



## Extraction of precious metals in fly ashes

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### Abstract

Although fly ash disposal is of environmental concern the quality of residues can be improved with respect to high value applications. Fly ash is considered as a potential source of aluminium and other strategic metals. Leaching and metal extraction behaviour of fly ash collected from Thermal Power Station have been thoroughly studied using as extractant. Coal fly ash is generated during the combustion of coal for energy production. Its utilisation as an industrial by-product has received a great deal of attention over the past two decades as more sustainable solutions to waste problems have been sought. The present paper reviews the potential applications for coal fly ash as a raw material: as a soil amelioration agent in agriculture, in the manufacture of glass and ceramics, in the production of zeolites, in the formation of mesoporous materials, in the synthesis of geopolymers, for use as catalysts and catalyst supports, as an adsorbent for gases and waste water processes, and for the extraction of metals. The review then analyses the impact that a multi-stage process could have by examining the technology capable of a series of separations to produce hollow microspheres, enriched carbon, magnetic spheres, fine ash product, and coarse ash product. The applications for these coal fly ash derived products were also reviewed. Since Our Common Future popularized the concept of sustainable development, researchers and industrialists have searched for ways of making industrial processes.

*Key words- Power plant, Coal, Fly Ashes, Precious Heavy metals*

### Introduction

A precious metal is a rare, naturally occurring metallic chemical element of high economic value. Chemically, the precious metals tend to be less reactive than most elements historically; precious metals were important as currency but are now regarded mainly as investment and industrial commodities. Gold, silver, platinum, and palladium each have an ISO 4217 currency code. The best-known precious metals are the coinage metals, gold and silver. Although both have industrial uses, they are better known for their uses in art, jewellery, and coinage. Other precious metals include the platinum group metals: ruthenium, rhodium, palladium, osmium, iridium, and platinum, of which platinum is the most widely traded. The demand for precious metals is driven not only by their practical use but also by their role as investments and a store of value. Historically, precious metals have commanded much higher prices than common industrial metals. The growth of industries in developing nations has turned, prompted generation of more and more power, resulting in generation of huge amount of fly ash.

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The initiatives under taken by many researchers through technology development have around the perception of fly ash from a "waste material" to that of "resource material". Application of fly ash in the manufacture of bricks, cement, concrete, ceramic products, building materials, composites, construction fill, road base, mineral filler in asphaltic mix, waste land reclamation and in agriculture has been proved to be beneficial. The low percentage of utilization of Fly ash in India is reflected in the low and medium value applications like bricks, cement and non-cement uses (Fig.1). For the purpose of high value application a programme has been initiated to evaluate some fly ashes of different thermal power plants. Since the coal combustion particulate products are principally inorganic substances, Coal-based thermal power stations have been the major source of power generation in several countries around the world. Combustion of coal in thermal power plants results in the emission of SO<sub>x</sub>, NO<sub>x</sub>, other toxic gases, and enormous quantities of fly ash. The fly ash is a powdery particulate material that is carried off in the flue gas, from which it is collected by means of mechanical or electrical devices. As the good quality coal reserves get depleted, the low quality (high ash) coals will have to be utilized for power



generation, leading to the production of larger amounts of fly ash. The disposal of such enormous amount of fly ash is a major problem in areas around power stations. Major mineral groups like sulphides (epigenetic and syngenetic pyrite), carbonates (epigenetic calcite and syngenetic siderite), clay minerals (kaolinite and illite), and tonsteins of various origin, *Pickhardt (1989)* has established environmental relevance of trace elements like As, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Mo, Ni, Sr, U, V, and Zn. *Turiel et al., (1994)* have demonstrated that these metals get enriched up to 10 times during combustion of coal. The bulk ash (88%) produced by coal combustion in Thermal Power Plants is in the form of bottom ash *Swaine, 2000* and contain large number of elements

including Cd, Cr, Pb, Zn invariable concentrations. The extraction of metals usually involves one of two possible aims. First, high extraction efficiencies of all metals are desired for the cleaning of, for example, fly ash or contaminated ground. For other applications (e.g., separation of metals from a mixture of metals), a highly selective extractant would be desired. Ideally, one or more desired elements are extracted reasonably well while few of the undesired elements are extracted from the material which they are faced with. More economy based on these metals, so extraction of these metals very necessary to growth of the society as well nation (*Tolhurst, 2015*).

