

Introduction

In recent times, it has been a significant increase in global interest for the reduction in pollution to save the environment and ecosystem. Many scientists have devoted their efforts, in particular, to finding sustainable solutions for recycling hazardous industrial pollutants [1–7]. The utilization of industrial by-products as a source of raw materials in their different form is an effective approach for their recycling. Coal fly ash is a waste by-product formed from raw coal combustion in thermal power plants and different production factories. The enormous utilization of coal as an energy source in coal-fired thermal power plants results in vast volumes of waste material produced in the form of fly ash. It poses major storage and environmental pollution problems in many countries. To dispose these waste materials required special remedial techniques which causes an extra economic burden to the manufacturer. A vast quantity (750 million tonnes) of fly ash has been generated every year worldwide, and in India, 196.44 million tonnes of fly ash was generated in 2017-18 [8,9]. Major quantity of electricity in India is produced from coal-fired thermal power plants using low-grade coal, which generally contains an ash content of 30–45 wt.%. This low-grade coal combustion produces a large quantity of fly ash which is a serious concern for the green environment. The Central Electricity Authority (CEA), Government of India, reports that in the years 2019–20, approximately 226.13 MT of fly ash were produced, of which 187.81 MT is utilized [10]. The unutilized fly ash is considered a waste material that needs special treatment for dumping and it consumes

a large area of land. The utilization of fly ash is shown in **Fig. 1.1** and this figure will be increased with time due to the rapid growth of industrialization and modernization [11,12]. These complex and ample anthropogenic materials need to dispose of with proper protocol; otherwise, they can cause environmental pollution, interrupt the eco-system [11]. The use of landfills, the main option in many countries for coal fly ash waste disposal, leads to serious pollution such as air, water and land pollution, which could foster the socio-economic problems [13].

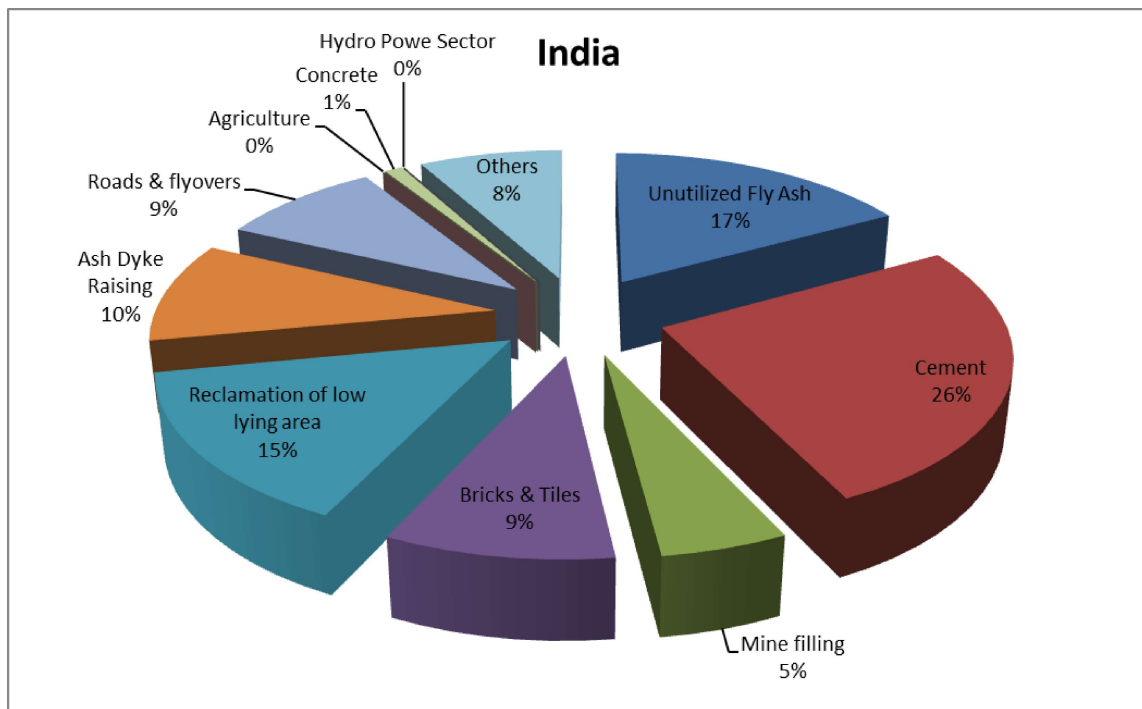


Fig. 1.1: Utilization of fly ash in India.

The environment would be benefited from the applications that make use of this waste product. Depending on the source of coal and combustion conditions, the chemical and phase compositions of fly ash are often changed their characteristics. Despite its diversity, it can be used for plant growth and contains macronutrients (P, K, Ca, and Mg) as well as micronutrients (Zn, Fe, Cu, Mn, B, and Mo) [14–16]. The

fly ash's ability to bind lime allows it to be used in cement production, concrete building materials, and other construction-related items. Fly ash has a substantial amount of silica (60-65%), alumina (25-30%), magnetite, and Fe_2O_3 (6-15%) in its chemical composition. Because of this, various authors believe it can be utilized to make zeolite, alum, and precipitated silica, ceramics tiles, glass-ceramics, cordierite, mullite [17–20]. Fly ash has been suggested as an adsorbent with the right physiochemical characteristics [21]. Fly ash can also be used to make agricultural and different technical materials. Fly ash has the potential to be employed as a low-cost material source in the glass and ceramic industries as a result of compositional varieties. Waste fly ash can be used to alleviate a significant environmental problem while simultaneously producing high-value-added commodities and conserving natural resources.

Researching the utilization of these solid wastes in order to create new or alternative uses to exploit them as raw materials for processing useful products rather than dumping them where future occupants are at risk of health problems is of economic and social relevance [22]. Akar et al. studied that fly ash can be utilized in a useful manner to treat domestic wastewater with basic methods and minimal expense adsorbents [23]. Ram et al. used fly ash for the soil amelioration [24]. González et al. reported that the fly ash can be used as a replacement for cement and other building construction application [25]. Obada Kayali et al. found that the mechanical properties of fly ash bricks are better than that of clay bricks [26]. Yao et al. prepared Li glass-ceramic from fly ash with well crystallized and small grain size [27]. He et al. reported that instead of kaolinite fly ash can be used to produce cordierite ceramics [20].

The fireclay category dominated the global market in 2020 and shown by chemical composition in **Fig. 1.2**, and is expected to increase at a CAGR of 4.7 percent over the forecast period. This is due to the fact that fireclay refractory material accounts for over 75% of total refractory material production and is an incredibly flexible and cost-effective refractory material utilized in sectors such as iron and steel, cement manufacturing, and other high-temperature operations. These factors are boosting the global refractory material market's fireclay segment's expansion [28]. Therefore, the production of fireclay bricks has been constantly increased to meet up the high demand. From the industrial point of view, the reduction in production cost is very much important. One of the ways to lower the production cost is to use the cheaper raw materials.

