturing processes of replaced products such as cement in the construction industry. The maximum utilization of fly ash can also save valuable landfill space for other nonbeneficial waste materials.

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