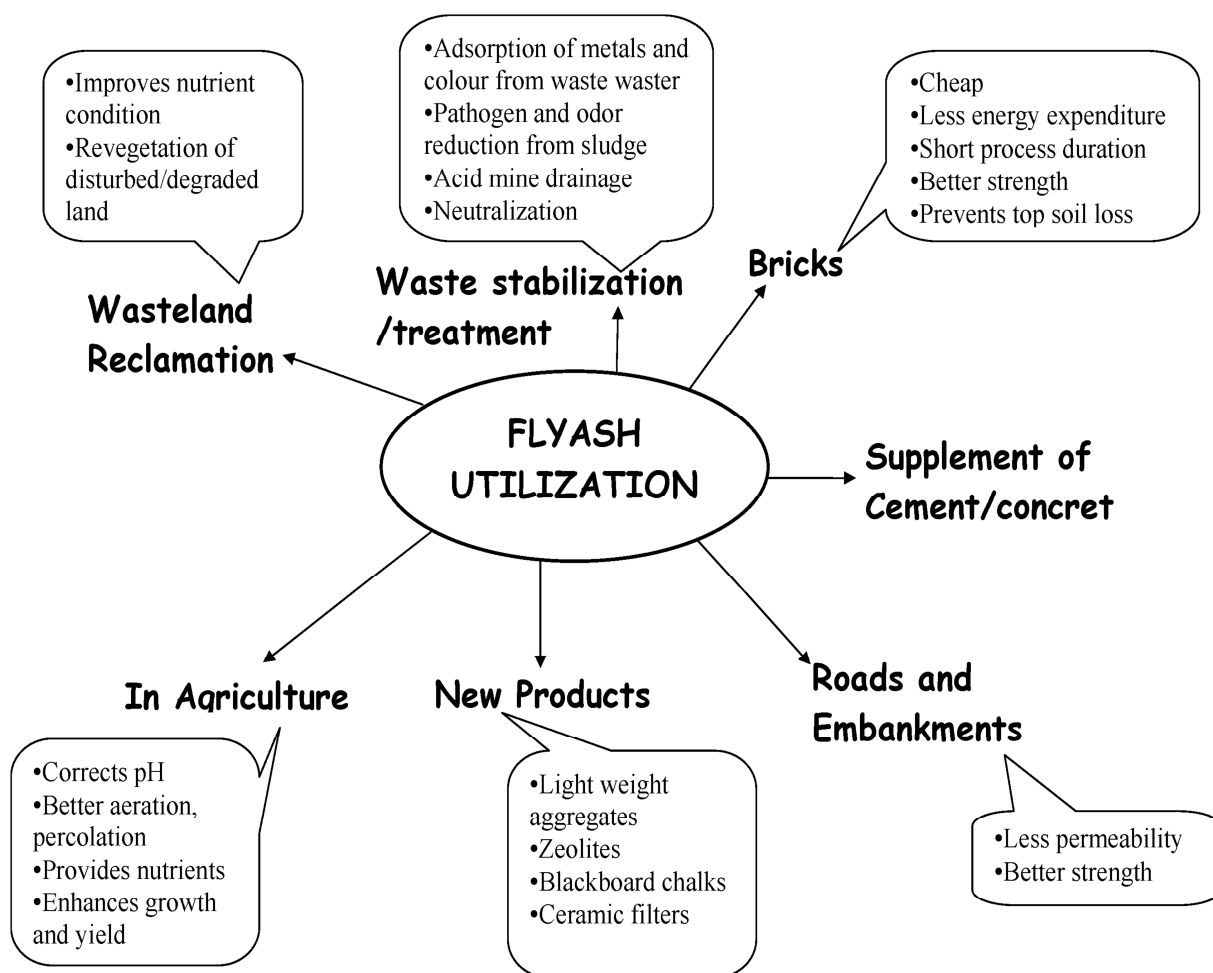


Figure 1. Fly ash utilization options.

## Material and Methods

Leaching procedures are known to remove heavy metals from soil, sludge, or compost at atmospheric pressure. This often requires a large amount of solvents, which must afterward be treated with neutralizers and disposed of. This is of both economic and environmental concern. Supercritical fluid extraction (SFE) with CO<sub>2</sub> has become a promising alternative to conventional solvent extraction for the cleaning of environmental samples. Compared with conventional solvent extraction, SFE is relatively fast and its selectivity can be controlled. The selection of ligands is a key parameter in determining the effectiveness of the extraction process and greatly influences the costs of metal removal. Many complexing ligands have been developed over the last years. Most of the ligands are used for solvent extraction with organic solvents at ambient pressure and only a few of them for SFE. Ligands may be characterized in terms of four classes, which are based on the type of reaction that occurs between the metal and the ligand. These classes are (1) acid ligands, (2) acid chelating ligands, (3) anion exchangers, and (4) solvating ligands. A suitable ligand for SFE shows a high complexation with heavy metals and is highly soluble in SC CO<sub>2</sub>. Ideally the ligand is also selective for specific metals and is easy to recycle.