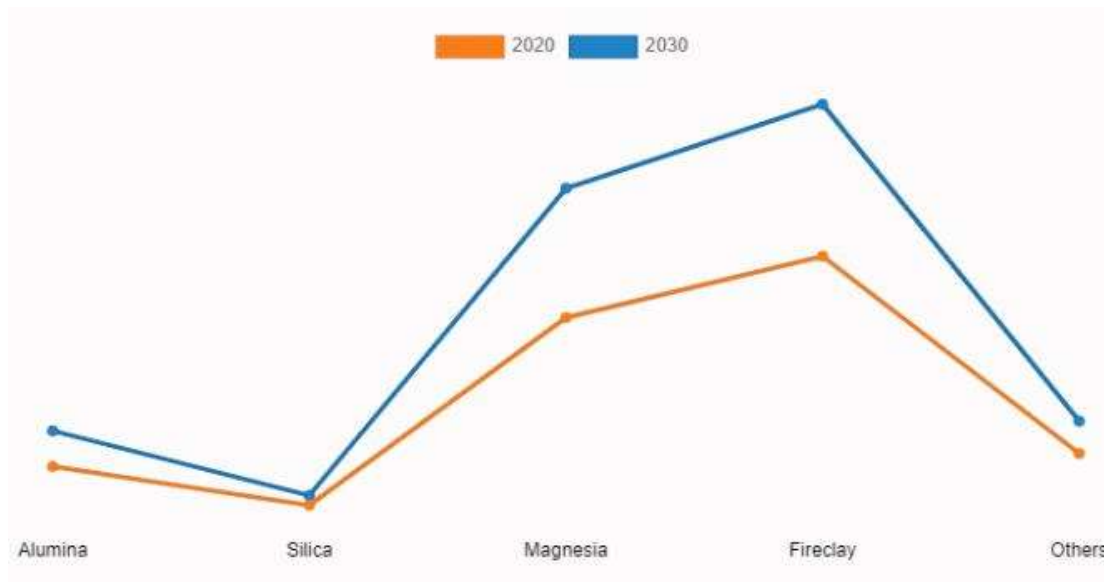


Fig. 1.2: By Chemical composition [28].

For refractory manufacturing, there is an excellent use of virgin raw materials. Still, with the increase in price and reducing raw material sources, it will be

challenging to continue in the future. While, the environmental concerns in a coal-fired thermal power plant are increasing rapidly, such as global environmental pollution, natural resource conservation, and the most significant increase in landfilling costs. Therefore, achieving zero waste by proper usage of material from waste is necessary for economic and environmental reasons in the future. So, the use of fly ash as an alumino-silicate raw material can be beneficial for the reduction in the environmental pollution in one way and in another way, it can reduce the cost of the refractories.

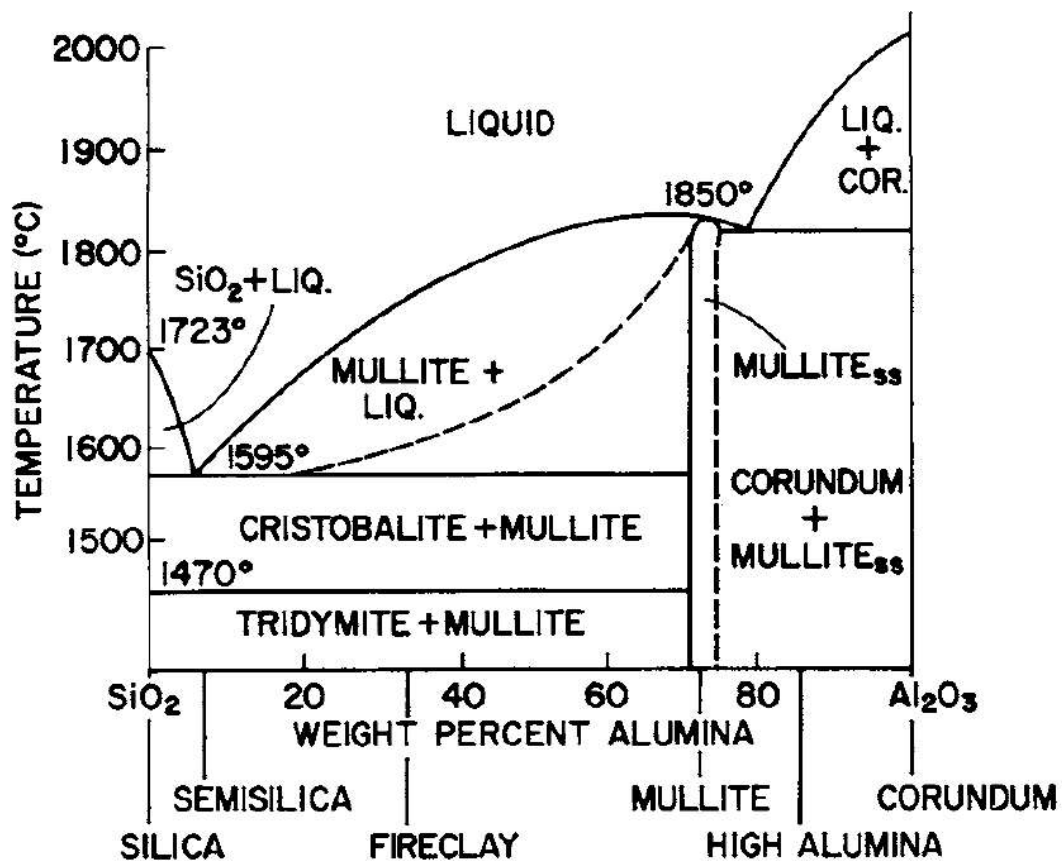


Fig. 1.3: Al₂O₃-SiO₂ phase diagram showing common refractory compositions

[29].

Al₂O₃-SiO₂ binary phase diagram

The compositions of a wide range of alumino-silicate refractories are included in the Al₂O₃-SiO₂ system. Silica, semi-silica, fireclay, low alumina, mullite, high alumina, and corundum are some of these. The phase diagram (**Fig. 1.3**) [29] can explain a lot of the high-temperature behaviour of these refractories. The diagram is defined by two end members, Al₂O₃ and SiO₂, as well as an intermediate compound, 3Al₂O₃.2SiO₂.

The Al₂O₃-SiO₂ binary phase system (**Fig. 1.3**) is of special importance because it aids in the understanding of mullite production, which has excellent thermo-mechanical properties. The Al₂O₃-SiO₂ binary phase system also includes fireclay refractory materials [30]. Mullite, an alumino-silicate mineral with moderate thermal expansion and conductivity, is a technologically appealing material for refractory ceramics. Mullite and alumino-silicate minerals are interesting in applications such as refractory materials because of qualities such as chemical inertness and excellent mechanical properties at high temperatures [31]. The greatest temperature feasible without forming a liquid phase throughout this composition range, according to the Al₂O₃-SiO₂ phase diagram (**Fig. 1.3**), is 1587 °C. Mullite and silica are the equilibrium phases found below this temperature (cristobalite). The presence of a tiny amount of liquid phase during refractory duty may be permissible without jeopardizing mechanical integrity. The amount of liquid phase present above 1587 °C is determined by the refractory composition. Increasing the alumina content raises the maximum service temperature, allowing a little amount of liquid to develop.

