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# A multi-directional utilization of different ashes

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## Abstract

The prospective uses and applications of coal fly ash, bagasse ash and rice husk ash, being generated in different types of industries are compared and reviewed. Several new applications of the ashes as a raw material for the preparation of different new materials like glass, hollow micro spheres, cement, ceramics, geopolymer and zeolite, as an adsorbent for different waste water processes, and removal of heavy metals etc. There is a considerable potential for the increased utilizations of all such ashes in its raw, additives and refined state for making industrial process economical and environment friendly which is strongly suggested.

Key words: Ashes, Porous material, Geopolymers, Micro spheres, Enriched carbon, Magnetic spheres

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## 1. Introduction

Coal fly ash is generated in thermal power plants during the combustion of coal as a waste or by-product and is considered to cause environmental pollution. This ash is generated at as high temperature as 1200-1700 °C from the combustion of various organic and inorganic constituents of the raw coal used in different plants as a fuel. Because of the variety of components, coal fly ash is one of the most complex anthropogenic materials that can be characterized. For example, approximately 316 individual minerals and 188 mineral groups have been identified in different coal fly ash [1]. Most estimates in the current literature put global coal fly ash production somewhere in the region of 500 million tones per annum [2].

To maintain the most effective way to accomplish a sustainable development through the imitation of natural world, which may be called as Industrial ecology, has gained sufficient attraction over the past two decades. To preserve the natural resource consumption, the worker of industrial ecology would advocate that the waste and byproducts produced in one industrial process would be assimilated by the other industrial process which would considerably minimizes the consumption of energy and raw material for a specific products and reduces both economic cost of production and environmental hazard [3].

In the mid of 1980s, in order to bridge the gap between environmental and socio-political concerns concerning the issues of human being development, the concept of sustainable development was emerged [4]. Industrialists and researchers have been searching for ways to make industrial activities more sustainable as our common future popularized the concept of sustainable development [5].

Due to shortage of fuel reserves, the consumption of coal has been increased to 50% of the total fuel including industries and transportation [6]. The annual production of ashes is estimated as 750 million tones, while its consumption is only 25% [7]. In US 39% while in Europe only 47% of the ash is utilized in different activities. The remaining coal ash is being disposed of without any benefit causing a number of environmental problems [8-9]. The disposal of coal fly ash is only expected to get worse as the demand for energy grows. The present forecasts envisage that the installation of the same amount of power generation capacity will occur in the coming twenty years as have been installed in the whole of the 20th century. Some part of the energy demand is likely to be fulfilled by renewable energy sources; but still in some energy intensive countries like China, Pakistan and India, coal is likely to become a progressively more dominant fuel for the production of power [10]. Though a number of reviews on the utilization of coal fly ash have been written [11-12], but the overview on the multi-component utilization of coal fly ash can be found in the past 10-15 years [13-14]. The aim of the present review is to establish the advancements in processing technologies that have been used to recover some useful constituents from not only coal fly ash, but all other such ashes like bagasse ash and rice husk ash and then to examine the potential applications of these recovered constituents.

## 2. Physico-Chemical study of ashes

### 2.1. Mineralogy and Chemistry

The major, minor and trace constituents of coal fly ash from different countries are shown in table 1. coal fly ash may consists of silica ($SiO_2$), alumina ($Al_2O_3$), ferrous oxide ($Fe_2O_3$), and calcium oxide (CaO) as a major constituent in a little variable amounts. The loss on ignition test shows that there is a variable amount of carbon as well. [5]. From the table it is evident that the components present in the fly ash are in the order of $TiO_2 < Na_2O < K_2O < MgO < CaO < Fe_2O_3 < Al_2O_3 < SiO_2$. The table shows that there is a significant difference in the composition of ash collected from different countries and even in the same country which mainly depends upon the type of coal from which ash is produced. For example ash produced from lignite and sub-bituminous coals are having a higher amount of CaO, MgO, and $SO_3$ and smaller $SiO_2$ and $Al_2O_3$ as compared to anthracite and bituminous coals. The amount of lime in the coal fly ash play important role in the physico chemical composition. For example, when the amount of lime is less than 10%, it may often consist of aluminosilicate glass and do not contain any crystalline compounds of calcium and in case if it contains more than 15% CaO, calcium aluminosilicate glass is present in addition to considerable proportions of crystalline calcium compounds like $C_3A$, $C_4A_3S$, CS and coal fly ash [15], which make the bases of its suitability for its use in cement replacement. coal fly ash is classified in two classes according to the American Society for Testing and Materials (ASTMs), class F fly ash and class C fly ash, the former has $SiO_2$, $Al_2O_3$, and $Fe_2O_3$ contents greater than 70% while the latter has greater than 50% as shown in table 2. The chemical composition of coal fly ash mainly depends upon the type of coal from which it is obtained. Chemical composition of coal fly ash obtained from different types of coal is given in table 3 [16].

Table 1.Analysis of coal fly ash obtained from different regions [15].

| Component | Range (wt. %) |
|---|---|

| | Europe | US | China | India | Australia |
|---|---|---|---|---|---|
| LOI | 0.8-32.8 | 0.2-11.0 | *BDL | 0.5-5.0 | *BDL |
| $SiO_2$ | 28.5-59.7 | 37.8-58.5 | 35.6-57.2 | 50.2-59.7 | 48.8-66.0 |
| $Al_2O_3$ | 12.5-35.6 | 19.1-28.6 | 18.8-55.0 | 14.0-32.4 | 17.0-27.8 |
| $Fe_2O_3$ | 2.6-21.2 | 6.8-25.5 | 2.3-19.3 | 2.7-14.4 | 1.1-13.9 |
| CaO | 0.5-28.9 | 1.4-22.4 | 1.1-7.0 | 0.6-2.6 | 2.9-5.3 |
| MgO | 0.6-3.8 | 0.7-4.8 | 0.7-4.8 | 0.1-2.1 | 0.3-2.0 |
| $Na_2O$ | 0.1-1.9 | 0.3-1.8 | 0.6-1.3 | 0.5-1.2 | 0.2-1.3 |
| $K_2O$ | 0.4-4 | 0.9-2.6 | 0.8-0.9 | 0.8-4.7 | 1.1-2.9 |
| $SO_3$ | 0.1-12.7 | 0.1-2.1 | 1.0-2.9 | BDL | 0.1-0.6 |

*BDL= below detection limit

Table 2

Classification of Coal fly ash on the basis of chemical composition [16].

| | Wt % | | |
|---|---|---|---|
| Class | $SiO_2+Al_2O_3+K_2O+TiO_2+P_2O_5$ (%) | $CaO+MgO+SO_3+Na_2O+MnO$ (%) | $Fe_2O_3$ (%) |
| Sialic | >77 | <11.5 | <11.5 |
| Calsialic | <89 | >11.5 | <11.5 |
| Ferrisialic | <89 | <11.5 | >11.5 |
| Ferricalcsialic | <77 | >11.5 | >11.5 |

Table 3. Chemical composition of coal fly ash on the basis of coal type [16-17].

| Component (wt.%) | Bituminous | Sub-bituminous | Lignite |
|---|---|---|---|
| *LOI | 0-15 | 0-3 | 0-5 |
| $SiO_2$ | 20-60 | 40-60 | 15-45 |
| $Al_2O_3$ | 5-35 | 20-30 | 10-25 |
| $Fe_2O_3$ | 10-40 | 4-10 | 4-15 |
| CaO | 1-12 | 5-30 | 15-40 |
| MgO | 0-5 | 1-6 | 3-10 |
| $Na_2O$ | 0-4 | 0-2 | 0-6 |
| $K_2O$ | 0-3 | 0-4 | 0-4 |
| $SO_3$ | 0-4 | 0-2 | 0-10 |

* Loss on ignition

Bagasse is a cellulose fiber remaining material after the extraction of the sugarcane juice from sugarcane. It is used as a fuel source in the boilers of the sugar mills. Bagasse ash is a biomass and valuable byproducts of sugar mills which use bagasse as a primary fuel source to supply energy to run the plants. Burning of bagasse produce energy and ash, which is considered as a waste causing a number of environmental problems. It is a recognized fact that bagasse ash is an alternative source of energy with high silica content [18]. A number of studies have been carried out to investigate the potential applications of bagasse ash like raw material for producing silica gel as adsorbent, raw material for ceramic, cements and concrete additives, catalyst, cosmetics, paint and coating, etc based on its characteristics as given in table 4 . The silica contents of bagasse and its ash are varied depending on the type of soil and harvesting [18]. The chemical composition of bagasse ash obtained from different regions is given in table 4, while the SEM photograph of bagasse ash obtained at 800 °C is shown in figure 1.

Table. 4. Analysis of bagasse ash from different Countries [19]

| Component (wt. %) | Brazil | Pakistan |
|---|---|---|
| LOI | 0.42 | 13.45 |
| $SiO_2$ | 78.34 | 87.87 |
| $Al_2O_3$ | 3.55 | 2.47 |
| $Fe_2O_3$ | 3.61 | 4.05 |
| CaO | 2.15 | 2.86 |
| MgO | 1.65 | 1.10 |
| $Na_2O$ | 0.12 | 0.17 |
| $K_2O$ | 3.46 | 0.44 |
| $SO_3$ | BDL | 0.16 |

Rice husk ash is the most silica rich material used as a raw material for the manufacture of a number of materials and contains about 90-98% silica as shown in table 5. Rice husk is a popular boiler fuel and the ash generated usually creates disposal problems. The chemical composition of rice husk as received, heated at 700°C for three hours and six hours is shown in table 5.

Table 5. Chemical composition of RHA before after burning [20]

| Components | Rice Husk Ash | | |
|---|---|---|---|
| | As-received | After burning out at 700 °C for | |
| | | 3 Hours | 6 Hours |
| LOI | N/A | 0.01 | 0.02 |
| $SiO_2$ | 96.51 | 97.86 | 98.14 |
| $Al_2O_3$ | 0.15 | N/A | N/A |
| $Fe_2O_3$ | 0.17 | 0.07 | 0.07 |
| CaO | 0.66 | 0.52 | 0.46 |
| MgO | 0.77 | 0.29 | N/A |
| $SO_3$ | 0.04 | 0.07 | 0.07 |

Substances which contain more than 70% combined $SiO_2$, $Al_2O_3$, and $Fe_2O_3$ is called pozzolona, which is not cementitious itself, but when mixed with cement, it becomes cementitious. So all these three ashes on the basis of its composition can act as pozzolona and can be mixed cement and concrete. In a very finely divided form however, it will chemically react with $Ca(OH)_2$ at ordinary temperatures and in the presence of moisture to form compounds exhibiting cementitious properties. The high CaO content of many of the lignite and sub-bituminous fly ashes will result in the formation of cementitious products in the absence of $Ca(OH)_2$; as such, they are not true pozzolans [19].

Based on the mineralogy classification, coal fly ash may be divided into four main classes like Pozzolanic fly ash represented as (P), inert coal fly ash (I), Active fly ash (A), and Mixed mixed coal fly ash represented as (M). The major phases consist of mullite, quartz, and hematite [9]. Bases on the major phases and behavior, fly ash may be glass, quartz + mullite and the sum of any other mineral bearing phases such as Fe-Ca-Mg-K-Na-Ti-Mn oxyhydro oxides, sulphates and carbonates. This classification of coal fly ash helps to simplify the choice of applying of each fly ash composition. The chemical properties of coal fly ash have been studied and it is understood that fly ashes contain many elements at a variable concentration sometimes greater than 50 mg/kg in which some are of environmental concern [20-21].

## 2.2. Morphology

Scanning electron microscopic study reveals that coal fly ash is composed of solid and hollow spheres and irregular unburned carbon contents. Mineral aggregates with quartz, corundum and magnetite particles have also been studied [22]. The particle size of fly ash is controlled by different factors, including combustion temperature and subsequent cooling rate. The formation of coal fly ash takes place in many steps as shown in figure 2. In first step, coal is converted into char. The char material burn out at higher temperatures. At such a high temperature the fine minerals gradually reduce and are released from within the char as it fragments. At this point decomposition of minerals and conversion into gases occur and finally condense to solid ash particles. The formation of ash particles between 0.02-0.2μm occur as a result of homogeneous condensation. The formation of predominantly spherical particles in the size of 10-90 μm as a result of a series of complex transformation [14]. The possible reason for particle sizes exceeding 90 μm is that, it is made up of organic constituent or the unburnt coal (char) components. It has been shown that the larger fractions of a coal fly ash have a greater content of carbon particles [23]. The chars are represented by particles which are slightly changed, semi-cooked, or cooked produced as a result of the complete and partial melting of the various organic constituents respectively, while the faintly changed particles are those which are exposed to temperatures lower than 550°C. These faintly changed particles are typical for coarse-grained fractions over 100 µm in size.