The complexing agents used in conventional solvent extraction processes can also be used in SFE complexation of metal ions, provided they are soluble in SC CO<sub>2</sub>. A variety, but insufficient number of ligand solubilities have been tested for the SFE of metals. SFE is carried out using the acid ligands Cyanex 302 [bis(2,4,4 trimethylpentyl) monothiophosphinic acid], D2EHPA [bis(2-ethylhexyl)phosphoric acid], D2EHTPA [Bis(2-ethylhexyl)monothiophosphoric acid], DiOPA (diisooctylphosphinic acid), the acid chelating ligand NaDDC (sodium diethyldithiocarbamate), the anion-exchanger Aliquat 336 (methyltriocetyl ammonium chloride), and the solvating ligand Cyanex 923, a mixture of tertiary octyl- and hexylphosphine oxides. Efficiency was defined as-

$$\text{Efficiency} = \frac{(\% \text{ extraction}) - 1 - \text{metal on treated spiked sand or fly ash (PPM)}}{\text{metal on untreated spiked sand or fly ash (PPM)}} \times 100 \%$$

By this way Each experiment is performed three times. The maximum deviation of the analysis from

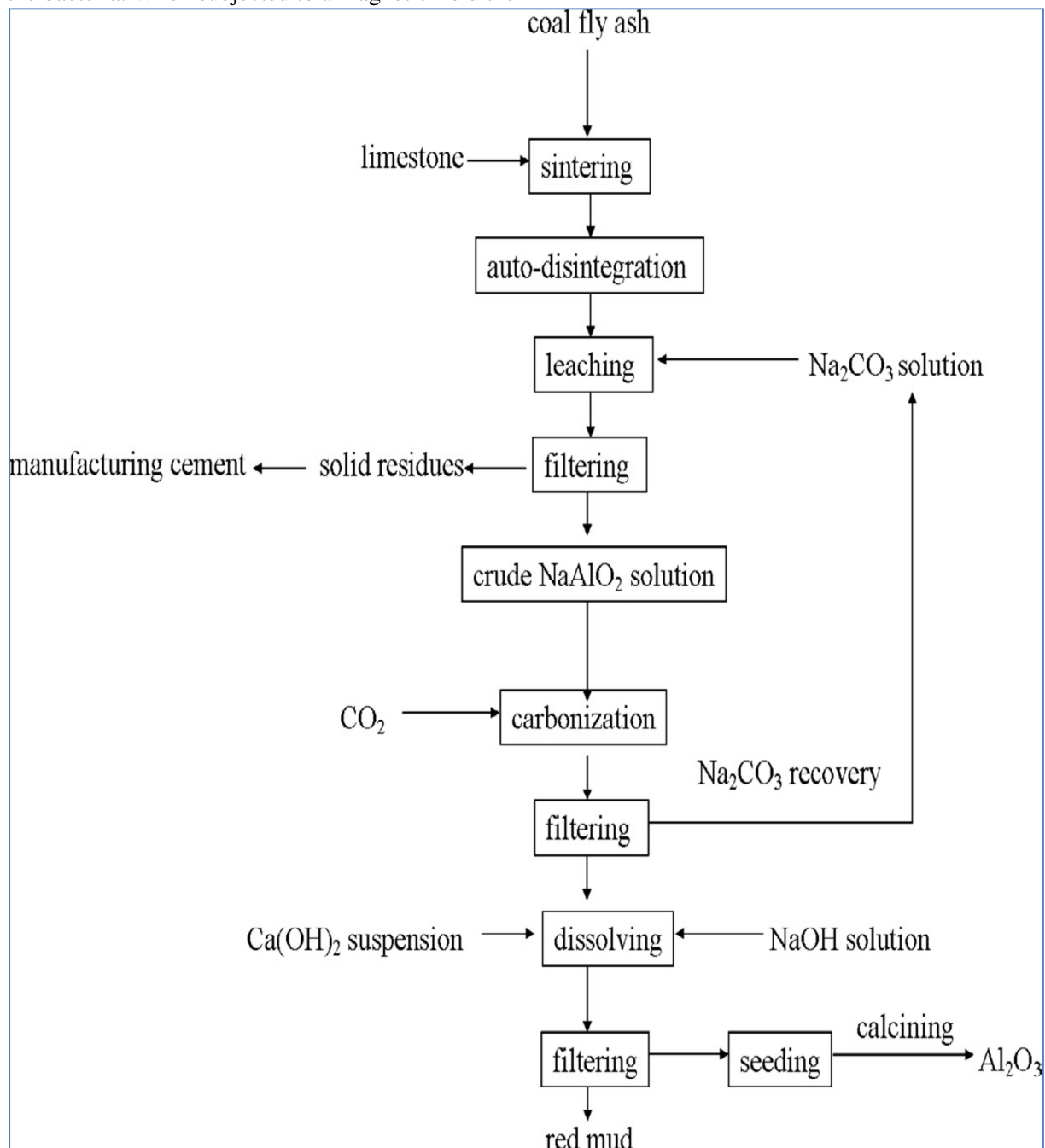
the average is defined as reproducibility. In addition to the influence of different ligands, the effect of variables such as pressure, entrainer, and matrix humidity on the extraction efficiency from fly ash and spiked s and was studied. Hg can be extracted by a continuous cold-vapor mercury generation assembly from a Leeman PS200 automated mercury analyzer was used to generate mercury vapor at known concentrations. The gas-liquid separator was used as supplied by the manufacturer and run according to instrument specifications. Reagents were fed to the gas-liquid separator using a variable- speed peristaltic pump so that the concentration of mercury vapor could be continuously varied as required. Mercury vapor from the vapor generation apparatus was continuously monitored using a Brooks Rand CVAFS-2 atomic fluorescence mercury analyzer.