Jung et al. reported that low density (63%) mullite ceramics which can be fabricated by the reaction sintering of the mixtures of coal fly ash and Al₂O₃ powders

at about 1500 °C [32]. Chakraborty et al. reported that kaolinite to mullite transformation at around 600°C, where the initially formed amorphous meta-kaolinite transformed to poorly crystalline spinel and mullite at around 1000 °C. The final step was formation of 3:2 mullite from the spinel phase and poorly crystalline mullite phase. Two growth steps were reported - one from 1050 to 1150 °C and another from 1250 to 1350 °C. Mullite peak intensity increased with increase in temperature up to 1550 °C. Dong et al. prepared low-cost mullite from natural bauxite and fly ash with complete mullitization above 1400 °C [33]. Park et al, prepared well developed mullite whiskers by the firing of appropriate mixtures of coal fly ash and $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ with the addition of 2 wt.% $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ at 1300 °C for 10 hrs [34]. Dong et al. used industrial waste coal fly ash and bauxite as starting materials to fabricate porous mullite-whisker structured ceramic membrane at sintering temperatures ranging from 1100 to 1400 °C with addition of AlF_3 and MoO_3 [8]. Dong et al. fabricated mullite ceramics at relatively low sintering temperatures (1500-1550 °C) rather than 1600-1700 °C from recycled fly ash and bauxite with MgO addition as raw materials [35]. As for the current requirement of the world, waste materials that are dumped into landfills are needed to be utilized in some useful applications. Fly ash main constituents like Al_2O_3 , SiO_2 have excellent refractory properties, which can be very useful for many ceramic refractory applications

With the consumption of traditional fireclay products, the refractory industry could be a substantial source for the use or application of these alumino-silicate waste materials. Kumar et al. synthesized mullite aggregates from a fly ash and alumina mix that have a dense mullite and corundum crystal network and can be safely utilized in castables up to 1400 °C [36]. Fly ash can be utilized as a substitute for clay in the

synthesis of cordierite for refractory applications, according to Kumar et al [37]. Nguyen et al. reported that synthesis of forsterite-spinel ($2\text{MgO}\cdot\text{SiO}_2/\text{MgO}\cdot\text{Al}_2\text{O}_3$) refractory ceramics from fly ash and alumina [38]. López-Cuevas et al. synthesized cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$), mullite ($\text{Al}_{4+2x}\text{Si}_{2-2x}\text{O}_{10-x}$) and cordierite-mullite ceramic materials after using stoichiometric mixture of coal fly ash (CFA) as a source of SiO_2 and Al_2O_3 , and high-purity of MgO and Al_2O_3 [39]. Gusti et al. investigate that fly ash could be used as an alumina and silica source to prepare acid-based castables after proper treatment [40].

It should be able to create alumino-silicate refractories ceramic materials from fly ash waste materials that may be utilized as a component in the manufacture of refractories by carefully determining the proportions of the mix [30]. The strategy of the three Rs, which stands for recycle, reuse, and reduce, has been encouraged by more strict rules for specific waste dumps, in tandem with the rising recycling philosophy. Because of its mineralogical, physical, and chemical makeup, as well as the presence of various elements and compounds, coal fly ash is a suitable clay substitute in a variety of industries.

The chemical composition of Indian origin coal fly-ash from Barsingsar, Bikaner, Rajasthan, the main waste materials in our investigation, is similar to the fireclay currently used in refractories [30]. The fly ash comprises of 67.20% SiO_2 , 23.89% Al_2O_3 , and 5.53% Fe_2O_3 . Thus, it can be thought that fly ash could be potential source of raw materials for alumino-silicate refractory. So, therefore it is essential to make a thorough study to understand the role of fly ash and ball clay on the properties of fireclay refractory produced at high temperature. The present study was undertaken to use the lignite fly ash of an Indian origin for the fabrication of fireclay refractories

to meet up the industrial requirements. The successful application will lead us to the utilization of waste product lignite fly ash that needs special care for redemption and effective use of this fly ash as a refractory raw material. These two different roles can cater to the Indian refractory industry in terms of cost-saving and environmental issues. To develop fireclay refractory bricks Indian-origin lignite fly ash was utilized which can be a value-added product for the refractory industries. Also, to produce semi-silica insulation refractory brick, the lignite fly ash was used. Ball clay and sawdust were used to produce semi-silica insulation refractory by using fly ash, which was an eco-friendly and low-cost material.

Using fly ash waste as raw materials has three main advantages. First, the use of a zero to very low-cost raw material, secondly, the conservation of natural resources, and finally the elimination of solid waste.

Literature Review

ASTM C71 defines refractories as "non-metallic materials having those chemical and physical properties that make them applicable for structures, or as components of systems, that are exposed to environments above 1,000 °F (811 K; 538 °C)" [41]. In addition, the ability to provide thermal insulation is often an important consideration. Refractory materials are marketed in a variety of forms, but bricks are the most common. Chemical composition (acid, basic, and special), form of implementation (shaped and unshaped), technique of fabrication (sintered and fused), and porosity content (dense and porous) can all be utilized to classify refractory materials. These materials are designed to withstand high temperatures and are subjected to varying degrees of mechanical stress and strain, liquid and gas corrosion, and mechanical abrasion [42]. Depending on the nature of the raw materials and the procedure utilized, many types of refractory materials can be manufactured. Refractory has a wide range of applications that are dependent on the qualities of each variety. In reality, the texture and richness of raw materials for fabrication of refractories such as alumina, mullite, doloma, periclase, spinel, and corundum are strongly related to the performance of a refractory (excellent resistance to heat and thermal shock) [43]. The overall classifications of refractories are shown in **Fig. 1.4** [44].