## 2.3. Uses of ashes

Being the complex composition, coal fly ash has been proved to have its bulk utilization in many fields. Some components may be useful or inert in some particular applications, but actively unfavorable in the others. For instance, excess char content in the ash hinders its use in cement replacement in concrete formation due to its susceptibility to adsorb the surfactants which are used in concrete to stabilize air bubbles in the mixtures [24]. On the other side, the adsorption capacity of the char in the fly ash may be beneficial in the control of pollution.

It has already been published that the composition of coal fly ash principally contains some mixture of quartz-mullite, glass, Calcium silicate oxyhydroxide, char, iron rich compounds, and some salt fractions. A variety of techniques in a sequential separation process as shown in figure 3, have been applied to fully characterize the coal fly ash fractions as follows; [25].

1. Ceramic Cenosphere concentrate (CCC)
2. Magnetic concentrate (MC)
3. Water soluble salt concentrates (WSC)
4. Improved coal fly ash residue (IFA)

5. Char concentrates (CC)
6. Heavy concentrates (HC)

Cenosphere is the lightweight fraction the coal fly ash. It is basically hollow from inside due to which it is lightweight. These particles, whether they are spherical or non-spherical, porous or non-porous are less dense than water, and therefore float on the surface of water and are collected in a sink/float process, all particles less dense than water, whether they are spherical or non-spherical, porous or non-porous, are considered to be ash cenosphere products. Magnetic sphere is rougher than that of the cenospheres. These are extracted from ash by using a wet magnetic drum separator technique which exerts a medium intensity magnetic force on coal fly ash slurry and lifts the magnetic fraction out. The magnetic particles are primarily spherical in nature. In comparison to the carbon which is a larger porous structure exhibiting a more irregular shape. The causes for this difference in morphology are mainly explained by the mechanism of the formation of coal fly ash.

The huge porous nature of carbon particles is due to the incomplete oxidation of the burning coal. Due to the increased porosity, carbon has a higher surface area relative to the inorganic matter contained in the coal fly ash. It has been shown that the surface area of the mineral matter in coal used in concrete varies from 0.7 to 0.8 $m^2/g$ coal fly ash, which is significantly lower than the 45-400 m2/g found for carbon [26].

## 3. Current applications of ashes

The use of bagasse ash and rice husk ash in different materials is given in tables 6-7 respectively. The author of this review has a greater contribution in the use of bagasse ash in different materials as clear from references.

Table. 6. Use of bagasse ash in different materials.

| S. No | Use of bagasse ash | Benefits | References |
|---|---|---|---|
| 1 | Raw material | • $CO_2$ emission<br>• 6.46% of energy | [27] |
| 2 | Raw material | • 1.73% Reduction in | [28] |
| 3 | In cement | • compressive strength,<br>• consistency, setting time<br>• chloride diffusion | [29] |
| 4 | thermally activated bagasse ash | • 30 % replacement<br>• 18% increase in compressive strength | [30] |
| 5 | Chemically activated with quick lime | • Enhanced compressive strength<br>• Chloride resistivity | [31] |
| 6 | Chemically activated with $CaCl_2$ | • 20% replacement<br>• Enhanced properties | [32] |
| 7 | Cement concrete | • 20% replacement<br>• Enhanced early and late strength | [33] |
| 8 | Cement and concrete | • Simulation study for the use of bagasse ash in concrete. | [33] |

| | | | |
|---|---|---|---|
| 9 | Low cost adsorbent | • For the removal of dyes | [34] |
| 10 | Fertilizer additive | • Wheat production in calcareous soil | [35] |
| 11 | Low cost adsorbent | • Removal of heavy metals from water | [36] |
| 12 | Production of activated carbon | • Removal of copper | [37] |
| 13 | mesoporous silica xerogels | • Purity 99%<br>• Surface area 69 to 152 $m^2\ g^{-1}$<br>• Excellent adsorbent | [38] |
| 14 | Silica gel | • Excellent adsorbent | [39] |

Table. 7. Use of Rice husk ash in different materials.

| S.No | Use of rice husk ash | Reference |
|---|---|---|
| 1 | flexible self-supported sodium silicate films | [40] |
| 2 | silica xerogel with lower sodium | [41] |
| 3 | cheaper and reinforcement filler in natural rubber | [41] |
| 4 | Pozzolona in concrete | [33] |
| 5 | extraction of silica | [42] |
| 6 | Extraction of silica | [43] |
| 7 | Thermally activated rice husk at | [44] |

| | | |
|---|---|---|
| | different temperatures | |
| 8 | silica nanoparticles | [42] |
| 9 | green route for the preparation of silica powders | [45] |
| 10 | Simultaneous production of silica and activated carbon | [46] |
| 11 | ZSM-11 zeolite | [47] |
| 12 | Silica powder by recyclable technology | [48] |
| 13 | Clay replacement in bricks | [49] |
| 14 | Activated with $Ca^{++}$ in concrete. | [50] |

### 3.1. Construction industry

Fly ash has a number of uses in the construction industry [51]. It has been used in high strength Portland cement. It has been used in cement at different stages like before clinkerization as a raw mix and after clinkerization as a cement replacement in mortar and concrete. The reasons for partially replacing cement in mortar and concrete with pozzolanic materials are diverse [52], including strength development, improvement in durability, good compaction, and low heat evolution during hydration. Its use greatly improves the water tightness; fills in voids and act as filler reducing the total surface area to be covered with cement. Indeed, cement production is highly energy intensive process involving significant environmental damage with respect to $CO_2$ production and raw material acquisition [52].

The author of this paper has used bagasse ash as a raw mix and in cement mortar as a cement replacement. Coal fly ash has also been used as additive in the cement industry [53]. Because coal fly ash has pozzolanic properties, it is widely used as partial replacement for clinker the major component in Ordinary Portland Cement. The use of coal fly ash in blended cements is a well recognized expertise, but its use should be under strict standards the American Society for Testing Materials ASTM C 618 and the European Standard EN 450-1. Several concerns have been raised regarding the utilization of ashes in concrete as a cement replacement, for example according to [54], construction industry, which uses coal fly ash in cement and the coal fired power plants that produce the coal fly ash are seasonal. The production of ashes and utilization in construction industries does not match with one another. The construction industry requires cement in the summer months when building conditions are optimum, whereas most of the ashes are generated during the winter season. Similarly the composition also does not remain the same throughout the year. For example, in the summer season coal generators tend to be restricted to double shift as to satisfy the demands and in doing so the Loss on ignition of the ash is going up, which is the direct measurement of the increase of un-burnt carbon [30,54]. The variation of unburnt carbon in ashes changes its adsorption behavior in terms of the air entrainment admixture in the cement mixes. The increase in the loss of ignition reduces the adsorption quality of the fly ash as per both ASTM C 618 and EN 450-1. Another factor which contributes to the increase in the loss on ignition is the changes in the coal fired power generation like the introduction of low-NOx burners and selective catalytic reduction with SCR supported by the ammonia inoculation. Similarly

High carbon in the ash may also lead to the discoloration of the mortar and concrete segregation [55].

Fairbairn et al. [56] used sugarcane bagasse ash in mortar and concrete as a cement replacement for the reduction of carbon dioxide emission. A simulation was carried out to estimate the reduction of $CO_2$ emission and the viability to issue certified emission reduction (CER) credits. The simulation was developed within the framework of the methodology established by the United Nations Framework Convention on Climate Change for the Clean Development Mechanism.

The production of carbon dioxide is associated with the cement manufacturing process. Bagasse ash has been used in cement manufacturing process in the partial replacement of raw material and the production of carbon dioxide has been reduced. It has been investigated that 5% of bagasse ash can be used in the raw mix and 1.73% of the emission can be reduced by having any adverse effects on the clinker potentials. More over the use 5% bagasse ash in clinkerization can save 6.46% of energy [57] which is the greatest achievement in cement production technology.

Amin [58] studied thermally activated bagasse ash in high strength Portland cement with for different physical and chemical properties of mortar. The pozzolonic reactivity of bagasse ash was enhanced using thermal activation technique by curing mortar specimens containing bagasse ash, at 20, 40 and 60 °C and the samples were tested for compressive strength at the age of 3, 7 and 28 days. Results indicated that bagasse ash is very sensitive to temperature rise and therefore the application of thermal activation is very important when strength development at early stage is desired. Bagasse ash replacement by 30% at 40 °C and 60 °C increased the mortar strength at 7 days by 10 and 18% more than the control, respectively.

Bagasse ash has been chemically activated using industrially produced quicklime and used in cement mortar and the strength development and pozzolanic reaction rates of Bagasse ash/Cementitious systems was investigated by the same author [59]. It has been found that the addition of quicklime increased both the early and later strengths of the cement-bagasse ash specimens. A 3% addition of quicklime was found to be the optimum dosage both for short and longer curing periods.

The effect of bagasse ash as a pozzolanic material for the partial replacement of cement in the presence and absence of calcium chloride as a chemical activator has been investigated [28,60]. It has been found that the strength of the cement increase very significantly with the use of calcium chloride. Moreover the addition of $CaCl_2.H_2O$ decreased the evaporable moisture and the pH of the extract from hardened cement paste, which is an indication of enhanced pozzolanic reaction between the lime and bagasse ash. The optimum amount of bagasse ash replacement for cement in the mortar was found to be 10% without and 20% with 4% $CaCl_2.H_2O$ respectively. The results from both the strength and water extraction suggest that $CaCl_2.H_2O$ is a good chemical activator.

Bagasse ash has been found to enhance the compressive strength of mortar, the effect of bagasse ash content on the physical and mechanical properties of hardened mortar was studied, which include compressive strength, consistency, setting time and chloride diffusion [61]. Results indicated that bagasse ash was an effective mineral admixture and pozzolana. The optimum replacement ratio of bagasse ash was found to be

20% of the cement, which reduced the chloride diffusion effectively up to more than 50%, without any adverse effects on other properties of the hardened cement mortar.

Bagasse ash has also been used in Portland concrete by the same author [62] which endow with an adequate solution to environmental anxiety linked with waste management. The impact of bagasse ash as a partial replacement of cement has been investigated on physical and mechanical properties of hardened mortar and concrete, including compressive strength, splitting tensile strength, chloride diffusion, and resistance to chloride ion penetration. The results of the studies indicate that bagasse ash is an efficient mineral admixture and pozzolana with the optimal replacement ratio of 20% cement, which reduced the chloride diffusion by more than 50% without any unfavorable effects on other properties of the hardened concrete.

Rice husk ash has also been utilized as a partial and full replacement of clay in the preparation of bricks and different properties like compressive strength, water absorption and size and shape of the resulting bricks have been studied [40]. The optimum replacement level of clay with rice husk ash in bricks was found to be 30%. The resulting bricks were found to exhibit high compressive strength and low weight. The replacement level and compressive of rice husk bricks is shown in figure 4.

Arayapranee et al, [63] utilized rice husk ash in a natural rubber as cheaper and reinforcement filler. Two commercial reinforcing fillers like silica and carbon black were also used for comparison purposes. The effect of such fillers on cure and mechanical properties of natural rubber at different loadings, ranging from 0 to 40 phr, was investigated. Results showed that rice husk ash filler resulted in lower viscosity and shorter cure time of the natural rubber materials. Further impacts on the properties of the rubber with rice husk ash include increased hardness, decreased tensile strength and tear strength. Some of the properties like Young's modulus and abrasion loss, showed no significant change. Rice husk ash showed a better resilience property than that of silica and carbon black.

For the past few decades, the use of pozzolana as cement replacement in concrete and mortar has been very common for a number of reasons including cost reduction, performance & durability enhancement or environmental reasons [30,64]. With the addition of water, the pozzolonic material, acts as cement, while in some instances providing a stronger bond than cement alone. This can allow for cheap building material without the loss of performance, which is crucial for any developing nation to continue its growth. The addition of rice husk ash to a concrete mixture, apart from other positive impacts, has been proven to increase corrosion resistance. It has a higher early strength than concrete without rice husk ash, which forms a calcium silicate hydrate gel around the cement particles which is highly dense and less porous [65]. This will prevent the cracking of the concrete and protect it from corrosion by not allowing any leeching agents to break down the material. Song and his colleagues found that the incorporation of RHA up to 30% replacement level reduces the chloride penetration, decreases permeability, and improves strength and corrosion resistance properties.

Pushpakumara et al [66] 2012, tried to increase the content of rice husk ash in concrete by activating it with $Ca^{++}$ to concrete. Solid masonry blocks, having the size of 360 mm x 100 mm x 170 mm, were cast with the mix proportion of 1:6 Cement - Sand. Blocks were manufactured in two series. In the first series, RHA was used as addition with respect to weight of cement. In this series, four different RHA contents (i.e., 0%, 5%, 10%, and 15%) were used with constant lime content (10%). In the second series, RHA was used as partial replacement for cement with four different RHA contents (i.e., 5%, 10%, 15% and 20%) with constant lime content (10%).The blocks were tested for 7, 14 and 28 Day compressive strength. With the presence of lime (10%), the optimum 28 Day compressive strength was found at the level of 10 % RHA. When RHA was used as an addition, the optimum 28 Day average compressive strength of the block was found as 4.937 $N/mm^2$. When RHA was used as partial replacement for cement, 28 Day average compressive strength of the block was found as 3.467 $N/mm^2$. Thermal performances of the RHA lime based blocks were also investigated. It was found that thermal conductivity of RHA lime based block was lower compared with that of the conventional block. The RHA lime based blocks showed better structural and thermal performances.