Aluminium and titanium extraction can be proceeded by this way- Several methods for the recovery of aluminium from CFAs have been proposed. Direct sulphuric acid leaching at low concentration and ambient temperatures does not yield high aluminium recoveries, and the non-target metals readily leach into the acid causing purity issues (Nayak *et al.*, 2010). A 2005 study of direct sulphuric acid leaching yielded an aluminium extraction of just 18% (Matjie *et al.*, 2005). In contrast CFA pelletized with fine coal and lime and calcined then leached with sulphuric acid yielded an 85% recovery. Three extraction methods were compared: selective pH precipitation, crystallization, and solvent extraction. The only viable method was found to be solvent extraction using Primene JMT in illuminating paraffin as the solvent extractant. The aqueous leachate was contacted with the organic solvent, and this selectively loaded Ti<sup>4+</sup> and Fe<sup>3+</sup> ions into the organic phase. The product obtained was a high purity alumina (99.4%). A 92–97% TiO<sub>2</sub> by-product could also be produced. Shabtai and Mukmenev (1996) described a novel biomagnetic titanium- aluminium extraction process. The authors used concentrated sulphuric acid to leach both valuable and toxic elements from the CFA. The pH was lowered until titanium precipitated from solution. This was carried out concurrently with a biomagnetic adsorption process. The bacteria *Rhodococcus* GIN-1 (NCIMB 40340) was