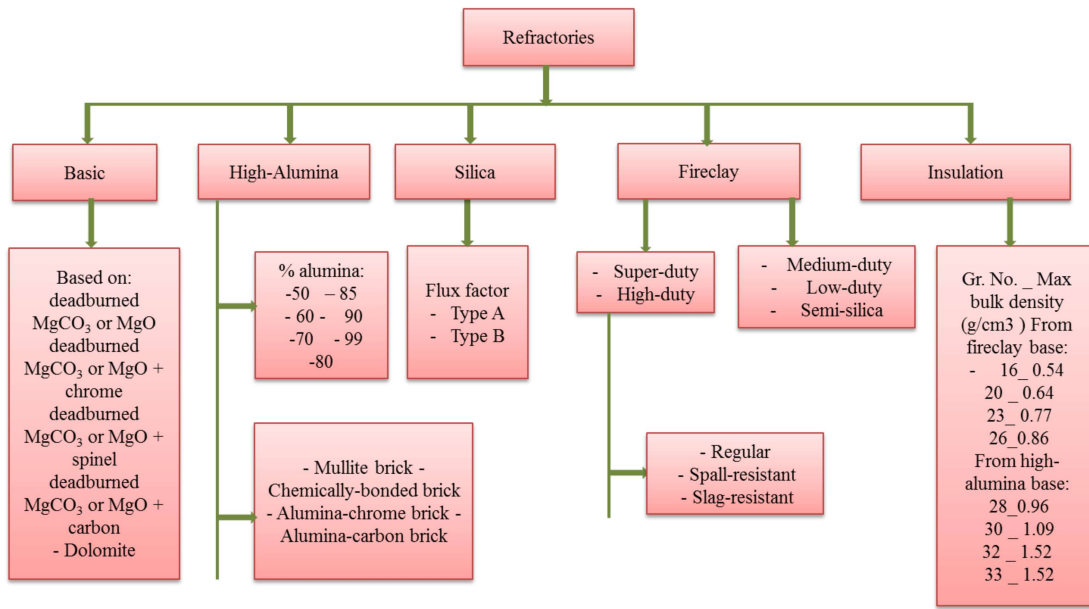


Fig. 1.4: General classification of refractory materials.

The alumino-silicate refractories are a type of material that is becoming increasingly popular, and their production requires the formation of mullite phase. Compared to other bricks such as special carbon refractories, zircon, zirconia, fused-cast refractory, alumino-silicate have the advantage of being relatively affordable. Furthermore, alumino-silicate refractory can be used in a variety of applications, including refractory supports, laboratory furnace coatings, food production-related industries, thermal insulating, chemical producers, industrial ceramics and pottery, pulp and paper, and anything else involving heat and/or hot products [42].

Fire clays, bauxite, sillimanite minerals, and combinations of alumina (Al_2O_3) and silica (SiO_2) sand are used to make alumino-silicate refractories. They will mention as common crystalline compound with a fusion temperature of at least 1500 °C [45]. Fire clays, high alumina, and silica are the three main types of classical refractories. The main component of refractory fireclay is hydrated aluminium silicates, with tiny amounts of other minerals. There are five standard grades of fireclay

brick, according to the American Society for Testing Materials (ASTM): (i) super-duty, (ii) high-duty, (iii) medium-duty, (iv) low-duty, and (v) semi-silica [46]. The typical properties of fire clay refractories are shown in **Table 1.1**. These classes include materials with alumina content ranging from 18 to 44 % and silica content ranging from 50 to 80 %. In the production of high-duty and super-duty fireclay brick, a mixture of clays is typically employed. Flint clays and high-grade kaolin have a high refractoriness, whereas calcined clays limit drying and fire shrinkages, and flexible clays help with forming and bonding. The amounts of clays used in a blend are determined by the quality and character of the brick to be manufactured [47].

Table 1.1 Properties of fireclay refractories [48].

Properties	Unit	Low duty fireclay	Medium duty fireclay	High duty fireclay	Super duty fireclay
Maximum service temperature	°C	1000	1200	1350	1550
Physical properties					
Porosity	%	19–21	18–20	16–18	14–16
Bulk density	g/cc	2	2.1	2.12	2.35
Mod. of rupture at RT	MPa	5–5.5	5.5–5.8	7.5–8.5	8.5–9.0
Cold crushing strength	MPa	25–28	30–33	34–36	35–38
Permanent linear change @ 1400 °C @ 1550 °C	%			(±) 0.3	(±) 1.2
Refractoriness under load under 2 kg/cm ² load	(ta) °C			1400	1600

With an alumina content of 40 to 44%, super-duty fireclay bricks have good strength and volume stability at high temperatures. When exposed to fast temperature changes, some super-duty bricks have a higher resistance to cracking or spalling. In the super-duty fireclay class, various changes are conceivable, including brick burnt at temperatures hundreds of degrees higher than the standard product. Higher amount of

fire clay improves the brick's high temperature strength, stabilizes its volume and mineral composition, boosts its resistance to fluxing, and renders it virtually impervious to carbon deposition breakdown in carbon monoxide gas atmospheres.

Large volumes of high-duty fireclay brick are utilized in a variety of applications. High-duty fireclay brick can frequently be utilized more economically than medium-duty brick for the linings of furnaces that are operated at moderate temperatures for lengthy periods of time but are subject to frequent shutdowns because of their superior resistance to thermal shock. Medium-duty bricks are suitable for applications that are subjected to moderately severe circumstances. Within their usable temperature ranges, medium-duty brick can endure abrasion better than many high-duty bricks. Low refractoriness fireclay brick is used as a base for higher-refractoriness fireclay brick, as well as for other applications requiring moderate temperatures. Semi-silica fireclay bricks have an alumina percentage of 18 to 25% and a silica content of 72 to 80%, with a low content of alkalis and other impurities. They offer great load-bearing strength and volume stability at relatively high temperatures, as well as a high resistance to shrinkage. Traditional refractory material selection, like advanced material selection, was and continues to be centred on balancing cost and performance lifetime [47].

Manufacturing of fireclay refractory bricks

The major ingredients of fireclay refractories are alumina and silica. Fe_2O_3 , TiO_2 , CaO , MgO , K_2O , and Na_2O are the additional oxides that remain as impurities. All of these oxides function as flux, lowering the refractory's softening temperature. Although undesired, the presence of these oxides is unavoidable due to their inherent existence in naturally occurring raw materials. Most fireclay refractory bricks are

produced using mixes of at least two clays. Some refractory bricks, particularly those of the low-duty class, are made of solo clay. The blends for super-duty and high-duty refractory brick usually contain raw flint and bond clay, with or without calcined clay. In making refractory brick of kaolin and different clays, a huge extent of the blend is pre-calcined to control sintering shrinkage and balance out the volume and mineral composition of the item [47].

In making fireclay refractory brick, the particles of ground clay should incorporate a range of reviewed sizes, each in appropriate extent. The clays are ordinarily ground in a "dry container," which is a turning, pan-shaped crushing mill having opened openings in the base. The batches are sifted to the ideal sizes and completely blended in with right proportion of water. The moistened batch is then fed to a mechanically or hydraulically operated press in which the brick are formed under pressure. Typical flowchart for manufacturing process of fireclay refractories showed in **Fig. 1.5**.

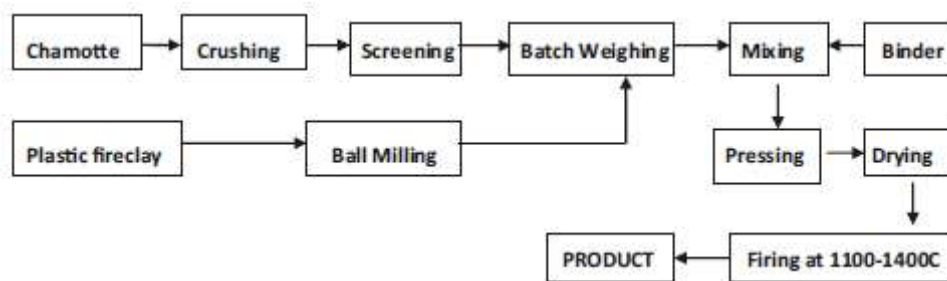


Fig. 1.5: Flow sheet of the process of manufacturing of fireclay-shaped refractory [49].