## 3.2. Geotechnical application.

The use of coal fly ashes in Geotechnical application is second to that of cement and concrete. Geotechnical is a broad term which includes grouting, asphalt filler, sub-grade stabilization, general engineering fill, pavement base course, structural fill and soil amendment [66-67]. Coal fly ash is being used as stabilizer for soil due to its beneficial properties. It is found that fly ash addition to soil tends to reduce the susceptibility for water absorption and swelling of the soil. When montmorillonite content in the soils is high, severe swelling problems may occur, they tend to expand and shrink in wet and dry condition respectively. This expansion shrinkage causes a movement which exerts pressure causing ultimately the crack of pavements, basement floors, driveways, pipelines and foundations. With The addition of coal fly ash to the soil the mineralogy changes due to pozzolonic reaction due to which the soil becomes more granular and holds less water as a result of which swelling associated with water absorption is decreased [47,67].

## 4. Future applications of ashes in applied fields

### 4.1. Adsorbents

Coal fly ash can be used as an excellent adsorbent both for gaseous and aqueous applications in pollution control. In early 1984, coal fly ash was thought as an excellent adsorbent for the removal of Copper (II) ions from industrial effluents and other waste waters of environmental importance [68]. An investigational analysis of a particular coal fly ash resulted good Langmuir isotherm, which created good design data suitable to produce pilot scale reactors. Later on, different metal ions from waste waters like Cu 49]; Pb [69]; Zn [70]; Mn [71]; Cd [72]; Cr [73]; and Ni [74] were removed by using coal fly ash with different compositions.

Irfan Hatim and Umi Fazara [56] reported the technical feasibility of commercial sugarcane bagasse based activated carbon (SBAC) and chemically treated sugarcane bagasse based activated carbon for the removal of $Cu^{2+}$ from samples. A batch wise process using simulated wastewater was developed. SBAC with particle size 1-2mm containing 4.8 wt % ashes was treated with an aqueous mixture of hydrofluoric acid (HF) and nitric acid ($HNO_3$). The ash content was reduced to 0.3 wt % respectively. The modified adsorbent was physically and chemically characterized using scanning electron microscopy (SEM), BET surface area analysis and Boehm’s titration. The BET analysis shows that chemically modified sugarcane bagasse based activated carbon can reach the surface area of 1120 $m^2/g$ from non- treated sugarcane bagasse based activated carbon that is 837$m^2/g$.

Dyes production industries and many other industries which use dyes and pigments generate wastewater, characteristically high in color and organic contents. Presently, it was estimated about 10,000 of different commercial dyes and pigments exists and over 7 x $10^5$ tones are produced annually worldwide [75]. These dyes causes water pollution, the removal of which is of great interest. Different techniques are being used for the removal of these dyes.

Aquatic environment has been very much polluted by the presence of heavy metals which is of great concern. Some of the metals are mutagens in nature like copper, zinc, and chromium and are highly toxic. Due to the high cost of treatment methods, the removal of such toxic metal ions is a very tricky job. Recently, researchers have taken an interest in the production of low-cost adsorbent like activated carbon from bagasse ash which remains an inexpensive material. Taha [76] used bagasse ash as a low cost and effective adsorbent for the removal of $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, and $Cr^{3+}$ from industrial waste water. The adsorption capacity was studied as a function of pH, adsorbent dose, metal ion concentration, shaking time, and diver's ions. Under the optimum conditions used, more than 95% of some of the ions under study were successfully removed.

### 4.2. Catalysts

Catalytic applications of coal fly ash has been reported by a number of authors. The objectives of the catalytic applications of coal are to reduce the consumption of materials having limited reserves and are costly to manufacture [9]. The use of fly ash as a material to be used in heterogeneous catalysis has been receiving a great deal of importance. Heterogeneous catalysis is very much attractive due to its easy recovery and the catalysts after the completion of the reaction is relatively homogeneous. As in heterogeneous catalysis, catalytic materials are supported on some other materials so its activity mainly depends both on the active component and its interaction with the support material. Usually a catalyst support materials include a range of metal oxides such like alumina and silica [77]. Coal fly ash can be employed as support material in various catalytic activities. It has been used as the catalytically active component. Coal fly ash has been used as a support material for nickel in different synthetic reactions. It was shown that treatment of the ash with lime earlier to Ni loading could produce catalysts capable of high conversion and stability with activities close to the well reported Ni/$Al_2O_3$ and Ni/$SiO_2$ systems [10,34,78]. Coal fly ash being made up of $Al_2O_3$ and $SiO_2$, it may offer desirable properties such as thermal stability to be used as a support. It has been studied that the potential for the selective catalytic reduction of NO by ammonia with ash supported Fe, Cu, Ni, and V catalysts; the Cu loaded coal ash displayed the highest activity [79]. Coal fly ash has also been coated with a $TiO_2$, which is very effective for photocatalytic

Coal fly ash with a loaded sulphated Zirconia by a sole-gel technique has been used for the synthesis of a highly active nano-crystalline thermally stabilized solid acid catalyst. The catalyst has been used for its performance in a number of processes, like liquid phase benzylation of benzene and toluene with benzyl chloride. The conversion of benzene and toluene were reported as high as 87% and 93%, respectively [72,80].

It has been demonstrated that the activation of $H_2O_2$ can be carried out with a $Fe^{3+}$ loaded on fly ash and is used for the oxidation of dye organic dye. For this purpose coal ash with high iron content has been used for the preparation of photocatalyst by leaching iron ions under acidic conditions and then precipitating amorphous FeOOH on the surface of the residual ash. The catalyst was studied for the determination of its activity in the effective photocatalytic degradation of organic dye methyl orange up to a pH of 9.0 [81].

Coal ash has been widely used for the catalytic oxidation of volatile organic compounds like oxychlorination and the deep oxidation reaction of phenol and monochlorophenols [82].

Coal fly ash with acid activation has been used to produce a nano crystalline solid acid catalyst which has been used for the estrification of salicylic acid with acetic anhydride and methanol to produce acetylsalicylic acid and methyl salicylate in a single step, without using any solvents. During this process the purity and yield were reported greater than 90% [83]. Similarly synthesis of solid base catalysts from coal fly ash using NaOH pre-treatment followed by thermal activation has been described which were found to have as high conversion as 70% and selectivity as high as 80% during the condensation reaction of benzylaldehyde and cyclohexanone to di-benzylidene Cyclo hexanone [84].

The oxidation of sodium sulphide in the air, has been investigated which is emitted from different industrial processes, including paper mills and tanneries [25,84]. The increase in the reaction rate factor was reported as 3.5 factor increase in reaction rate with a 4 wt%. Fly ash loading as compared to 4.52 relative to no fly ash addition at the same loading and temperature, but using $H_2O_2$ as the oxidant.

Coal fly ash has been assessed for its potential to be used as a photocatalyst in the removal of dyes from water under visible light. It has been reported that the removal of thionine up to 60% is possible after four hours from a starting concentration of $10^{-4}$ M [85].

## 4.3. Ceramics and Glass

Coal fly ash has received attention as a low cost and good material for the manufacture of ceramics, glass ceramics, and glass materials as is made up of oxides like $SiO_2$, $Al_2O_3$, CaO, and $Fe_2O_3$ [86], schematically shown in figure 5. The basis for the manufacture of such ceramics is the temperature activation of the raw coal fly ash with variations in temperatures and co-reagents directing the final form of the glass or ceramic.

Erol et al. [86] has manufactured glass, glass-ceramic and ceramic material from coal fly ash without the addition of any other additive. Physical and mechanical studies of these prepared material revealed that the these materials obtained from the waste fly ash was in good comparison with literature values for glasses and ceramics derived from waste and non waste sources. Apart from basic raw material for the manufacture of above material coal fly ash has also been considered in the manufacture of the ceramic cordierite as a replacement for kaolinite [87].

Fly ash of particle size less than 44 µm was mixed with alumina and magnesium carbonate a powder which was milled with methyl cellulose and the blended components were then pressed into discs before sintering at temperatures between ranging from 900 to 1300 °C. The composition of the mixture was 64-68 wt% ash, 10% alumina, and 22-

26% magnesium carbonate. The mixture was heated at 1200 and cordierite was produced at sintering temperatures of over 1200°C.

Ceramic tiles of category BIII according to EN 14411 has been prepared by mixing coal fly ash with kaolinitic clay in the ration of with 60:40 [87]. Different varieties of Glass ceramics were made using different fluxes like $CaCO_3$ and $Na_2CO_3$ both with and without the addition of $HBO_2$. Glass ceramics made with different types of fluxes formed the main crystalline phases like wollastonite ($CaSiO_3$) and anorthite ($CaAl_2Si_2O_8$). Although both ceramics exhibited good mechanical properties, but the one made with fluxes, including the $HBO_2$ were very advanced.

Glass, ceramics have also been prepared by melting ash with CaO and $TiO_2$ as nucleating agents to decrease the temperature of melt process [88]. The melts were annealed at the glass transition temperature of (+10 °C). Glass, ceramics produced using the optimum conditions showed good wear resistance and fracture toughness which indicated their potential to be used as building materials. Another useful application of fly ash is the production of Ceramic micro-filtration tubular membranes, which was prepared with the objective to filter the effluents from textile dyeing processes [89]. Such membrane includes both a macro porous support and a micro filtration active layer. The manufacture of support occurs in two stages; in the first stage coal fly ash is calcined and in the second stage it is mixed with binding agents to form a paste which is molded into tubes and then sintered. The micro-filtration layer was applied using ground ash in the range of 0.5- 2 µm). slip-casting method was followed for the deposition on the support using a dip solution containing the fly ash powder and polyvinyl alcohol as a binder. The ceramic membrane, after preparation was used for the cross flow membrane treatment of textile dye effluent, which achieved as high as 75% removal of chemical oxygen demand (COD) and 90% removal of color. In another study [90] it has been demonstrated that a double coated membrane had a smaller pore size and narrower size distribution than a single coated membrane.

### 4.4. Geopolymers

Geopolymerisation was first developed in the 1970s by Joseph Davidovits in which a chemical reaction between aluminosilicate oxides and alkali metal silicate solutions occur under strongly alkaline conditions and give amorphous or semi-crystalline polymer structures (Si-O-Al) bonds. Geopolymers exhibit a good physical, chemical, and mechanical property which includes low density, micro and nano-porosity, low shrinkage, high mechanical strength, good thermal stability, durability, surface hardness, fire, and chemical resistance. Given these desirable properties they are seen as potential alternative cementing materials for ordinary Portland cement in mortar and concrete [91].

The alkaline activation of alumino-silicate material can be described as the reaction of a liquid with a high alkaline concentration and a solid with a high proportion of reactive silicate and aluminate. When the liquid to solid ratio in the mixed is in the range of 0.2-1, the resulting paste set and hardens like ordinary Portland cement. The alkaline activated binding material forms a gel with the composition $Na_2O.Al_2O_3.rSiO_2.nH_2O$, or simply N-A-S-H, with r ranges from 2-5 [92]. On Nano scale these gels show three dimensional arrangements and of an amorphous nature as determined by XRD. Many studies have shown that there is often observed in the crystalline and semi crystalline phases, but these are generally zeolitic material which appears to be more prevalent when the synthesis conditions are kept hydrothermal. It is thought to be as a result of improved solution phase transport [93].