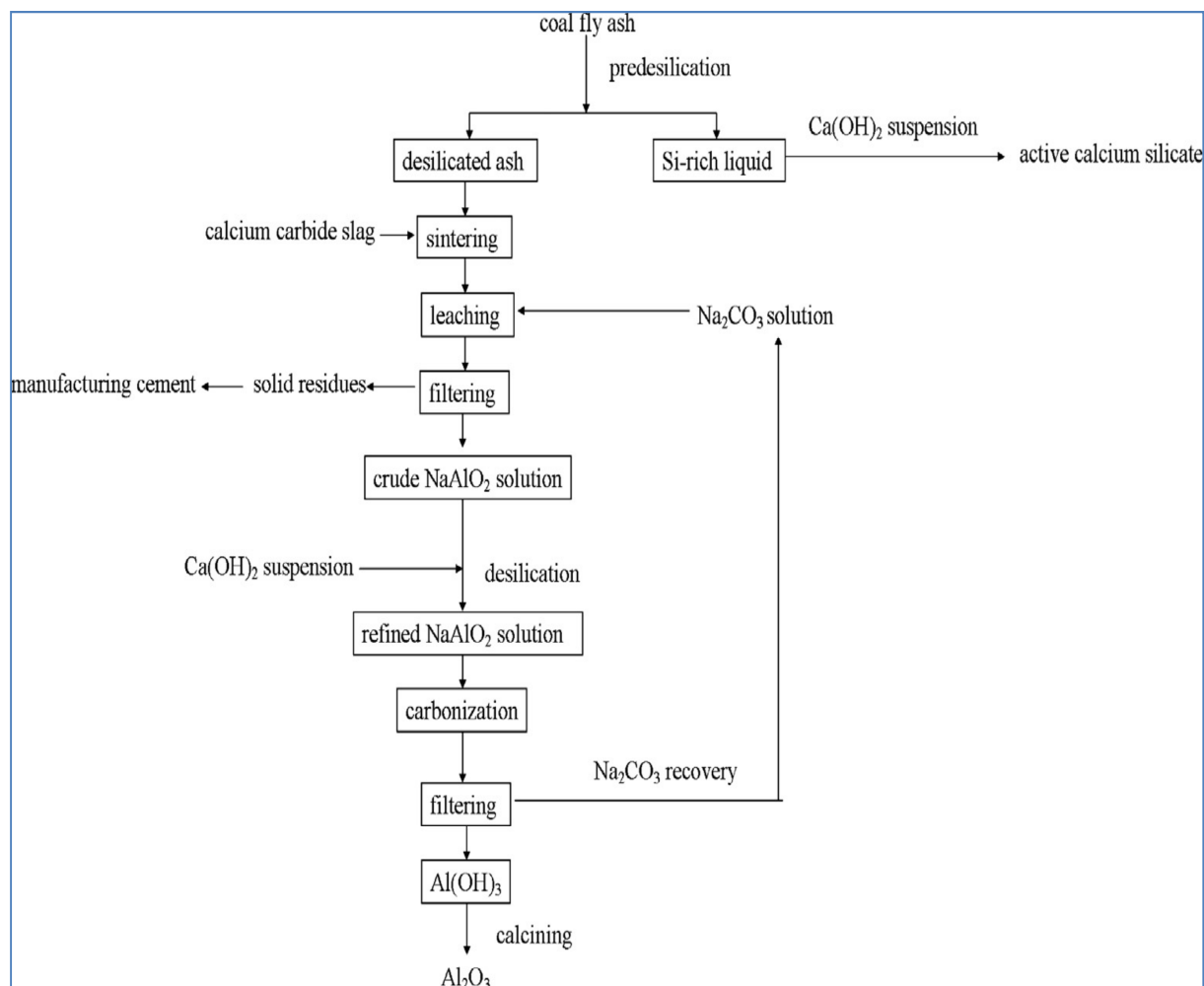
cultivated and added to a suspension containing magnetic particles which resulted in the adsorption of the bacteria onto the magnetic particles. The suspension was added to the leachate prior to precipitation. As the titanium precipitates out of the solution, it adsorbs along with the magnetite onto the bacteria. When subjected to a magnetic field the

titanium is lifted selectively out of the precipitate. This biomagnetic separation procedure is carried out twice to yield a titanium dioxide rich product with ferrous, silicate, and sulphate impurities. An aluminium rich precipitate was obtained by raising the pH to 6.5.



**Schematic diagram of lime sinter followed by Bayer process**

### Extraction of precious metals



**Schematic diagram of predesilication followed by lime-soda sinter process.**

In a more recent study, a CFA reported to have an extremely high aluminium content of 40–45% was assessed for its potential to produce aluminium commercially (Bai G, et al., 2010). In order to increase the  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio of the ash, a silica extraction step was carried out first using a NaOH solution. The desilicated ash was then mixed with lime and sodium carbonate and sintered before alumina extraction with a sodium carbonate and sodium hydroxide solution. Using this method, essentially a lime-soda sinter alkali leach process, an extraction efficiency of 90% was reported. High purity alum (>99.9%) has also been prepared from CFA and ammonium sulphate (Park et al., 2004). The ammonium sulphate and the CFA were

reacted at 400 °C. The product from this reaction was hydrothermally leached with sulphuric acid. The leaching liquor was mixed with ammonium hydroxide and aged for 24 h. The purity of the precipitate was increased via a method of dissolution precipitation. Zeolites extraction by this procedure Zeolites comprise of an important group of crystalline aluminosilicate minerals; they possess an infinitely extending three-dimensional anion network made up of  $(\text{SiO}_4)_4^-$  and  $(\text{AlO}_4)_5^-$  tetrahedra that link at the corners via their shared oxygen atoms. The three-dimensional nature of the framework is what 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 that make zeolites particularly suitable materials for adsorption processes. The substitution of Si (IV) by Al (III) in the structure is what accounts for the overall negative charge; this means that the zeolites have the potential to show high cation exchange capacities (CECs) (up to 5 meq g<sup>-1</sup>) (*Querol et al., 2002*) 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 synthesis to proceed.