The fireclay refractory's microstructure examination suggests that it can contain up to 50% glassy phase with embedded cristobalite and mullite crystals. With larger fluxes and a higher firing temperature, the fraction of glassy phase increases.

With mullite 55% and cristobalite 20 to 25% in a fireclay brick with 40% Al_2O_3 , utilizing raw materials with modest amounts of alkali and fluxes, the glassy phase can be decreased to 20%. The thermomechanical behavior of the refractory is influenced by the existence of glassy phase and mullite crystals, as well as their sizes. At high temperatures, fireclay refractories exhibit strong volume stability, good abrasion resistance, good thermal shock resistance, and extremely good resistance to alkali attack. In fireclay and high alumina refractories, mullite is always a desired phase [49].

Dense and Porous Refractories

Refractories can be divided into two types based on the amount of porosity they contain: dense and porous refractories. Porosity in dense refractories ranges from 15 to 20%. These refractories were employed in hot liquid metal and gas applications. Porous refractories, on the other hand, can have up to 80% porosity. The porous refractories are low in weight and provide excellent thermal insulation. These refractories are utilized as furnace back-up linings or at high temperatures. Hot face insulation bricks are used for high-temperature insulation. Cold face insulation bricks are the backup insulation bricks [44].

Properties Insulation Bricks

The existence of a considerable degree of porosity in insulation brick distinguishes it. Most of the pores are closed. The thermal conductivity of the refractory is dramatically reduced when porosity is present. Insulation brick is the name for these porous refractories. Due to the existence of porosity in these bricks, their bulk densities are often low. The temperature at which these bricks are used is determined by their composition. Insulation bricks made of kyanite, for example, can withstand temperatures of up to 1250 °C. Insulation refractories made of fireclay are

typically employed at low temperatures.

Insulation Bricks

Insulation bricks should have a low bulk density and a high porosity, as this reduces the brick's strength. The thermal conductivity and heat capacity of these bricks were also relatively poor.

Raw materials for Insulation Bricks

Aggregates, binders, and combustibles/pore formers are the three types of raw materials used in the fabrication of insulation bricks [50]. Insulation bricks are made of rice husk/sawdust straw, polystyrene foam, naphthalene, starch, or low-cost biomaterial as combustibles or pore formers. Sawdust is a flammable material that, at high temperatures, produces channels and porosity [51–55]. Insulation bricks are often made with polymeric clay, ethyl cellulose, starch, and a molasses-based binder. In the production of paste insulating bricks, several binders are employed. During the casting and setting process, however, calcium oxide-based binder lime or, on occasion, gypsum is added to make insulation bricks [50].

Fabrication of insulation refractories

Insulation brick are manufactured by two different ways mainly casting and setting and pressing.

Casting and setting

Refractory aggregates and pore formers are mixed with binder, water, and plaster of Paris as a setting agent in this method. The plaster of Paris is hydrated during the mixing procedure. The vibro-casting technique is used to cast this hydrated product in a mold. The mold is allowed to set after casting. The product is remolded and slowly dried when the final setting is obtained. The dry item is progressively burnt to a

maximum firing temperature above the brick's service temperature. The included brick component burns off and produces pores in the brick matrix during the firing process; because the water demand for this processing is rather considerable, the brick does not revert to its original shape after firing. Cutting the surface of the fire brick prepares the final shape of the brick. For industrial production, this is the most common strategy [56,57].

Pressing

To make insulating bricks, aggregates, binders, and pore formers are mixed with 4-5% water and pressed uniaxially or hand-molded. The mix's plasticity is a crucial factor in producing a high-quality test brick. The plasticity is obtained by increasing the amount of binder in the raw mix. The manufacture of bricks in this procedure is prone to lamination. The quality of the press product may be improved if the composition and process parameters for pressing were carefully controlled. The pressed brick is dried in a hot air oven before being burnt at a higher temperature than the service temperature brick. The temperature at which the batch is served is determined by the qualities of the raw material used in the batch formulation. If green rejection is kept to a minimum, this method yields great output. Because the amount of water required for this operation is minimal. Surface grinding or cutting are not required in this procedure to make bricks [58].

Fly ash

Energy has become the essential element for progress and growth and the driving force of the current economy. Coal is the primary energy source, and the future will be so expected due to its abundance worldwide. The pulverized coal is generally

burned in coal-fired thermal power plants to produce energy. In the course of combustion, carbon and volatile matter are burned off along with coal impurities consisting of clay, quartz, feldspar, shale, etc., generally condense and remain in suspension. These condensed materials turned into fly ash in low temperatures [59]. India's total installed capacity for power generating is around 100,000 megawatts (MW). Thermal power plants generate 73 percent of total electricity. India has around 180 billion metric tonnes of coal reserves. As a result, it's worth noting that 88 percent of India's thermal power plants rely on this plentiful natural resource. There is various power-producing units in our country, with roughly 85 of them depending on coal. The physical significance of Indian coal is the large amount of ashes contained (35–50%) and poor calorific content (2,800–4,200 kcal/kg). To create the required energy, a high coal-fired rate is required, resulting in a larger ash accumulation. The current fly ash generation in India is about 226.13 MT which is supposed to be double in the upcoming decade [10].

Several physical features aid in the classification of fly ashes for diverse technical applications. Fly ash physical attributes vary greatly depending on coal type, boiler type, coal ash content, combustion process, and collector arrangement. The texture of fly-ash is typically silt loam, with 65–90% of the particles having a diameter of less than 0.010 mm [60,61]. Fly ash is made up of microscopic powdered particles with a spherical shape that might be solid or hollow. These particles are mostly glassy (amorphous), while some crystalline phases are possible. Because oxidation happens during coal combustion, a small quantity of carbon and nitrogen is contained in fly ash [62,63]. Because of the little amount of unburned carbon present in fly ash, its color ranges from grey to black [13]. Fly ash has a low bulk density (1.01–1.43 g/cm³), a

specific gravity of 1.8-3.2, and a specific surface area of 18 to 100 cm²/g.

Due to its physical features and sheer volume created, fly ash is a severe hazard.

Some of the issues are as follows [64]:

- Fly ash particles, both dry ash and pond ash, occupy many hectares of land in the neighborhood of the power station due to heavy disposal.
- Fly ash in a dry condition is difficult to handle due to its fineness. Fine ash particles in the air damage structural surfaces and have an impact on horticulture.
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Fly ash comprises silica (SiO₂), alumina (Al₂O₃), and iron oxides (Fe₂O₃), and the content of these oxides varies based on the coal deposit, coal preparation processes, burning process, and other factors. Fly ash also contains Na₂O, K₂O, MgO, CaO, P₂O₅, MnO, TiO₂, SO₃, and other oxides in addition to the significant oxides. Furthermore, fly ash contains elements such as B, W, Ga, Ni, Cr, V, Ag, Se, Au, Zn, Ge, Pb, Mo, U, and others in proportions less than 1% (by weight), as well as toxic and potentially harmful elements such as As, Be, F, Yg, and others [11,13,38,39,65–69]. The chemical composition of fly ash used in different places worldwide is shown in **Table 1.2**.