The desired properties of any geopolymer product are affected by many factors. For example the existence of metal cation in the alkaline activator plays an important role in the formation of the geopolymeric network while that of $OH^-$ ion acts as the reaction catalyst, the alkaline metal cation acts as the structure forming elements. It balances the negative framework charge carried by the tetrahedral aluminium. The silica and alumina in the alkaline solution are liberated from coal fly ash so it can be predicted from strong alkali like KOH exhibit greater dissolution ash comparatively weaker alkali like NaOH. It is also thought that the reason for this phenomenon is the smaller ion size and greater charge density of $Na^+$ relative to K+ due to which it has the ability to migrate more easily through the gel network or because of a higher charge density [29, 64]. It has been pointed out that KOH has much lower geo-polymerization potential as compared to NaOH. Moreover, both NaOH and KOH are still lesser than sodium silicate activators with respect to geo-polymerization [94]. Similarly, it has been studied that the leaching of fly ash in alkaline solutions of KOH and NaOH to assess the effect of the addition of soluble silicate solutions on dissolution rates. It was found that when the soluble silicate dosage was lower than 200 mm, the dissolution was retarded by secondary precipitation on the surface of coal fly ash particle. On the other hand, when the soluble silicate dosage was higher than 200 mM, the significant structural alteration was observed. The enhanced aluminosilicate dissolution was followed by precipitation of a new aluminosilicate gel phase; the mechanism is believed to be that of the formation of geopolymers. Panias et al. [95] concluded that the addition of sodium silicate increases the compressive strength of the formed geopolymer concrete linearly increases to a certain $SiO_2$ content. Above this value the compressive strength dropped off, which was attributed to increased viscosity of the geopolymer pastes hindering the molding properties and workability. It has also been investigated that the strength of geopolymers depends on the ratio of $SiO_2/Na_2O$. The strength of the alkali solution plays an important role in the overall strength of the manufactured geopolymer. The optimum concentration of sodium hydroxide solution for the production of high strength geopolymer was found to be 6.6M [96]. On the contrary, it has been found out that the compressive strength of geopolymers is highest with alkali concentrations of 14 M, and no deterioration of strength over a certain concentration was observed [96].

A number of factors are responsible to control the extent of dissolution of aluminium and silicon ions in strong alkaline solutions like particle size, morphology, vitreous phase of material and the chemical composition of the raw material [14, 97]. Previous researches have shown that the reactivity of the source material can significantly affect the strength of the prepared geopolymer. Two different fly ashes were used as source materials, a predominantly amorphous, and a significant crystalline one. The ash with a highly crystalline fraction produced geopolymer with a much lower early compressive strength than that with amorphous one [34,98]. Other studies have also shown that the chemical composition of the ash can affect the application of the geopolymer. For instance, it has been shown that a high iron contents in the ash appear to have an adverse effect on high temperature resistance performance of geopolymers. It seems that this is the result of the fact that there is an amorphous iron oxide particles within the ash due to which it does not dissolve into NaOH and silicate solutions [99] which results retention in the produced geopolymer as a filler particle.

4.5. Recovery of metals

Coal fly ash is considered as a potential source of different valuable metals which have important applications. For example germanium (Ge) and gallium (Ga) are considered as a critical strategic metal as are extracted in a few countries [100]. Germanium is a very important element used in the manufacture of photovoltaic cells, light emitting diodes, fiber optics and infrared devices. Moreover, it is used as a catalyst in the production of polyethylene terephthalate. This metal is usually present in as trace content in coal. It has been found that coal of UK contains 0.3 to 15 ppm, and it is suspected that it is associated with the organic matter in the coal [101]. When coal is burnt, this germanium is concentrated up to 10 times higher than in the original coal. The Ge content in coal and coal combustion ashes is regarded as a potential source. It has been suggested that the Ge and Ga content of coal ash exceeds production by a factor of 200. Different recovery methods have been used, including the use of the occurrence of Ge as water soluble species like $GeS_2$, GeS, and hexagonal $GeO_2$ in gasification of the fly ash [102]. Other methods used for the isolation of the said elements from coal ash include the complexing agent like catechol to bind the Ge. For the removal of Ge-catechol complex made with a synthetic aqueous Ge from the aquous solution, activated carbon was used as adsorbent. This method has a high selectivity for Ge in the presence of other metals in the solution. Torralvo and Fernández [103] used strong anionic ion exchange resins instead of activated carbon for the removal of Ge-catechol from aqueous solution.

A maximum yield of about 96% was achieved in this process. Reutilization of the resin was studied with extraction yields of 97.6-98.3%.

Solvent extraction is considered.

Another most acceptable method for the selective removal of the Ge - complex from the aqueous system. Arroyo et al. [104] designed a solvent extraction unit using data from a pilot scale investigation and achieved the production of 1.3 g/h of Ge, to economically evaluate the potential of scaling this design up to process 200 kg/ h of coal fly ash.

Like germanium, Gallium is also a very applicable element which is widely used in optoelectronics, aerospace, telecommunication, alloys, computers, and DVD. Ga is usually recovered from the refining processes of aluminium and zinc. The ore of aluminum, Bauxite is the largest source of Ga containing 0.003-0.008% of Ga and is the result of treating an effluent stream of the Bayer process [105]. Though crustal abundance of Ga is only 16 ppm, certain coals are enriched in Ga, and this content is further enriched when coal is combusted. The reported concentration of Ga in different coal fly ashes ranges from 37.5-320 ppm.

The use of coal fly ash for the recovery of metals like alumina and silica has been reported by several authors. Several methods for the recovery of alumina from fly ash have been reported. Direct sulphuric acid leaching with low concentration and ambient temperatures does not yield high aluminum recoveries [69], direct sulphuric acid leaching produced an aluminum extraction of just 18% [70] while coal fly ash containing fine coal and lime impurities and calcined at high temperature leached with sulphuric acid gave 85% recovery.

Three extraction methods have been reported like solvent extraction, selective pH precipitation and crystallization. The only feasible method was found to be a solvent extraction method. The aqueous leachate was contacted with the organic solvent, and this selectively loaded $Ti^{4+}$ and $Fe^{3+}$ ions into the organic phase. The obtained product alumina was as pure as 99.4%. 92-97% $TiO_2$ was obtained as a by-product. Concentrated sulphuric acid has also been used for leaching both the titanium and aluminium extraction process from the coal fly ash. With addition of concentrated sulphuric acid the pH was decreased till the precipitation of titanium from solution.

High purity alum (99.9%) has been prepared from fly ash with ammonium sulphate [106]. The reaction was carried at 400 °C. The product was hydro thermally leached with concentrated sulphuric acid. Ammonium hydroxide was added to the leaching liquor and was aged for 24 hours. The purity of the precipitate was further increased using a method of dissolution precipitation. Finally the precipitate was calcined using normal and conventional heating. α alumina and γ alumina were formed as a result of microwave and normal heating respectively.

### 4.6. Fly ash as a cement replacement in mortar and concrete

In the present world construction industry is growing very fast. Human beings use different types of ashes in cement at different stages for different purposes. It is clear from the finding of Flower and Sanjayan [107] that 80% of the $CO_2$ emissions from the concrete mixes are due to the inclusion of Portland cement. 7% of the global anthropogenic $CO_2$ emissions is made during the production of Portland cement. Production of one ton of cement produces one ton of $CO_2$ due to the raw material and fuel burning during the clinkerization. The use of ashes in concrete as a substitute of cement decreases the emission of greenhouse gases.

A different amount of ashes is being mixed in concrete as a cement replacement depending upon different factors including the chemical composition of ash, required properties of concrete. In general 40% and 35% replacement is made as per ASTM C 595 and EN 197-1 respectively. According to ASTM C 1157 no limit on the components of blended cements is fixed. Similarly the International Building Code states that the optimum amount of fly ash is determined by the required properties of the concrete and is to be established by testing [108]. In a Common practice, the optimum replacement of coal fly ash is limited to 15-20%. This replacement is sufficient to have a positive effect on the workability and cost economy of concrete. If this replacement is increased up to 25-30% further improvement in the workability of concrete can be achieved like durability to sulphate attack, alkali-silica expansion, and thermal cracking. The use of cement at such high level of substitution is said to be High Volume Fly Ash concrete and is constituted by a minimum of 50% fly ash, low cement content (<200 kg/m3), a low water content (130 kg/m3), and a low water/cement ratio (<0.4) [109-110]. High Volume Fly Ash concrete has become of high interest because of the environmental and economic benefits associated with its use. A high level replacement up to 50-75% has been reported with good properties like Enhanced workability, Early strength up to 7 days, High gain in Later strength at 28 and 90 days, Better dimensional stability, Increased resistance to thermal, autogenous, and drying shrinkage, High electrical receptivity, Resistance to chloride attack and penetration, Greater durability to concrete reinforcement corrosion, Alkali silica expansion, Resistance to sulfate attack.

Though the later strength development is very much important with respect to making concrete, it also results in a significant disadvantage of using high volume fly ash concrete in practice. In spite of the use of these mixtures in the field, increasing, it is commonly remarked on by concrete workers that HVFA mixes can be vulnerable to long delays in finishing and occasionally lack the required early age strength.

The rate of strength development setting times decreases with the increase in the coal fly ash incorporation into high volume fly ash concrete. Setting times can be increased by as much as 2 hours with high volume fly ash concretes using different treatments [111]. For example, this problem can be alleviated to some extent by incorporating rapid hardening cement or $Ca(OH)_2$ powders. The reduction in setting time is ash specific and requires further field study. Berry et al. [112] showed the performance of 100% ash concrete manufactured using a high calcium class C ash with respect to its performance in workability, short and long term strength development, structural behavior and durability. Short and long term strengths were achieved as 27.5 and 55.2 MPa respectively.

## 4.7. Extraction of amorphous silica

Rice husk ash is used as a source for the extraction amorphous silica. Nittaya Thuadaij 2008 [113] used rice husk ash for the extraction of silica. The reaction completed in two steps. The initial step is the extraction of silica from ash as sodium silicate using caustic soda. This reaction is carried out at a temperature in the range of 180-200 $^{\circ}$C and pressure ranging from 6-8 atm.

The reaction is

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

But low reaction temperature and pressure can be used if ash obtained by burning rice husk at 650°C is used. This ash obtained is mostly amorphous silica, which is reactive with NaOH solution at around 100°C to yield sodium silicate. A viscous, transparent, colorless sodium-silicate solution is obtained after filtration of the reacted slurry. In the second reaction, amorphous silica is precipitated from sodium-silicate using sulphuric acid. Controlled conditions are required for the addition rate of sulphuric acid and temperature of reacting mass in a neutralizer. The temperature is in the range of 90-100°C and pressure is the normal atmospheric pressure.

The reaction is:

$$Na_2SiO_3 + H_2SO_4 \text{ -------------> } SiO_2+Na_2SO_4+H_2O$$

Silica is digested from ash using caustic soda as sodium silicate. Reaction of sodium-silicate with sulphuric acid precipitates silica. The purification and drying produce silica in white amorphous powder form. This work presented a laboratory studies on the preparation of rice husk ash by burning at 700°C for 3 and 6 hours, respectively. Consequently, silica content obtained after heat treatment at 700 °C for 6 h was 98.14%. Rice husk ash (RHA) was purified by alkaline extraction method used 2.0, 2.5 and 3.0 N sodium hydroxide. Percent yield of silica extracted by 2.5 N. NaOH, was 90.3% and the infrared spectral data supported the presence of the hydrogen bonded silinol group and the siloxane groups in silica. Subsequently, the RHA was subjected to precipitation method in order to produce nanosilica. The precipitation was done by refluxing silica from RHA in boiling 2.0, 2.5 and 3.0 N NaOH, respectively. TEM results showed that 2.5 N NaOH for 10 h provided agglomerate particles with dimension of 5-10. The specific surface area was found to be 656 m2/g. From X-ray diffractograms and diffraction pattern showed that the obtained products were amorphous nanosilica.

Kalapathy et al, [114] used rice husk ash silica extract for the production of flexible and self-supported sodium silicate films. Silica was extracted from the rice husk ash using 1 N NaOH. The extract was concentrated by volume reduction and adjusted to 3 N NaOH. Concentrated silica extracts in 3 N NaOH solutions were used to produce flexible silicate films. XRD analysis showed that silicate existed in an amorphous form in the film. Methyl oleate was used as plasticizers. The effect of this plasticizer in the presence and absence of the emulsifier lecithin on the film properties was also investigated. The interaction of silicate and methyl oleate (MO) in the films was mainly due to siloxane groups as indicated by FTIR data. Percent elongation for silicate film alone, silicate film with MO and silicate film with MO and lecithin were 12, 15 and 17, respectively as measured by a texture analyzer. Mechanical strength of silicate films was not significantly affected by the addition of MO and lecithin. All the silica based films were permeable to water vapor and excellent barriers for hexane and iso-octane.

Kalapathy et al, [115] developed an improved method for the production of silica xerogel with lower sodium. The previously published methods for producing silica xerogel involved the dissolution of rice husk ash silica with an alkali solution to form sodium silicate and afterward forming silica aquagel when hydrochloric acid is added to lower the pH from 11.8 to 7.0, followed by washing and drying the aquagel to form xerogel. The silica xerogel had over 4% sodium as a contaminant while the improved method involved the production of silica aquagel by adding silicate solution to pH 1.5 hydrochloric, in the citric, or oxalic acid solutions till the pH of 4.0 was reached. The aquagel was washed and dried to form silica xerogel. Silica xerogels were also produced at pH 7.0 using the same protocol for comparison purpose. The silica, sodium, carbon and oxygen content of silica xerogels were varied depending on the pH and the type of acid used for the preparation of these xerogels. Sodium content in the silica xerogels obtained by the improved method with citric and oxalic acid was 0.52% and 0.22%, respectively.