### Magnetic sphere recovery

The removal of magnetic concentrate (MC) from CFA is also a significant opportunity to create added value. The amount of magnetic material varies in each particular CFA depending on the coal source and operating conditions of the coal boiler, but it can vary from between 0.5% and 18% (*Zyryanov et al., 2011*). There is little in the literature about the specifics of magnetic material recovery from CFA. However, magnetic separation of materials is a mature and well established technology emerging from the mid 19th century. Magnetic filtration has been used to capture 15% of CFA emanating from a power station, but this was for the purposes of pollution control rather than ash beneficiation. The basic principle behind magnetic separation is straightforward; it relies on the fact that materials with different magnetic moments experience varying forces in the presence of magnetic field gradients. In this way, an externally applied magnetic field can lift out those materials with similar magnetic properties (*Yavuz et al., 2009*). Fly ash samples are collected from the electrostatic precipitator of coal fired thermal power stations. The as received samples are subjected to various investigations like mineralogy, morphology, particle size and chemical analysis. Flame Photometer, Atomic Absorption Spectrophotometer, Inductively Coupled Plasma Spectrophotometer, Fly ash samples are collected from the electrostatic precipitator of coal fired thermal power stations. PLASMA were used for elemental analysis. The particle size analysis was carried out by particle size analyser. Scanning Electron Microscope attached with an Energy Dispersive X-ray Analyser has been used for morphological analysis and crystal structure determination of fly ash. The phase analysis of fly

ash has been carried out by X-ray diffractogram using Cu Ka radiation. IR spectra of the samples were recorded on spectrometer. Glass Ceramic extracted by Ceramic microfiltration tubular membranes were produced from CFA with the objective of filtering the effluent from textile dyeing processes (*Jedidi et al., 2009; Jedidi et al., 2011*). The layer was deposited on the support using a slip-casting method in dip solution containing the CFA powder and polyvinyl alcohol as a binder. When the prepared ceramic membrane was used for the cross flow membrane treatment of textile dye effluent, it achieved a 75% removal of chemical oxygen demand (COD) and 90% removal of colour. A separate study suggested the use of Cr<sub>2</sub>O<sub>3</sub> as a nucleating agent in order to prepare glass ceramics (*Vasilopoulos et al., 2009*). Samples Cd and Cu were analysed for their chemical composition using flame atomic adsorption spectrophotometry. The fly ash was melted with a mixture of 1: 1 w/w boric acid and lithium carbonate at 950°C. Then, the fused mixture was treated with deionised water and concentrated nitric acid to obtain the sample solution. X-ray diffractometry showed a small signal for quartz in both samples. The adsorption method consisted of mixing, in polyethylene bottles, fly ash with copper and cadmium metallic solutions prepared in the laboratory. Chromium (Cr), lead (Pb), zinc (Zn), nickel (Ni), cobalt (Co), copper (Cu) and manganese (Mn). The method used for the analysis of the heavy metals was atomic absorption spectrometry (AAS).

### Results and Discussion

The high extraction efficiency of Hg<sub>2</sub><sup>+</sup> probably originates from the high volatility of Hg<sub>2</sub><sup>+</sup>. Cyanex 302 was better able to extract Zn<sub>2</sub><sup>+</sup>, Cd<sub>2</sub><sup>+</sup>, and Cu<sub>2</sub><sup>+</sup> rather than Pb<sub>2</sub><sup>+</sup>. Aliquat 336 shows poor extraction efficiencies, with the exception of Cd<sub>2</sub><sup>+</sup>. With D2EHPA or DiOPA, the extraction efficiency of Zn<sub>2</sub><sup>+</sup> was moderate, while small amounts of Cu<sub>2</sub><sup>+</sup> and almost no Pb<sub>2</sub><sup>+</sup> and Cd<sub>2</sub><sup>+</sup> were extracted. One aim of this study is to remove heavy metals from sludges, e.g., river and harbor sludges. An important parameter for sludge treatment is the water concentration in the matrix. The water content in the sample was defined as Prior to extraction, ultrapure water was added to vary the humidity. For all metals, a maximum efficiency is obtained for water concentrations between 5 and 10



wt %. The most significant rise in efficiency was noted for  $Pb^{2+}$ . At 10 wt % sand moisture,  $Cd^{2+}$  and  $Cu^{2+}$  are extracted almost completely. The efficiency of  $Zn^{2+}$  is maximal at 5 wt % and decreases linearly with increasing humidity. (C. Kersch *et al.*, 2000).