Table 1.2 Chemical composition of fly ash used in different places worldwide.

Composition (wt.%)	Renukoot, India [70]	Andhra Pradesh, India [66]	Asturias, Spain [67]	Candiota, Brazil [68]	Hefei, China [69]	Mělník, Czech Republic) [38]	Nava, Coahuila, México [39]
SiO ₂	69.35	57.37	53	68.48	51.7	57.3	60
Al ₂ O ₃	26.32	29.78	28	20.21	26.24	29.3	27.6
CaO	0.07	8.41	1.6	1.27	11.1	2.2	2.8
Fe ₂ O ₃	1.16	1.83	6.1	6.7	3.28	5.1	3.7
Na ₂ O	--	0.54	0.6	0.41	0.57	1.7	--
K ₂ O	--	0.32	3.9	1.59	1.14		1.3
P ₂ O ₅	1.13	--	--	0.05	--	--	--
MgO	0.25	0.68	1.6	0.56	0.65	1.4	--
TiO ₂	--	1.07	--	0.61	1.36	--	2
S	0.36	--	--	--	3.54	--	--

Renowned characteristics of fly ash are low cost, low alkali content, pozzolanic properties, spherical texture, and moisture insensitivity, simple handling, consistent quality, low carbon content and good shear strength. The driving force behind the application-oriented studies on fly ash is upon the improvement of products with technical and industrial value. The processing of coal fly ash is a good alternative to

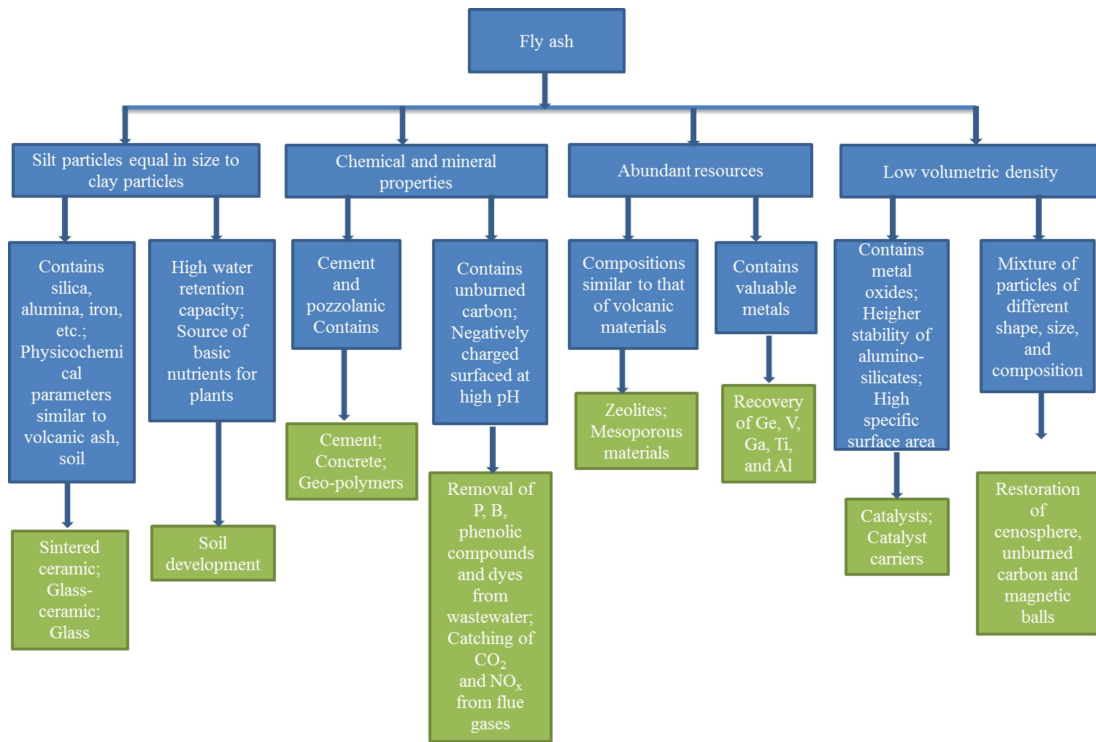


Fig. 1.6: Some physicochemical characteristics and application of fly ash.

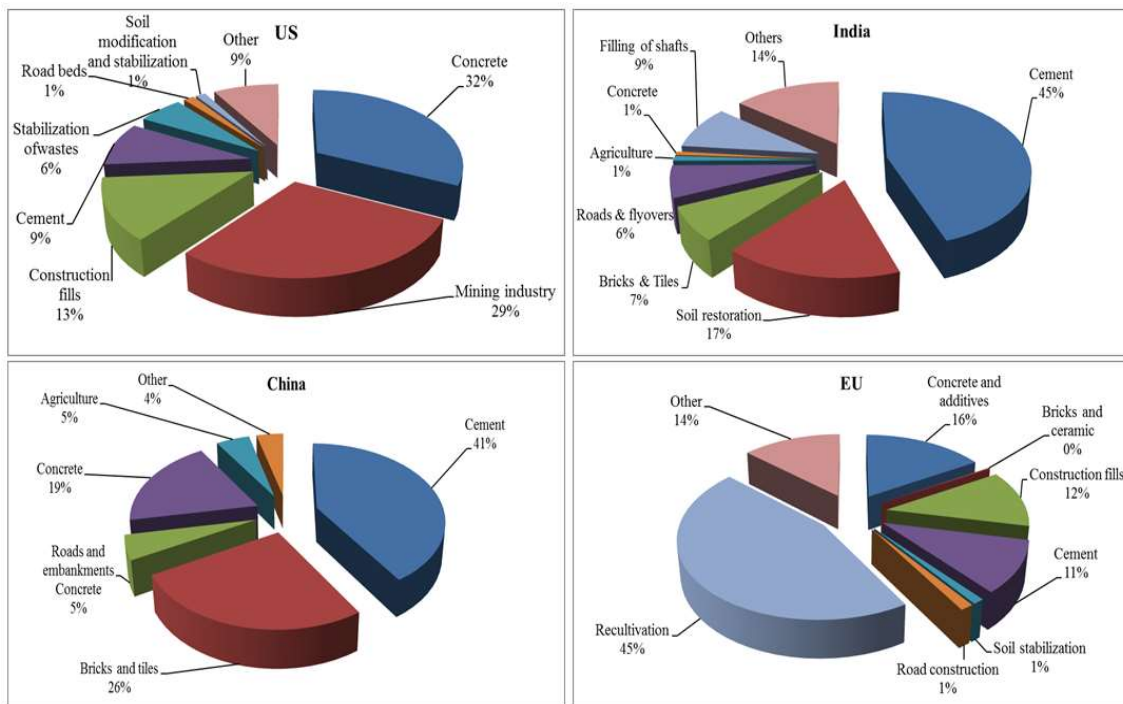


Fig. 1.7: Fly ash usage technique in US, India, China, and EU [11].

recycling and can bring significant economic and environmental benefits [11]. Some physicochemical characteristics and application of fly ash is shown in **Fig.1.6**. The usage of fly ash in US, India, China, and EU amounted to 46.74%, 55.79%, 67.96%, and 93.74%, respectively in 2011 [11,71]. The fly ash usage techniques in these countries are exhibited in **Fig. 1.7**.