Zaky et al [116] used the semi-burnt rice straw ash as a waste material provided from gas production unit of rice straw for the preparation of silica nanoparticles. Box-Behnken statistical experimental design was used to optimize the factors affecting the dissolution efficiency of the silica such as stoichiometry (NaOH: $SiO_2$), reaction time and reaction temperature, and to determine the optimum conditions for the extraction process. X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) have been used for the characterization of the SBRSA while UV/VIS/NIR Spectrophotometer was used to measure the concentration of the silica in the solution. The results show that the main constituent of SBRSA is silica (62%). Statistical design shows that the dissolution efficiency was in an agreement with the generated model and the experimental results. It is observed that the dissolution efficiency of silica was increased by increasing leaching temperature, time and stoichiometry. At stoichiometric value 1 and 2, the dissolution efficiency of silica was increased by increasing leaching temperature and time and did not reach 99% efficiency. The dissolution efficiency reached 99.88% at 100 °C and 4 hours with increasing the stoichiometric value up to 3, Rice husk ash has been used for the extraction of silica [34]. Precipitated silica has found a number of applications in various industries like food industries, tyre industries, paint industries, cosmetics industries and many others. All these industries need silica of different grades, which are characterized by grain size, adsorption capacity, purity and depth density. The schematic diagram for the silica extraction is shown in figure 6.

## 4.8. Mesoporous materials

In a number of separation and catalytic processes, porous solid materials have their importance. A number of researchers have reported the discovery of many such materials like M41S containing uniform mesopores for such applications. The newly designed materials are getting very importance due to the high cost and toxicity of conventional reagents [117]. Coal fly ash has been getting very importance for such purposes as having a potential as a source of silica for the manufacture of mesoporous silica. The methods of manufacture of these materials have very similarities to that of zeolite synthesis. Kumar et al. [118] manufactured the same material in two stages. In the first stage zeolite was prepared by the alkaline fusion method and in the second stage the fused material was mixed with water and aged for 24 hours, the solution was filtered and the supernatant was mixed with cetyl trimethyl ammonium bromide and ammonia solution. The mixture was hydrothermaly treated for about for 4 days. MCM-41 was obtained using the same method and was subsequently aluminated using trimethyl aluminum to produce another porous material Al-MCM-41, which incorporates aluminum into the framework. It is suggested that Al-MCM-41 material is very suitable material for the use in the cracking of cumene but that it is not as effective a materials synthesized from pure reagents.

Mesoporous silica SBA-16 has also been synthesized using coal ash as a source of silica and subsequently employed it as a template to manufacture mesoporous carbon [119]. With the additional sodium metasilicate solution to the supernatant prior to reaction, the surface area was reported to be 649 m2/g. This method was comparable to the conventional methods of synthesis which produced materials with a surface area of 683 m2/g. However the pore volume was as high as 5.4 nm with the use of coal fly ash as a silica source as compared with using pure raw materials (4.1 nm). Different methods for the preparation of mesoporous material based on a two-step hydrothermal synthesis of zeolites have been reported. First the extraction of silica was conducted hydrothermally using a NaOH solution. The solution was then mixed with cetyl trimethyl ammonium bromide with the addition of ethyl acetate. The silica extraction method is more economical extraction conditions in addition to ethyl acetate being both cost effective and environment friendly. There was no reference to how pure reagent materials performed in the study so. It is difficult to judge its efficacy, although a wide range of pH reaction conditions were studied as there was no reference to how pure reagent materials performed in the study. It is generally known that material synthesized at a higher pH had a larger pore size and are more hydro thermally stable. Although much attention has been paid to the manufacture of mesoporous silica derived from coal ash, there has been little scrutiny of the potential applications for such materials. However, MCM-41 was synthesized using the alkaline fusion method and cetyl trimethyl ammonium bromide as the template [22,65]. It was tested for its utility in the catalysis of the classical Mannich reaction. The MCM-41 derived from coal ash is more favorable as compared to other catalysts studied by the author.

### 4.9. Zeolites

Zeolites is one of the most important group of crystalline aluminosilicate material, which may contain an infinitely extending three-dimensional anion network made up of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedron, which are linked at the corners by a shared oxygen atoms. The three-dimensional framework gives rise to the special properties of zeolitic materials. The voids and internal channel of the network allow easy access of molecules leading to fast diffusion rates, which make zeolites suitable materials for adsorption. The substitution of Si (IV) by Al (III) in the structure accounts for the overall negative charge; which means that the zeolites have the potential to show high cation exchange capacities up to 5 meq/g [120] leading to possible applications in ion exchange or as a molecular sieve.

Zeolites require a source of Si and Al ions, an alkaline environment, and usually an elevated temperature for the synthesis. Time for the Zeolite formation may be in the order of hours, days, weeks, or even months, depending on the nature of the reactants and the temperature of the reaction [35]. For the first time zeolite was synthesized by the application of alkaline hydrothermal using coal fly ash as a source of Al and Si ions by [13,33]. The flow sheet diagram for the synthesis of zeolite using alkaline hydrothermal method is shown in Fig. 7. Using the same procedure as developed by Höller and Wirsching, many attempts have been made to synthesize zeolites from fly ash using a one stage hydrothermal method. but all faced the only problem that reaction can not be sped up and temperature of about 125-200 °C must be applied in order to dissolve the silica and alumina. Under such conditions the formation of larger pore, and more valuable, zeolites is slowed down.

However, phillipsite, herschelite K-chabazite, and other high-CEC zeolites have been obtained with a maximum yield of the synthesis at a temperature of 125-200°C [121]. Different experimental conditions, activation solution/fly ash ratio, temperature, pressure, and reaction time results with different types and yields of zeolite.

The two stage hydrothermal methods for the synthesis of zeolite, which has been the subject of considerable subsequent interest, has been introduced by [122], which is much similar to alkaline fusion. In the first stage silica is extracted from the ash using sodium hydroxide solution. The silica to alumina ratio (Si/Al) of this solution is adjusted. In the second stage zeolite crystallization is achieved at a temperature below 100 °C.

Kartick et al, [123] prepared ZSM-11 zeolite particles through in-situ extraction of silica from rice husk ash using sodium aluminate and tetrabutyl ammonium hydroxide as aqueous-based precursors following a simple hydrothermal condition at 100 °C. The synthesized zeolite was characterized using different techniques like X-ray diffraction, Fourier transform infrared spectroscopy, thermogravimetric analysis, differential thermal analysis and field emission scanning electron microscopy (FESEM). The crystallization of ZSM-11 obtained at 100 °C for 12 days was confirmed from XRD pattern. The presence of double 5-ring in the pentasil zeolite structure of ZSM was confirmed from the vibration bands at around 548 and 1221 $cm^{-1}$. The exothermic peak at 463 °C in DTA curve confirmed the removal of tetrabutyl ammonium ion which was used as a structure directing agent. FESEM image showed that nano-sized ZSM-11 particles were agglomerated in the crystals. The Si/Al ratio of ZSM-11 particles was found to be 51 as indicated by the elemental analysis with energy dispersive X-ray (EDX).

Different applied conditions are responsible for different types of pure zeolites (A and X) which can be obtained from fly ash. The solid residue is mixed with the solution from the second step of the process to form further zeolitic material, which may have lower purity. The disadvantages of such manufacturing of the zeolite in this way may include the intensive usage of water, the extra costs of reagents and long incubations times. In spite of some disadvantages good CEC values like 3.6 to 4.3 meq/g were obtained for the pure zeolites as compared to the residual fly ash contaminated zeolites (2.0-2.5 meq/g). Anyhow the single step process is comparatively less expensive as compared to the two step process, but the high cost of the two step process may be justified by its greater application potential in wastewater treatment for heavy metal ion removal. Some authors have reported the two step process for the manufacture of pure zeolites from waste stream from the aluminium industry to provide the source of Al ions. Extraction of pure silica from Fly ash in pure form up to 190 g $SiO_2$/kg in a single step process and six hours time was achieved.

Samsudin Affandi et al [124] reported the synthesis of mesoporous silica xerogels in high purity from bagasse ash. The bagasse ash was chosen as the raw material due to its availability and low-price, and environmental considerations also were important. Silica was extracted as sodium silicate from bagasse ash using NaOH solution. The sodium silicate was then reacted with HCl to produce silica gel. To produce high-purity silica xerogels, three different purification methods were investigated, i.e., acid treatment, ion exchange treatment, and washing with de-mineralized water. High purity silica

(>99 weight %) was produced by washing the produced gels with either de-mineralized water or with ion exchange resin. The specific surface area of the prepared silica xerogels ranged from 69 to 152 $m^2 g^{-1}$ and the pore volume ranged from 0.059 to 0.137 $cm^3 g^{-1}$. The pore radii were 3.2-3.4 nm, which indicated the mesoporous nature of silica xerogels. The obtained silica xerogel was studied for its adsorption capacity. The maximum adsorption capacity by high-purity silica xerogel was 0.18 g-$H_2O$/g-$SiO_2$. It has been demonstrated that the potential of bagasse ash in mesoporous silica production with its excellent adsorptive capacity, which makes it beneficial as an environmental solution.

### 4.10. Direct applications of coal fly ash

In many applications coal fly ash has been used without any further pre-treatment like in agriculture, as an adsorbent, or in some circumstances as a catalyst. Many benefits are associated with the direct use of Coal fly ash, but this may come at the expense of effectiveness. For instance, though fly ash is applied to soil as amelioration agent there are issues regarding potentially mobile toxic elements being applied to soil which may be used in the growing of crops. To avoid such problems, the pre-treatment steps have been considered [15,67]. Moreover the chemical nature and morphology of different ashes may also hinder their direct use. The indirect applications of ash may combine a number of chemical, thermal, and mechanical methods of activation in order to produce the required formulation. A number of variable products can be formulated by the simple processing of coal fly ash as shown in figure 8. This diagram shows the potential significance of coal fly ash with respect to the design of different new derived products. In order to improve the productivity and decrease the wastes in ash, it is important to identify where multiple products might be obtained from the same processing step.

## 5. Recovery of other value added materials

### 5.1. Carbon recovery

Carbon recovery using electrostatic separation has been attempted by several investigators [125] for the reduction of loss on ignition of fly ash in beneficiation process in many respects. This process may operate on the principle of bipolar charging of dry particles by different ways like particle-particle contact or particle-wall collision under turbulent conditions. The separation of positively charged carbon particles from the negatively charged ash particles becomes possible in an electric field. Though this technology has now been commercialized in many respects, it has to be ensured that the ash is sufficiently dry prior to the beneficiation process which means that the separation efficiency can be significantly diminished. Other beneficiation technologies which have been commercially applied are that of fluidized bed reactors, which are capable of processing a continuous stream of fly ash using a thermal process designed to burn out the remaining carbon. The heat from the flue gas and product ash is recovered and used to pre-heat the steam condensate from the power station and reduces the thermal load on the power station.

In order to achieve good yield, high grade of carbon and primarily for the purpose of characterization studies a combination of sieving and froth flotation has been employed. Another similar technology to froth flotation is that of oil agglomeration which relies on the preferential wetting of oleophilic/hydrophobic particles of oil added to aqueous slurry. This would involve the carbon particles wetted by the oil and the ash mineral particles remaining in suspension. The vessel is then agitated, which causes the oil coated particles to collide with each other and form agglomerated particles. These agglomerates rise up to the top of the vessel due to the lesser density as compared to the ash suspension. Using this method with cyclohexane as the solvent, the carbon purity and yield achieved was (66-71%) and (55-57%) respectively [126]. Carbon purity in the same range has also been reported by other researchers using vegetable oil as solvent but, as this was a characterization study, no recovery data was included. On comparing the three different isolation and separation techniques like a flotation column, an oil agglomeration column, and a triboelectrostatic separator, it was found that the flotation column was the best with purity grades of 61% and yield recoveries of 62%, but the ash product was only benefitted up to loss of ignition of 8% so further optimization of the flotation column and multi-stage process was suggested to improve the high yield and low LOI ash product. The author gives new directions to the researchers working on materials science/chemistry to work in the area and this will open a broad spectrum in the future.

### 5.2. Cenosphere recovery

Cenospheres are hollow spherical particles and are considered to be one of the most important value-added components of coal fly ash; they are similar in composition to the ash though they tend to have a larger particle size [55,127]. The exceptional characteristics of cenospheres, like their spherical nature and low density relative to water, make them acquiescent to a number of different applications. The techniques of cenospheres extraction have traditionally relied on the storage of ash large lagoons and the cenospheres can be removed from the surface of the water.