Holler and Wirsching (1985) are widely credited with the first application of alkaline hydrothermal synthesis of zeolites using CFA as a source of Al and Si ions. summarises the subsequent approaches that have been taken to the synthesis of zeolites from CFA. Following Holler and Wirsching (1985), many attempts have been made to derive zeolites from CFA using a one stage hydrothermal method (Kikuchi *et al.* 1999, Berggaut *et al.*, 1996, Querol *et al.*, 1997, Hollman *et al.*, 1999, Querol *et al.*, 2001, Murayama *et al.*, 2002, Inada *et al.*, 2005, Walek *et al.*, 2008). The main obstacle to synthesizing zeolites from CFA is that, to speed up the reaction, temperatures in the range of 125–200 °C must be applied in order to dissolve the silica and alumina. Under these conditions the formation of many of the larger pore, and more valuable, zeolites (A and X) is hindered. However, KM (equivalent to phillipsite), NaP1, Nachabazite (herschelite), K-chabazite, Linde F, and other high-CEC zeolites have been obtained with high synthesis yields in the range of 125–200 °C (Querol *et al.*, 2002). The variations in zeolite type and yield tend to result from the combination of experimental conditions that are employed; activation solution/fly ash ratio, temperature, pressure, and reaction time have all been varied to synthesise up to 13 different zeolite types from the same fly ash (Querol *et al.*, 2001). In general it was found that a high activation temperature and alkaline concentration (200 °C and 5 M) led to the formation of low CEC zeolites such as sodalite, and conversely low activation temperature and alkaline concentration (<150 °C and 0.5–3 M) led to the formation of higher CEC zeolites such as NaP1, NaA, or chabazite (Querol *et al.*, 2002). A method of pre-fusion of the CFA with a solid alkali at high temperatures (>500 °C) prior to the conventional hydrothermal growth of the zeolites was introduced by (Shigemoto *et al.*, 1993; Berggaut and Singer, 1996), but more recently interest has been renewed in this method (Jha *et al.*, 2009; Molina & Poole 2004; Mishra & Tiwari 2006; Rios *et al.*, 2009; Yao *et al.*, 2009; Kazemian *et al.*, 2010).

Berggaut and Singer (1996) mixed NaOH and CFA into a paste with water prior to heating. This enabled the decomposition of all of the mullite phase of the fly ash precursor. Zeolites X and NaP1 were formed depending on whether the fused material was aged prior to the hydrothermal step. The purity of the zeolite was found to be high containing only small amounts of residual materials from the fly ash such as carbon and iron oxides. The schematic summarises research into the conditions needed in the hydrothermal crystallisation stage to form particular zeolites (Jha *et al.*, 2009). It was found that a higher concentration and longer reaction times favoured the formation of zeolite X, but at the highest NaOH concentration some sodalite formed as a by-product. Hollman *et al.*, (1999) pioneered the two stage hydrothermal method which has been the subject of considerable subsequent interest (Hui & Chao, 2006; Moreno *et al.*, 2002; Tanaka *et al.*, 2008; Font *et al.*, 2009; Kim & Lee, 2009; Tanaka *et al.*, 2009).

Nayak and Panda (2010) has observed the chemical analysis of major inorganic oxides found in TTPS fly ash are  $SiO_2$  (59.49%),  $Al_2O_3$  (29.09%),  $Fe_2O_3$  (3.9%),  $TiO_2$  (1.9%),  $CaO$  (0.99%),  $MgO$  (0.33%),  $Na_2O$  (0.13%) and  $K_2O$  (0.72%). The present study is not concerned with the contents of rare metals and hence, not included. Results from characterization indicate that pre-leached fly ash consists of spherical micron sized particles composed of mullite enclosed in a two phase glassy matrix (Sarkar *et al.*, 2005; Sarkar *et al.*, 2006; Nayak & Panda, 2007). The exterior reactive glass is embedded with surface salts like Ca, Mg, Fe and Al. The interior glass matrix is composed primarily of Si and a major portion of Na and K. Leachate characteristics are primarily controlled by dissolution of the external glass matrix after rapid dissolution of surface salts. Similar results were obtained for Ni oxidative extraction. In Puertollano IGCC fly ash, Ni occurs mainly as fine reduced species, mainly Fe–Ni sulphide species, nickeline and breithauptite (Font *et al.*, 2005). These Ni-bearing species are easily oxidised into Ni-sulphate/arsenate/antimoniate species that are soluble in water, giving rise to relatively high water soluble fractions of Ni (Font *et al.*, 2005; Font O. 2007). Consequently, similar Ni extraction yields were obtained at different oxidative gas atmospheres, while low Ni extraction yields were