Construction industries use fly ash as substitute materials. Fly ash is also used as aggregate in the fabrication of geopolymer, concretes, and cements [72–77]. Gonzalez et al. reported that fly ash can be used as raw material for the pavement base course foundation material production, drying agent for wet soils and structural fill [25]. Lin et al. reported that fly ash is suitable raw materials for brick production [78]. It is also used as low cost adsorbent for organic compounds, flue gas (NO_x , SiO_2) and metals (As^{+5} , As^{+3} , Zn^{+2} , Pb^{+2} , Cd^{+2} , Cu^{+2} , Cr^{+6} , Cr^{+3} , Ni^{+2} , Hg^{+2}) removal from industrial effluents [79–85].

Notwithstanding certain heavy components, fly ash additionally contains significant metals like germanium (Ge), gallium (Ga), vanadium (V), titanium (Ti), aluminium (Al), gold (Au), and platinum (Pt), which can be extracted by proper developed technology [11,86–89]. Fly ash with huge amount of silica (SiO_2), alumina (Al_2O_3), calcia (CaO), and iron oxide (Fe_2O_3) (see Table XX) is utilized in the ceramic business to substitute excellent quality raw materials. The finely distributed fly ash powder particle required no special treatment for the industrial processes. As a result, the ceramic product which can be obtained from fly ash are ceramic tiles [18,90–93], zeolite [94–97], glass-ceramics [20,98–100], ceramic fibre [101], and refractories [66–68,102–104]

Otero et al. (2004) studied on the fabrication of thermal insulating firebricks from coal fly ash. Fly ash was the principal component of the insulating bricks created. A sintering additive of ordinary clay was employed, as was sodium silicate as a binder to boost the mechanical strength of adobe bricks, as well as a foaming agent and water. Fly ash and clay were mixed together according to the proportions of the combination, then sodium silicate and water were added. The homogenized suspensions were then poured into metal molds and allowed to air dry. The molded samples were sintered at temperatures ranging from 900 to 1100 °C in a ceramic furnace with electric heating. The bricks formed have a high mechanical strength and a low thermal conductivity, making them good insulating materials. However, they lacked sufficient refractoriness [67].

Vilches et al. (2003) highlighted the use of coal fly ash and titanium waste in thermal insulation and fireproofing programs. Coal fly ash (>50%) and titanium waste (>35%) were used to create the plates. To make the material more porous and lower density, exfoliated vermiculite (10%) was added. The materials generated have a high porosity, with average pore diameters ranging from 0.5 to 10 μm, a density of 0.74 g/cm³, and compressive strength of 0.31 MPa. The material is stable at high temperatures (>800 °C) according to the results of differential thermal analysis (DTA) [105].

Refractories are only the start of until now one more field of application for coal fly-ash and its byproducts. Even though volumes used are currently unsure, these are bound to boom as the refractory, and greater specifically the consumer industries, comprehend the advantages that can be carried out. Development is persevering with on these materials and the boundaries have now not yet been reached.

Fly ash is utilized as the major material for complete or partial replacement of chamotte or clay in refractory manufacturing technology. Hossain and Roy reported that fly ash was used to partially or totally replace clay in the creation of an insulating refractory [66]. In addition to clay and coal fly ash, the composition included chamotte, rice husk, and rice husk ash. Samples were burned at temperatures ranging from 800 to 1000 °C after being manufactured by uniaxial hydraulic pressing at a pressure of 120 MPa. The insulating refractory's pore structure, size, and distribution were drastically altered when clay was replaced with fly ash. The material's open porosity increased as the quantity of fly ash in the composition rising from 38 to 53%, and its thermal conductivity reduced to 0.46 W/ (m.K), while its bending and compression strength declined by 52.9 and 36%, respectively. However, the scientists point to a sample made entirely of coal fly ash as a viable material for large-scale insulating brick production.

Bragança et al. examined the application of coal fly ash in refractory insulating material, which is typically made with kaolin, chamotte, and sawdust [68]. Coal fly ash was employed as a substitute for chamotte because of its low reactivity to water in the molding body, which makes it easier to dry. Fly ash was added to a commercial composition containing kaolin, chamotte, and sawdust in proportions of 5 and 10 wt.%. Hand pressing was used to create the samples, with a PVA aqueous solution as a binder. After drying, the samples were baked at 500 °C before being burned in a laboratory electric furnace at 1350 °C to burn away the binder. With the addition of fly ash, the mechanical strength of the refractory reduced somewhat (0.92 – 1.45 MPa). According to the authors of the work these values are comparable with the strength of refractory material based on a commercial composition (1.89 MPa). The presence of

ash contributes to a slight increase in thermal conductivity. This does not degrade the quality of the refractory product in terms of thermal insulation, because the value of this parameter is small.

Sukkae et al. made refractory bricks using refractory clay and fly ash [102]. Fly ash was added to the mixture in amounts 10 to 50% by weight. The samples were fired in the temperature range 1100 to 1400 °C. The introduction of coal fly ash into the composition of refractory bricks improved the thermophysical properties of the material. An increase in porosity and pore size with increasing coal fly ash content decreased the thermal conductivity of samples fired at 1250 °C from 1.6 to 0.8 W/ (m.K). However, the mechanical strength decreased from 26 to 6 MPa.

López-Cuevas et al. developed cordierite-mullite composites utilising fly ash as an alternate source of Al_2O_3 and SiO_2 was studied [39]. Iron impurities were removed from pre-comminuted fly ash, and calcium oxide was leached with acetic acid. Comminuted electrofused powders of MgO and Al_2O_3 were used as added raw materials. Uniaxial pressing with a load of 4 tonnes was used. The produced samples were heated in platinum crucibles before being burned at temperatures ranging from 1200 to 1600 °C. The composites had a cordierite matrix and interlaced mullite needles in their microstructure, with accelerated development of the last phase on the inner surface of the pores. The density of composites with higher nominal mullite content dropped, which was explained by a greater tendency to create porosity under those conditions. However, the complicated processing combined with the high cost rendered them unsuitable for industrial use.

Senthil Kumar et al. recognize coal fly ash as a substitute material for producing pure cordierite with a low synthesis temperature and enhanced mechanical

properties [106]. The cordierite phase was synthesized using magnesium oxide and coal fly ash as raw materials, with CeO_2 , TiO_2 , and ZrO_2 added in varied proportions as additives. The samples were produced at 240 MPa by hydraulic pressing, after burning the binder at 400 °C followed by firing at temperature range 800 to 1350 °C.

