

Recovery of metals and other beneficial products from coal fly ash: a sustainable approach for fly ash management

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Abstract Increasing production and disposal of coal fly ash (CFA) is a matter of serious environment concern. However, CFA contains various beneficial metals and mineral matters whose demand is increasing in the industrialized world, while natural supplies are diminishing. Therefore, recovery of these potential resources from CFA can be an alternative way to save mineral resources, as well as to reduce the environmental burden of CFA disposal. There are numerous methods developed for the recovery of beneficial products from CFA. Based on the US patents and journal literatures, the present review describes the recovery status and technologies of major elements such as Al, Si, Fe and Ti, and trace elements such as V, Ga, Ge, Se, Li, Mo, U, Au, Ag, Pt groups and rare earth elements (REEs) and other beneficial products such as magnetic materials, cenospheres, and unburned carbon from CFA. It also highlights the recovery efficiency and drawbacks for their extraction, and suggests future research to develop satisfactory results in terms of selective recovery and purification.

Keywords Coal fly ash · Beneficial elements · Recovery · Hydrometallurgical methods · Extraction efficiency

1 Introduction

Coal based thermal power plants are one of the largest sources of electricity, contributing around 39 % of the total electricity generated throughout the world (Fig. 1) (US EIA 2014). This is due the fact that coal is the most abundant fossil fuel, and it is comparatively much lower priced than other fuels such as oil and natural gas. However, growing use of coal in power plants is generating

huge amounts “waste”, known as coal fly ash (CFA), with China, the US and India being the largest producers (Heidrich et al. 2013) (Table 1). The current global annual production of CFA is approximately 750 million tonnes (Yao et al. 2015), and this is anticipated to increase in the near future. Thus, increases in the global production of CFA is a matter of serious environmental concern because of issues related not only to its disposal but also the threat to public health and potential damage to soil, agriculture and natural beauty. These problems are more critical in areas experiencing increasing land use competition. Fly ash can even reach the sub-soil and contaminate the groundwater with heavy metals (Prasad and Mondal 2009; Ramya et al. 2013). Thus, there is a pressing need of its recycling and utilization (Ilic et al. 2003; Yao et al. 2015). More efforts have been undertaken on concrete production, paving roads, mine fillings, building material production, land reclamation, soil stabilization, toxic element immobilization, and synthesis of polymers and agriculture etc. (Kruger 1997; Basu et al. 2009; Ahmaruzzaman 2010; Alam and Akhtar 2011; Loya and Rawani 2014). Taking

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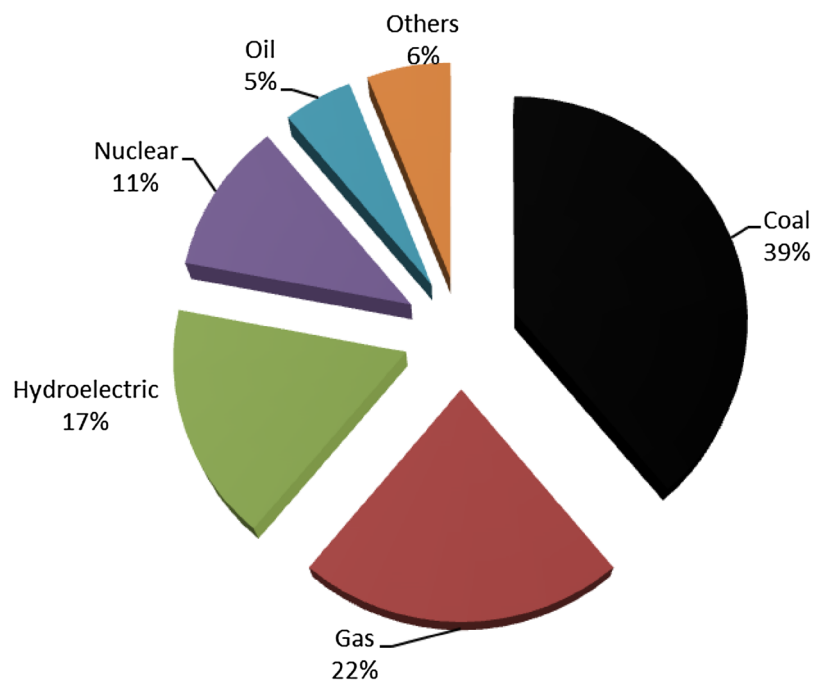


Fig. 1 World electricity production from all energy in 2014 (US EIA 2014)

Table 1 Worldwide annual production of coal fly ash (Heidrich et al. 2013)

| Country | Ash production (Mt) |
|------------------------|---------------------|
| China | 385 |
| USA | 118 |
| India | 105 |
| Europe | 52.6 |
| Middle East and Africa | 32.6 |
| Russian Federation | 26.6 |
| Other Asia | 16.7 |
| Australia | 13.1 |
| Japan | 11.1 |
| Canada | 6.8 |

this into account, on average only 25 % of CFA is utilized (Sommerville et al. 2013), wherein 38 % for US, 47 % for the EU and 15 % for India (Yao et al. 2014a, b; reference therein). The rest is considered as pollutant and disposed waste. Hence, there is an urgent need for developing of its novel applications (Blissett et al. 2014).