obtained in a  $N_2$  atmosphere. The leaching of As in oxidative atmospheres was totally different from those described above for Ge and Ni. Germanium successfully separated from coal fly ash efficiently by vacuum reduction metallurgical process (Zhang *et al.*, 2016 & 2017). Whilst As leaching in air or pure oxygen, with or without gas flow, fell from the maximum value, the leaching performed in a nitrogen atmosphere showed a slight increase. However, these maximum values were reached at different times of leaching, depending on the gas atmosphere used. On the other hand, it is very common to use lime (CaO) to treat industrial wastewater containing arsenic. In these cases, dissolved As can be precipitated as Ca-rich arsenates whose composition is related to the composition of the aqueous solution and can precipitate over a wide pH range (Harris, 2003). Although the neutralization with lime is not effective for completely removing As, the use of lime plus ferric iron achieves very good results in wastewater treatment (Harris, 2003). It should be noted that, besides containing a high percentage of iron sulphides IGCC fly ash also has a relatively high Ca content, both contributing to As removal from aqueous leaching solutions. For the different initial concentrations, adsorption equilibrium was rapidly achieved. Experimental results indicate that adsorption capacity increases as the initial Cu and Cd concentration decreases for both fly ashes, but the adsorption capacity of Abofio (CVA) fly ash is distinctly better than that of Cangas del Narcea (CVN). For the Abofio fly ash, the percentage metal removal was more than 90% (Ayala *et al.*, 1998). As CFA is made up of oxides such as  $SiO_2$ ,  $Al_2O_3$ , CaO, and  $Fe_2O_3$  it has received attention as a low cost material for the manufacture of ceramics, glass-ceramics, and glass materials Erol *et al.*, (2008). The basis of manufacture is the temperature activation of the raw CFA with variations in temperatures and co-reagents directing the final form of the glass or ceramic. Erol *et al.*, (2008) manufactured glass, glass-ceramic, and ceramic material from CFA using the general stages outlined in without the addition of any additives. Physical and mechanical property tests revealed that the three materials manufactured from waste CFA compared well with literature values for glasses and ceramics derived from waste and non waste sources. CFA has been considered as a

replacement for kaolinite in the manufacture of the ceramic cordierite (He *et al.*, 2005). Classified ash (<44  $\mu m$ ) was mixed with industrial alumina and magnesium carbonate powders. This mixture was milled with methyl cellulose and the blended components were then pressed into discs before sintering at temperatures between 900  $^{\circ}C$  and 1300  $^{\circ}C$ . Results show that a raw material composition of 64–68 wt.% CFA, 10% alumina, and 22–26% magnesium carbonate produced cordierite as the dominant phase at sintering temperatures of over 1200  $^{\circ}C$ . CFA has been used in a 60:40 weight ratio with kaolinic clay to manufacture category BIII ceramic tiles according to EN 14411 (Sokolar and Vodova, 2011). The authors hoped that using a CFA with high CaO content and lower particle size would decrease the firing shrinkage that is evident in classical CFA high temperature ceramics. The study reported that firing shrinkage was reduced but at the expense of an increase in porosity, a decrease in bending strength, and an increase in  $SO_2$  in the flue gases. The chemical composition of CFA makes it particularly suitable for the manufacture of structural glass-ceramics (Peng *et al.*, 2005).

## Conclusion

A number of recovery methods have been developed since the pioneering work of Grzymek. However, there are some drawbacks to all these methods and most reported work to date has been at the laboratory scale. Leachability tests after SFE will show a more detailed impact of SFE on the reduction of metals from fly ash. It has been demonstrated that SFE can be used for the extraction of divalent metal ions from either spiked sand or fly ash. The acid leach processes can dissolve aluminium and other metals with silicon-rich residues by-products. However, it requires acid-resistant and air-tight processing equipment, such as that used in the Shenhua Group Co., Ltd. plant, prepared from tantalum niobium alloy. In addition, alumina recovery and waste treatment can be quite complex. In the leaching process, a proportion of soluble impurities such as Fe, Ti and Mg contained in the ash are introduced into the pregnant solution, necessitating post-treatment to purify the aluminium; It is concluded that direct acid leaching at low concentration and ambient temperatures is not satisfactory for high recoveries





of these metals from this fly ash. The concentrations of the acids were varied from low to concentrated reagent. Hence, low to moderate recoveries of metal values from fly ash by direct acid leaching is not surprising since fly ash consists primarily of iron and aluminium-silicates together with silica fused into a refractory glassy mullite material. The leachability of metals from fly ash depends on the nature of leaching medium, solid:liquid ratio, temperature and leaching time. By acid routes silica remains substantially insoluble where as the aluminium is taken into aqueous solution as  $Al^{3+}$ . The acid leaching is not selective

for aluminium as Fe, Ti, K, Na, Mg and Ca generally dissolve simultaneously with aluminium. For any kind of specific use the impurities other than the desired metal need to be removed through a suitable process.

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