The ability of ash to leach toxic elements in such process is of high concern, but studies into the leaching behavior of a typical ash sample in the United State found that it was safe under natural leaching conditions [27,34,50]. However extraction of cenospheres from ash is both space as well as time intensive which does not allow for integration into a continuous fly ash processing unit. An alternative method for the extraction of cenosphere was reported by whereby a triboelectric separation system was applied. However, this method is dependent on the definition of the cenospheres as having a less than two specific gravity proposed by which is based on the fact that a solid particle of pure silica should have a higher density than that exhibited by the particles of ash. Taking into account that the gas bubbles could be trapped in particles with specific gravity of greater than 1. However, this definition is not the generally accepted definition in literature; despite, many of the high value applications for cenospheres rely on their very low density. Very few other studies have examined the extraction of cenospheres. A continuous operation is desirable in order to integrate the extraction of cenospheres into a wider beneficiation process of coal ash,

A theoretical treatment for the recovery process of cenosphere was carried out both on a wet and dry basis [72]. Dry process is comparatively more reliable as the wet processing causes a number of problems associated with environment. A comparison between the wet and dry separation can be made by using a size, density distribution of industrial cenospheres and ash. Making calculation of the terminal velocity of these particles using either water or air as the medium, the setting of an upward fluid flow rate is equal to the terminal velocity. The ration of particles reporting to the underflow and overflow can easily be found out. Density is the main factor in such separation. The important point in this experiment is that when water is used as a separating medium the cenosphere particles are moved upwards due to their positive buoyancy, causing a density separation. On the other side if air is used instead of water, then both the cenospheres and the ash particles have a density much larger than the air, so separation is not possible. For air separation, any disturbance in the size distributions of ash and cenospheres particles will reduce the efficiency of the separation. For water, the upward velocity that can be used is limited by the size of the smallest ash particles. Another finding of the theoretical analysis is that the performance of dry separation was marginally less efficient than that of wet separation.

## 6. Applications for fractioned ash products

### 6.1. Cenospheres

Cenospheres have a lot of inimitable properties like sphericity and their low density as compared to water. Such properties make cenospheres acquiescent to a variety of different applications. The ability that cenospheres float on the surface of water is of special interest to researchers working on the investigation of new photocatalysts. They can be used as a buoyant carrier to improve the catalytic activity as they increase the exposure of the particle to light sources [128]. Due to the fact that these particles float on the surface of water also means that they are easily recovered from water after the reaction. Cenospheres has also attracted interest for their use in water purification such as in the removal of excess fluoride from drinking water. This was achieved by producing cenospheres with loaded magnesia using a relatively simple wet impregnation method of magnesium chloride. This principle can be extended by applying functional layers onto the coal fly ash cenosphere. The properties of cenosphere have been changed by coating it with different metals. Some researchers have suggested the use of cenospheres as lightweight materials in the fields of electromagnetic interference shielding, electromagnetic wave absorbance, and high light reflectivity. Different methods of plating have been used but some of the most widely investigated are electrodless plating [81], magnetron sputtering [85], and heterogeneous precipitation [87]. Cenosphere has been used as a carrier and the advantage of using a cenosphere as the carrier are its sphericity, non-toxicity, high strength and light weight. This property makes it ideal for incorporating into materials like silicone rubber in order to improve the conductivity of rubber. Moreover, this enhances its suitability for its use as an electromagnetic wave absorbing material which can be used in electronic and radars [65]. Cenoshperes due to its lightweight nature renders them suitable for the design of lightweight composite materials. A number of different composite materials have been evaluated, like the incorporation of coal fly ash into concrete [129], polymers, resins [130], and metal alloys [131]. Their use in such applications reduces the extent to which energy intensive and resource dependent materials are used. Their use also confers some advantages to the composite structure in the case of the metal alloys. In cast metal the traditional porosity is undesirable property; however, by the use the cenospheres to enclose porosity inside strong hollow structures embedded inside metals, several properties of the composite are enhanced, and the density is decreased. Such types of materials are highly suited for the use in weight sensitive applications like automotive and aerospace industries [132]. In ceramic, composite foams the use of hollow spheres has also been of significant importance in which they are being investigated for their similarities to exhibit high temperature performance and low thermal conductivity especially for refractory materials [133]. Other research studies have evaluated the possibility of using such materials as coating materials for similar purposes in which such material has been coated onto a silicon carbide substrate using an electrophoresis method and exhibited a lower thermal conductivity relative to pure coal ash coatings, but they were extracted based on size rather than density [134].

## 6.2. Fly ash carbon

The recovery of carbon from coal ash has got a specific attention in the fast few decades. This recovered carbon has a purity of up to 70-80%, so it can be used as a coke in a number of industries like metallurgy etc due to which it has got much attention for researchers. The only problem associated with this is the presence of phosphorus, which must be reduced to less than 20 ppm. In order to achieve this goal chlorination of carbon has been performed which has reduced the phosphorus content in ash from 2000 ppm to 24 ppm [135]. Activated carbon has also been prepared from the enriched carbon from coal fly ash in which it has been used as a precursor. A number of methods have been used for the preparation like the use of steam in a fluidized bed at 900 °C, in a furnace with steam at above 850°C, and soaked in potassium hydroxide solution prior to activation at 780°C [136]. The effect of addition of ammonium salt solution pre-treatment using different ratios of solution/solid was reported. The effects of the addition of KOH on different parameters has been studied and it was found that pre-treatment with activated carbon samples produced with ammonium salt solution was having better adsorption properties as compared to samples produced with conventional steam activation, and that the addition of KOH is effective at increasing the specific surface area. The only negative factor with it is that it reduced the yield. Activated carbon prepared from coal fly ash has been proposed for a number of applications like the removal of sulphur dioxide (SO2) from flue gases which is an air pollutant and can cause a number of environmental problems like acid rain and photochemical smog.

For this reason it has been progressively more synchronized in the exhaust emissions of gases from combustion of fossil fuels. From the flue gases $SO_2$, $H_2O$, and $O_2$ are adsorbed onto the internal surface of the carbon, and the adsorbed $SO_2$ is then oxidized to sulphuric acid and stored within the pores [137]. In another similar application the adsorption capacity for the retention of NOx has been investigated. Another coal combustion pollutant that is attracting scrutiny is mercury emission. A hopeful improvement strategy is to inject fine carbon adsorbent upstream of the electrostatic precipitator that collects the coal fly ash. The recovered carbon is a cheap source of activated carbon and effective way of acting on mercury regulations [15,138]. Other used of activated carbons obtained from coal fly ash includes the treatment of liquid waste which is the subject of interest. Activated carbon obtained from the unburned coal in bottom ash was utilized to check for the removal of various organic compounds from an aqueous stream. The adsorption capacity of such carbon was found comparatively high to the raw ash [139]. The unburned carbon obtained from coal fly ash has been assessed for its suitability as a precursor in the manufacture of graphite. It was found that graphite made from coal ash, carbon was similar both in physical properties and in performance in lithium-ion batteries [140].

Graphite is the conventional choice for the majority of commercially available lithium- ion batteries due to its comparatively high specific charge capacity, high cycling efficiency, and low irreversible charge, which are the energy source of choice for most portable electronic device manufacturers. The increase in the demand for lithium-ion batteries the market of graphite will be affected both in terms of production and price [141].

### 6.3. High quality coal fly ash residue

Raw fly ash has a number of problems associated regarding its use in different applications like cement and concrete etc. For example, high carbon content in fly ash is not preferable for the high strength of cement mortar and concrete. Moreover the particle grain size is also important in most applications. High quality coal fly ash residue can be used for the highest quality EN 450-1 category (A) ash which has the highest market value. Most fly ashes have such particle size distribution that a fraction of the material would not conform to these specifications, so a classification required. So high quality fly ash residue is divided into a fine and coarse product. The coarse particles are greater than 45μm in size and are utilized in many applications like the manufacture of quality cement. A number of studies have been conducted, including that of author on utilizing bagasse ash that fly ashes are suitable raw materials for the manufacture of Portland cement while its residual carbon content can act as alternate fuel which may decrease the energy required in the cement kiln [18,32,34,142]. In the study of author, it has been found that 6% of fuel can be saved during clinkerization.

The use of Fly Ash in the production of zeolite could be very beneficial. With the decrease of iron oxide content the extent of its dissolution in the alkaline leaching of zeolite production would be reduced. Researchers have demonstrated that a reduction in iron oxide improves the cation exchange capacity of the zeolite [23,55]. It is also believed that the fine particles of fly ash would show increased zeolite yield due to its small size and increased area which should enhance silica reactivity with NaOH and hence its extraction capability. The use of a high quality fly ash is particularly relevant to its application as filler in polymer blends. In this case, it has been found that a particle size smaller than 5 µm is suitable. It extends the bulk polymer volume and also facilitates the compounding and processing. Moreover, it has been shown that the plastic products made of it have shown to improve the physical properties of [143] and surface modification of a purified fly ash in order to improve the interfacial bonding between fly ash and polymer has also been reported. They showed that the treatment of a purified ash with $Ca(OH)_2$ and $CO_2$ created a comparatively rough surface which improved the polymer- fly ash bonding.

### 6.4. Magnetic spheres

Magnetic spheres have been used in a number of applications. Groppo and Honaker [144] evaluated the possibility of incorporating a magnetic recovery process into an existing ash remediation plant in Kentucky to assess the magnetite derived from ash for its suitability to be used as a dense medium in coal cleaning circuits. It has been found that that the ash magnetite had almost similar or even better performance than conventional magnetite after the ash magnetite had been powdered for a period of time to increase its suspension stability. The use of Magnetite for dense medium separation in coal cleaning circuits could provide a good opportunity to employ the magnetic fraction of the fly ash and at the same time provide another good example of industrial synergy. Other uses for magnetite includes as a filler material for polymers used in recording media and a number of medical applications. Magnetic spheres obtained from coal ash have also been found suitable as catalysts for deeper oxidation of methane with limited success [35,45]. It can also be utilized as filler in thermoplastics and rubbers used in the automotive interior and building industries for its sound damping behavior, high density, and electrical and magnetic properties [145].

## 7. Role of coal fly ash in making the industrial process as environment friendly

### 7.1. Reducing greenhouse gases

It is a well known fact that coal fly ash is being used as an industrial by-product in many cases like cement production, mortar and concrete as a partial cement replacement because till this time no such process has been reported in which coal fly ash has been used as a 100% raw material.

Coal fly ash has no 100% utilization in any technology and is considered as a waste product, it can be regarded as to make the industrial process as environment friendly. The best way to measure the impact that fly ash utilization can have its use in applications where the relevant life cycle analysis has been carried out such as blended cements [146] and geopolymer concretes [24-25]. During clinkerization process calculations of limestone and the burning of fuel a huge amount of $CO_2$ is produced. Decomposition of limestone into equimolar quantities of CaO and $CO_2$ is an essential process in the production of cement clinker. Through stoichiometry, it can be shown that for every ton of CaO produced; about one ton of $CO_2$ is generated. When 25% coal fly ash is mixed with the raw mix of cement the production of greenhouse gases reduces up to 13-15%. The author of this review has used 15% bagasse ash in the clinkerization process and reduced the emission of greenhouse gases up to 15% [33]. It is not necessary that different coal ashes will have the same impact as there is some difference in the chemical composition; still it has been proved that up to 50% of the different coal fly ashes can be substituted in cement and concrete keeping all the properties within standard limits [147].

Habert et al. [18] and Chen et al. [148] have reported with strong arguments that coal fly ash fulfills the criteria for a by-product as per EU directive legislating for industrial waste materials [18, 24]. The authors argued that if coal ash meets all the criteria for a by-product, then it must take some allocation of the GHG and other emissions from the power station. In order to meet these criteria, it must have full utilization in different applications. Coal fly ash is the major fuel in the thermal power plants in most regions of the world so we argue that no allocation of the power station emissions to the ash is justified. McLellan et al. [20] have reported reduction in GHG emission in the range of 44-64% with the use of Australian coal ash in geopolymers. The difference in the emission of gases depends upon the types of geopolymer for which the calculation was made. Moreover, they reported a relative cost range of 7% lower to 44% higher than Ordinary Portland Cement. Similarly, in another study [24] a 45% saving in GHG relative to OPC has been reported. However, they have also reported the higher environmental impact based on the sodium silicate.

### 7.2. Industrial re-cyclization

From the present review, it is clear that coal fly ashes have a number of uses in different industrial applications. It is very much important to increase the reuse in industrial process. One way to significantly increase the re-use of materials is to increase industrial synergy by closing the loop on industrial processes. Fig. 9 illustrates this concept. The figure shows that by placing the coal fly ash processing plant at the center of an industrial ecosystem, the net material input to the system could be lessened and consequently less virgin material used. The waste streams should be significantly reduced in quantity, although they will not completely be reduced by such a system. The use of waste streams from the aluminum finishing industry is an exhilarating panorama for the production of useful industrial products. Aluminum etching waste water may contain 100 g/L NaOH and 60 g/L of Al, which is conventionally disposed of by mixing it with the acidic waste from the anodizing process and then discarding to the sewer. Making use of these streams with fly ash can be of mutual advantage in the production of geopolymerization and zeolitising and aluminum anodizing industry [44,148]. Moreover, materials are often required in order to improve the properties of ashes in the ceramics preparation. In spite of using the routine materials for this purpose, the use of industrial wastes has been considered [149]. During the coal fly ash sintering, metal finishing wastes obtained from different industrial sources have been used as a fluxing agent. By using metal finishing wastes, the scientific and marketable feasibility of ash ceramics has been improved as a result of the lower sintering temperature. When the factor of disposal cost of the waste is taken into consideration, it is possible that the cost of raw materials will significantly be reduced.