Kumar and Kumar Singh reported in a study that the cordierite was produced using calcined alumina, coal fly ash, and talc [104]. Magnetic and flotation separation process were used to enhance the original fly ash. Materials were comminuted to the necessary fineness in the needed quantities. Samples made from a granulated body were burned at 1350 °C in air after being uniaxially pressed at 250 MPa. After fire at 1250 °C, cordierite was manufactured using pure fly ash, and the modulus of rupture for a commercial sample was found to be 72 MPa.

Wang et al. described the effective manufacture of a low-cost single-phase porous cordierite ceramic [107]. MgCO_3 (Magnesite) and SiO_2 (quartz) were added directly into fly ash to fabricate ceramic by solid state reaction. MgCO_3 (Magnesite) served as both a pore-forming agent and a source of MgO. To maintain a stoichiometric composition, quartz contributed extra SiO_2 . Ceramic samples molded at 20 MPa using uniaxial pressing were sintered at temperatures ranging from 1100 to 1300 °C. The best sintering temperature obtained for generating single-phase cordierite using fly ash (1300 °C) was substantially lower than the sintering temperature required when using pure oxides based on the experimental results. This is owing to the fact that the impurities in the raw material act as agglomeration additives, which improve phase separation and cordierite crystallization. The synthesized materials have high compressive strength (72.64 MPa) and bending strength (23.92 MPa), as well as high open porosity and bulk density (33.16 % and 1.61 g/cm³, respectively).

He et al. made cordierite refractory glass-ceramics with coal fly ash as the major raw material and industrial aluminium oxide (Al_2O_3) and basic magnesium carbonate (MgCO_3) powders as additives [20]. Water and methylcellulose were used to granulate comminuted powders of aluminium oxide, fly ash, and basic magnesium carbonate (MgCO_3). The samples were produced at 15 MPa using uniaxial pressing followed by firing at temperature range 1125 to 1320 °C. Fly ash cordierite glass-ceramics have a number of appealing qualities, including compressive strength (35 MPa) and heat resistance (37 thermal shock cycles 1200 to 28 °C). This material can be used to replace commercial cordierite goods such honeycomb carriers for catalysts, kiln furniture, and heat exchanger parts due to its low linear thermal expansion coefficient and strong compressive strength.

Tabit et al. used a dry mixture of fly ash, $\text{Mg}(\text{OH})_2$ (magnesium hydroxide), and $\text{Al}(\text{OH})_3$ (aluminium hydroxide) to make cordierite precursors. [108]. After mechanical comminution, the resultant mixture was homogenized, and the samples were made using uniaxial pressing at 15 MPa. The firing temperature ranged from 900 to 1200 °C. Sintered ceramics based on the cordierite phase with a heat conductivity of 1.12 W/(m.K) and a compressive strength of 128 MPa. According to the authors of the study, the materials made from fly ash are competitive in terms of specific heat and thermal conductivity with ceramic materials made from cordierite sourced from natural resources and commercial oxides.

Nguyen and Sokolář studied the comparison of refractory material of forsterite-spinel ceramics made with class-F fly ash to the refractory material of forsterite-spinel ceramics made with reactive alumina [38]. Raw ingredients included olivine, calcined caustic magnesite, and kaolin. To obtain optimal plasticity, the pre-comminuted

mixtures were homogenized in a rotating mechanical homogenizer and blended with water. The samples, which were made from a plastic paste and cast in brass molds, were burned in an air fired laboratory furnace at 1500 °C. With increasing fly ash content and no loss of refractory qualities, the modulus of rupture and heat resistance of the samples fabricated using fly ash samples increased. On the other hand, when the amount of alumina added to the samples increased, the rupture modulus and heat resistance declined.

Chen et al. studied the effect of the size of fly ash particles on the characteristics of lightweight insulating materials [109]. Fly ash, refractory clay, kyanite, sawdust, and polyvinyl alcohol were employed as raw materials for the organic binder. The samples were fabricated by uniaxial pressing at 2.5 MPa, then sintered at temperatures ranging from 1300 to 1400 °C after drying. The linear shrinkage, bulk density, and open porosity after calcination at 1350 °C are 4.5%, 0.81 g/cm³, and 70.84%, respectively, with an average fly ash particle size of 79.762 μm, corresponding compression strength of 1.74 MPa, and thermal conductivity at 900 °C of 0.281 W/(m.K). The qualities of lightweight insulating material are most affected by fly ash particles smaller than 60 μm, particularly particles between 20 and 30 μm. Fly ash particles of 20 to 30 μm contribute to improved physicochemical qualities by increasing density, thermal conductivity, and linear shrinkage, but fly ash particles of > 80 μm have the reverse impact.

Dai et al. investigated the effect of fly ash particle size on the qualities of a high-strength insulating material extruded from a mix of fly ash, clay, and PVA [110]. The ash particles ranged in size from 80 to 200 meshes. The bulk density, strength, and thermal conductivity of sintered specimens were all affected by the ash particle

size. The strength and density of samples in both works grow as the particle size of the fly ash increases, then drop. Fly ash particles with a mesh size of 120 to 160 produce the best strength and density results. With increasing size of the fly ash particles, the thermal conductivity of the material in [110] drops at first, then increases. With 120 to 160 mesh fly ashes, the best thermal conductivity is also reached.

Fly ash, which is produced in large quantities as a by-product of fuel combustion in power plants, pollutes the air, soils, wastewater, and other regions, and has a substantial impact on the environment. Its active use in the construction industry would mitigate negative repercussions by reducing existing ash slag waste build-ups and preventing the formation of new ones. It's also attractive to use it to remove heavy metals, organic compounds, radioactive pollutants, sulphur and nitrogen oxides, and other impurities from water and gases as catalysts, carriers of catalysts, or adsorbents. Fly ash can also be used to make refractory ceramics and thermal insulation as a raw material. Its usage as a main material or source of alumina and silica oxides will limit the use of non-renewable resources while also permitting the development of materials with improved thermophysical properties such as strength, heat resistance, and thermal conductivity. From the literature survey it can be seen that efforts have been given by the researchers towards application of fly ash as an alternative source of raw material. Thus, the application of fly ash as alternative raw material for the refractory field still in its young age and a lot of research are needed to make the fly ash as a viable material.

Objectives of the present work

Alumino-silicate refractory is a very crucial for high temperature application such as back up lining for high temperature furnaces, soaking pit and. Lignite fly ash is a waste material was used alternative raw materials for fabrication of alumino-silicate refractories. The primary objectives of the studies are as follows:

- The main objective of this study is to utilize lignite fly ash for fabrication of alumino-silicate refractories.
- To find an alternative resource of fireclay raw materials which will saves natural resources and help to protect the environment.
- Enhancement of cold crushing strength of alumino-silicate refractories by using lignite fly ash.
- Study the behavior of thermal conductivity of alumino-silicate refractories.