Keeping the chemical composition of coal fly ash, the author is strong supporter that it can be used 100 % in many applications. Examples of such use are provided from the study in which 100% coal fly ash concrete was made with recycled glass aggregate [150]. The work already done was on the pilot scale so more work is yet needed to go further than pilot scale, the size and $CO_2$ intensity of the concrete market will make this study more interesting. Another possibility to make use fly ash is during the two stage process of zeolite manufacturing, which leaves a residual low grade zeolite product, which potentially can adsorb nitrates and phosphates, and can be used as a treatment for farm effluent for the removal of such fertilizers. Although these studies are on laboratory scale, but need to be economically feasible and have a number of environmental benefits. This target can be achieved with larger scale studies which may examine the cost data of such processes and start to consider the life cycle impacts of the process, because fly ash may not necessarily have similar impacts in all applications. For example, the use of ash in concrete causes a considerable reduction of $CO_2$ emission, but may not have similar prevalent benefits in all other applications. In order to achieve the required functionality, the processing steps require more energy than the current best practice using conventional materials. The present study shows how the multi-processing component of ash is a good example of the practice of industrial synergy. The subject of industrial synergy is a new term in an academic field; therefore, it can be argued that these synergies are natural evolution as they emerged before the concept of sustainable development. On the other hand, it is obvious from industrial processes today that there is still a significant scope for loop closing in industry and it is not clear whether the present market mechanisms will be in a position to apply these changes to occur enough rapid to alleviate the ecological stress as a result of the increased economic growth. However the removal of existing policies which create obstacles to resource recovery such as price distorting subsidies and regulations that hinder the re-use of by-products can make it possible.

## 8. Conclusion

The present study provides an overview of the current and potential applications of coal fly ash, bagasse ash and rice husk ash and referred to a lot of work that is still limited to the laboratory scale and much more developmental work is required within these application areas to be commercialized, which will strengthen the industry academia collaboration. The review also discussed the latest advances in processing technologies which would make use of the multi-component utilization of different ashes. Hopefully making use of the processing technologies discussed in this review, the implementation of some of the applications will become more likely, in which cenospheres, magnetic spheres, residual carbon, and improved fly ash residue are some common examples. In order to assist some further developmental progress that is required to turn some of this research into commercialized work, much attention has to be paid to the driving factors at the research stage.

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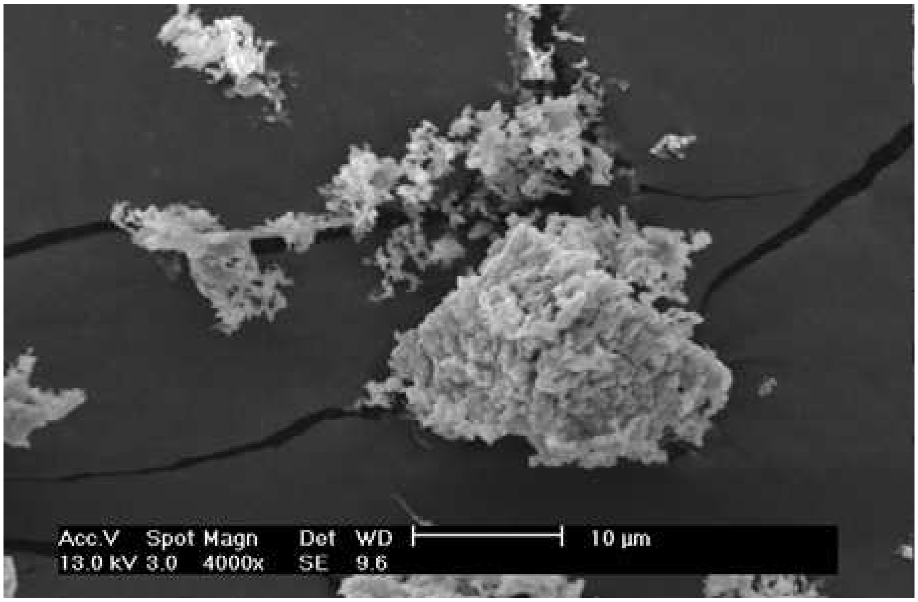

Fig. 1. SEM of bagasse ash under 800 °C for 3 hours

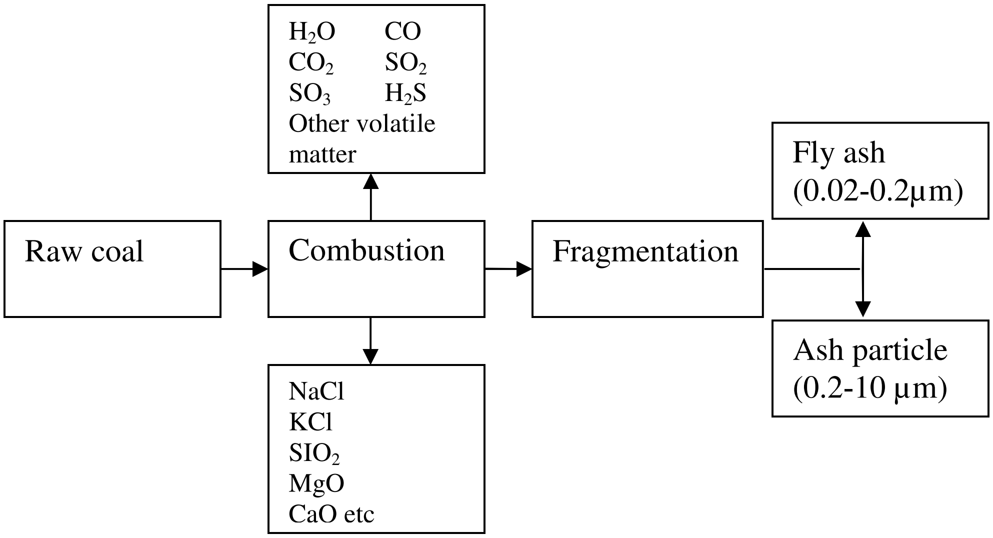

Fig. 2. Mechanism of coal fly ash formation from pulverized coal combustion

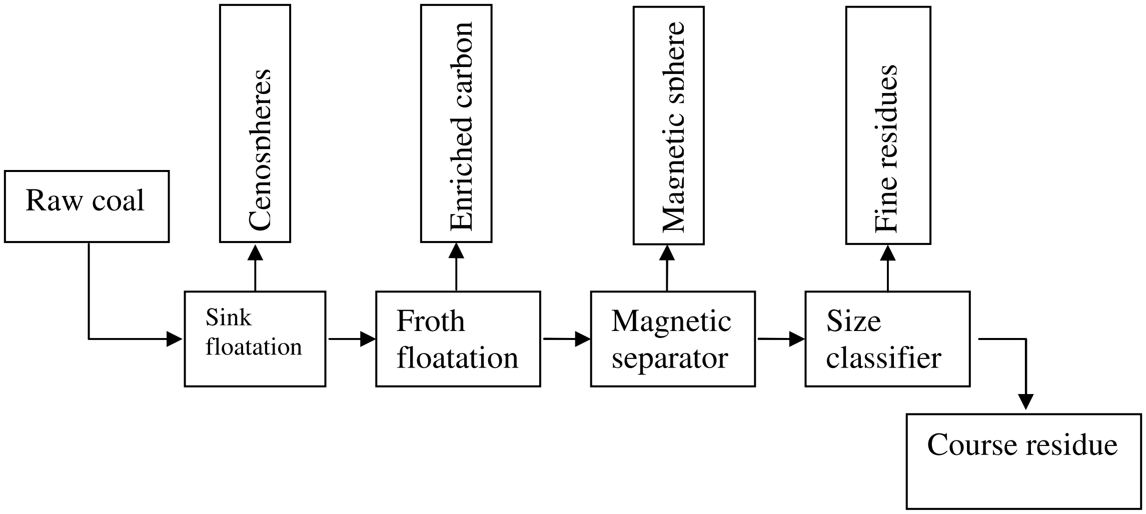

Fig.3. Sequential fly ash separation technique

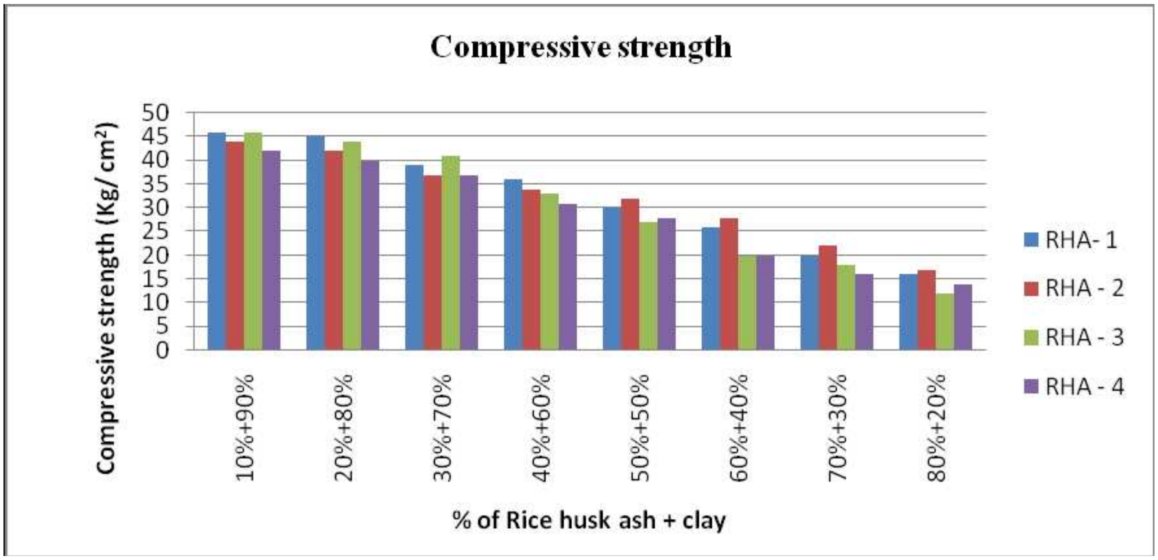

Fig.4. Compressive strengths (kg/ cm2) of bricks, cast with different rice husk ash and clay proportions [40].

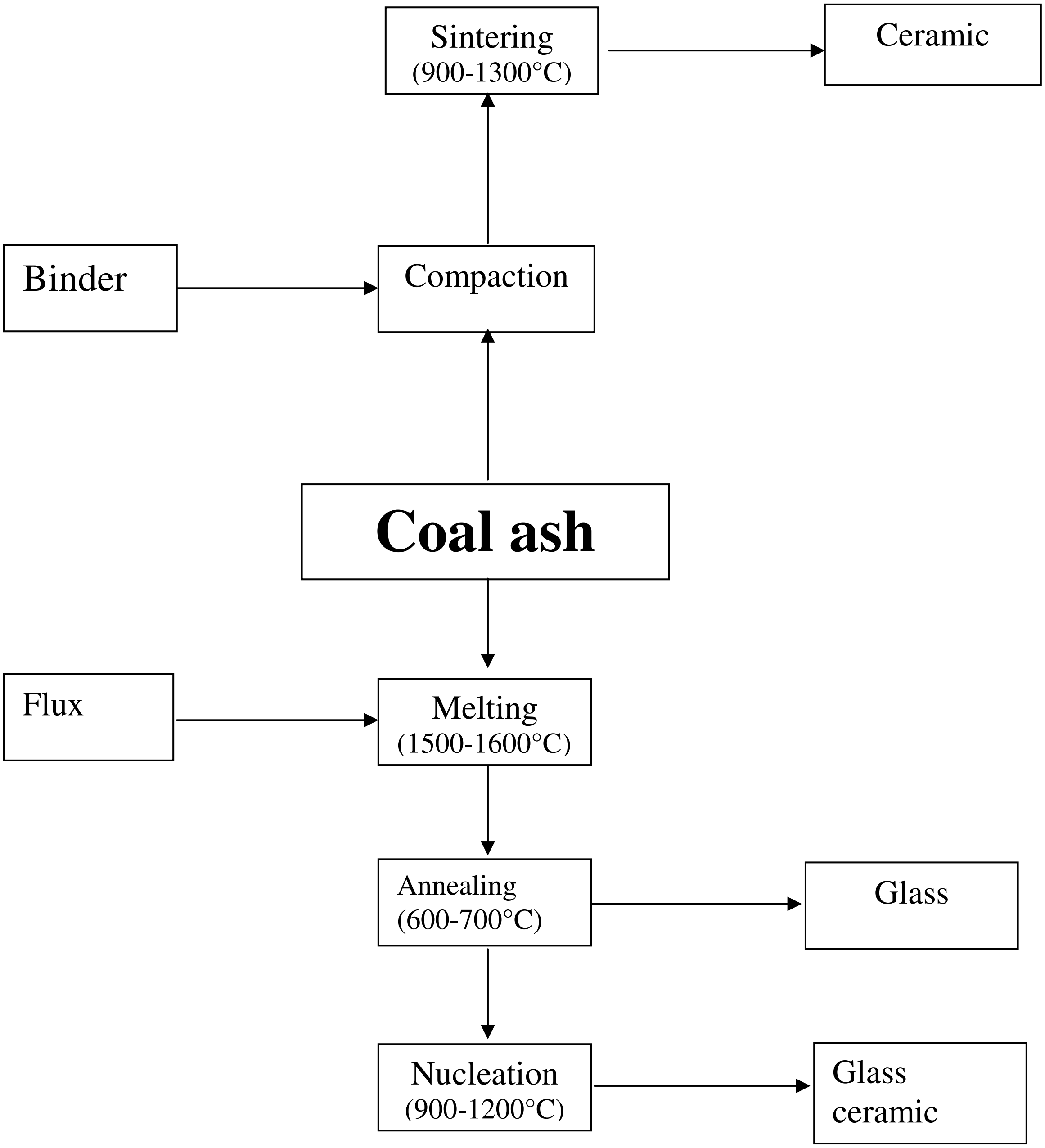

Fig. 5. Thermal process for the production of different materials from fly ash

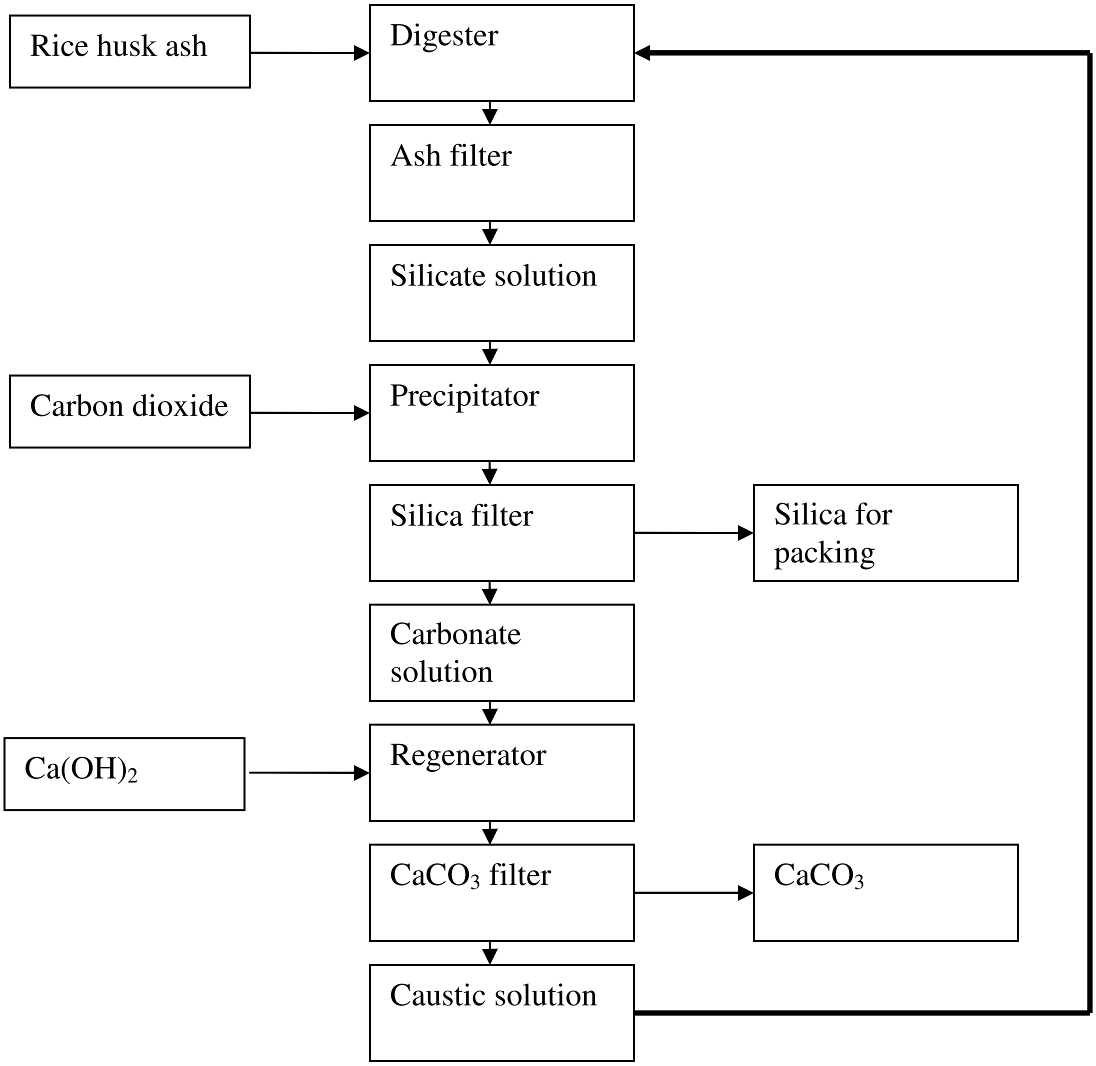

Fig. 6. Extraction of silica from rice husk ash.

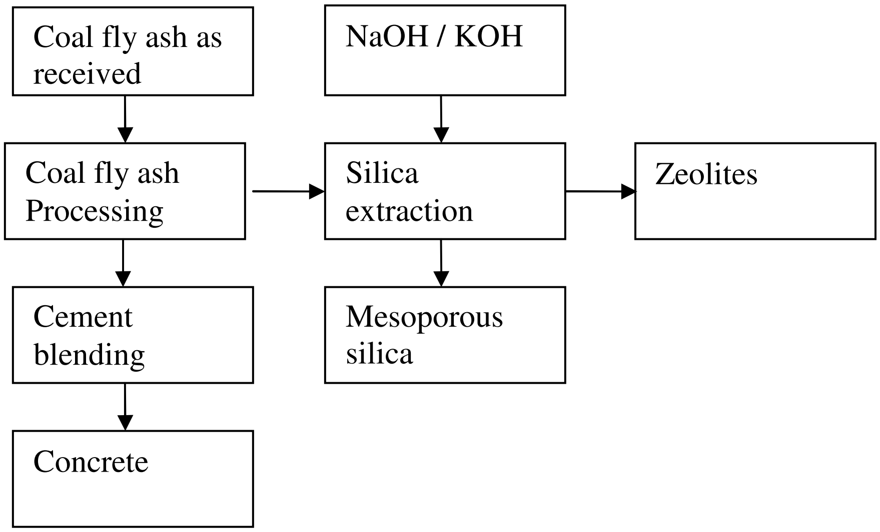

Fig. 7. Zeolites and mesoporous silica formation from coal fly ash

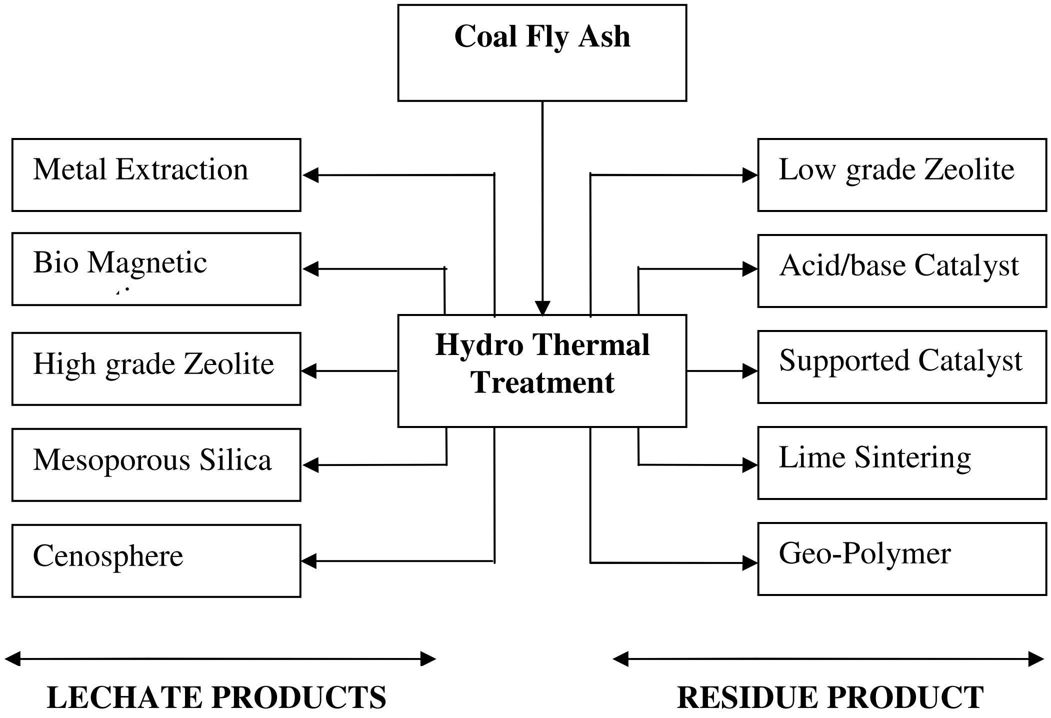

Figure 8. Ash products obtained through hydrothermal activation.

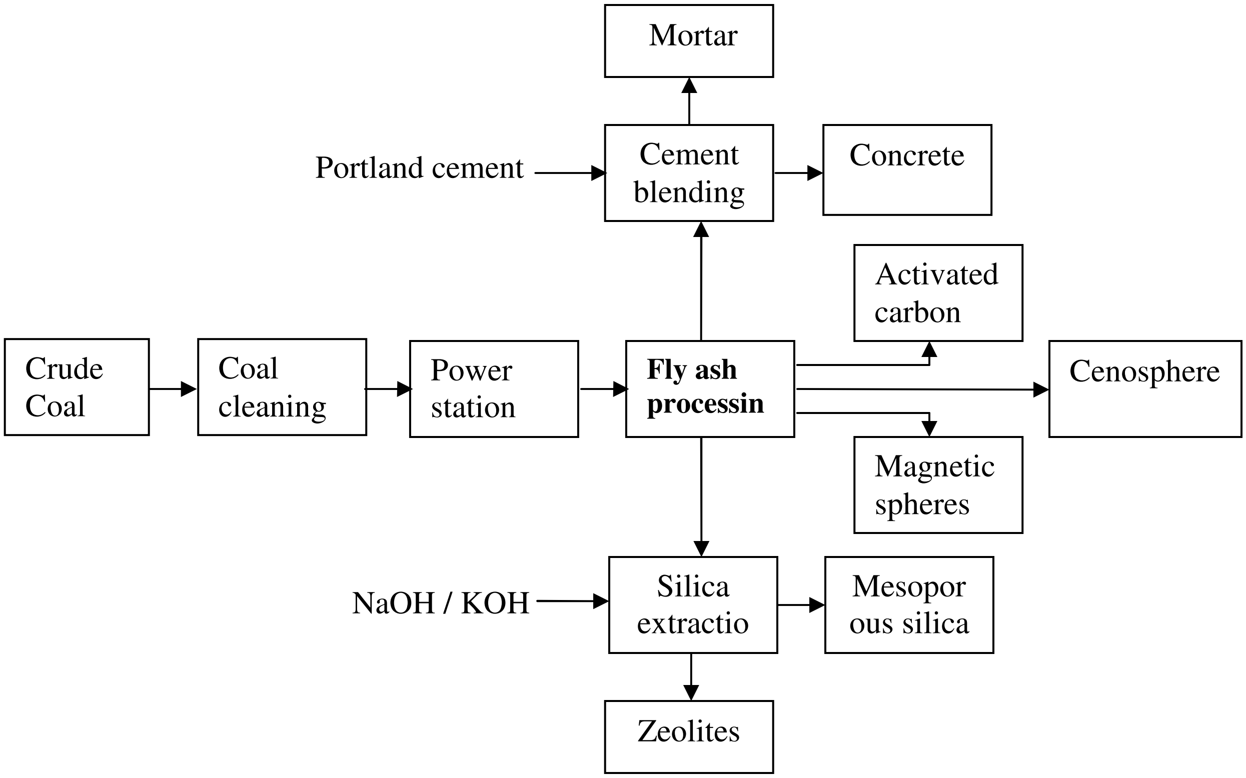

Figure 9. Reuse of coal fly ash in different industries for advanced materials.