Currently, CFA is being explored as an alternative source of valuable metals, since it mainly composes of a variety of oxygenated inorganic compounds, such as SiO_2 , Al_2O_3 , Fe_2O_3 and TiO_2 , with smaller amounts of trace elements (Lai-shi et al. 2011; Blissett and Rowson 2012; Seredin et al. 2013; Mayfield and Lewis 2013). With diminishing metal resources as well as ever-increasing their demand, recovery of these products from CFA would

be highly worthwhile and a challenging topic for current international research (Cao et al. 2008; Mayfield and Lewis 2013; Tolhurst 2015). Nevertheless, recovery of metals from CFA can reduce environmental risks associated with disposal and leaching of metals to surface and subsurface waters. There have been several reviews based on journal articles that focused on the recovery of beneficial elements and products from CFA (Jha et al. 2008; Cao et al. 2008; Meawad et al. 2010; Blissett and Rowson 2012; Yao et al. 2014a, b; Franus et al. 2015). However, the present review focused on US Patents, as well as journal articles to present an overview of the recovery status and technologies of metals and other beneficial products from CFA using several metallurgical and bio-metallurgical methods with the aim of evaluating their extraction efficiency, impact and applicability.

2 Properties of coal fly ash

The physico-chemical properties of CFA are highly variable depending on coal type, combustion temperature, combustion technique, air/fuel ratio, and particle size of the feed coal (Dhadse et al. 2008). The major oxides for CFA from different coal types are presented in Table 2 (Meawad et al. 2010). The principal components of all ash samples are SiO_2 , Al_2O_3 , and Fe_2O_3 , with varying amounts of carbon, reported as loss on ignition (LOI), CaO , and MgO . Higher concentrations of CaO and MgO , and lower concentrations of SiO_2 , Fe_2O_3 and carbon are found in lignite

Table 2 Major oxide concentrations in fly ash from different coal types (%) (Meawad et al. 2010; references therein)

| Component | Bituminous | Sub-bituminous | Lignite |
|--------------------------------|------------|----------------|---------|
| SiO ₂ | 20–60 | 40–60 | 15–45 |
| Al ₂ O ₃ | 5–35 | 20–30 | 10–25 |
| Fe ₂ O ₃ | 10–40 | 4–10 | 4–15 |
| CaO | 1.12 | 5–30 | 15–40 |
| MgO | 0–5 | 1–6 | 3–10 |
| Na ₂ O | 0–4 | 0–2 | 0–6 |
| K ₂ O | 0–3 | 0–4 | 0–4 |
| LOI | 0–15 | 0–3 | 0–5 |

and sub-bituminous CFA compared to bituminous CFA. According to the American Society of Testing Materials (ASTM C618 2000), two classes of CFA have been defined based on the coal usage. Fly ash produced from anthracite or bituminous coal is classified as class F, while class C fly ash is produced from lignite or sub-bituminous coal. This classification is based on differences in contents SiO₂, Al₂O₃, and Fe₂O₃, and LOI in the ash. In classes C and F, the SiO₂ + Al₂O₃ + Fe₂O₃ contents are >50 % and >70 % respectively, and LOI is <6 % and <12 %, respectively. In addition, class C fly ash corresponds to high-lime (10 % up to 40 %), while Class F fly ash has lime concentrations <10 % CaO. Coal fly ash is considerably rich in trace elements (Karayigit et al. 2001; Vassilev et al. 2005; Dhadse et al. 2008). The normal range of those elements is given in Table 3 (National Research Council 2006; USEPA 1999; Meawad et al. 2010). Elements in CFA are enriched mainly based on their organic/inorganic affinity and host mineralogy, followed by volatility (Xu et al. 2003; Vassilev et al. 2005). During fly ash gasification, the majority of mineral fractions hosting important trace elements is volatilized and then condensed on the surfaces of the fly ash (Clark and Sloss 1992; Querol et al. 1995). US Patent No. 0274886A1 (2007) illustrates the volatility classes of elements during combustion (Fig. 2). This indicated that elements such as As, B, Bi, Cd, Ge, Ga, Mo, Pb, S, Se, Sb, Sn, Te, and Ti are classified into Class II category. These elements have tendency to more concentrate in the finer particles of the ashes during the condense-volatilization process (US Patent No. 4686031 1987; Gieré et al. 2003).

3 Recovery of major element

There are a number of methods have been developed for the recovery of major elements from CFA (Table 4), which are discussed below.

3.1 Aluminum and titanium

Aluminum (Al) is an industrially important metal; it is light, corrosion resistant, and malleable and is mainly used in the aircraft industry. It is also used in the production of aluminum chemicals and in refractories (Matjie et al. 2005). Titanium (Ti) is used for various purposes in industry. In particular, it has been used in the aerospace industry. Titanium oxide is used as a pigment in the paint industry. On larger-scale, Ti and titanium alloy products are used for making automotive parts (Fontana et al. 2005). Coal and coal residues such as CFA are enriched with these elements (Halina et al. 2007; Seredin 2012; Dai et al. 2012a).

Several methods have been reported for recovering Al from CFA. Burnet et al. (1977) introduced a chlorinating process, where the fly ash is first separated into magnetic and non-magnetic fractions. The non-magnetic fraction of CFA was mixed with carbon and chlorinated in a fixed bed. The iron remaining in this fraction was removed by lowering the temperatures between 400 and 600 °C. The chlorinated aluminum fraction was recovered by increasing the temperature to 850–950 °C. Following Burnet et al. (1977), Mehrotra et al. (1982a,b) studied a high-temperature chlorinating process, and found that only 25 % of Al and 25 % of Ti in ash could be chlorinated at temperature above 900 °C. However, this process left about one-third of the iron with the nonmagnetic fraction. US Patent No. 4159310 (1979) gives a more thorough discussion of the chlorinating process for the recovery of Al and Ti. In this Patent the nonmagnetic fraction of ash was chlorinated in an oxidizing atmosphere and selectively separated Fe from other metals. The remaining residue was then chlorinated in a reducing atmosphere in the absence of solid carbon to suppress the chlorination of Si and vaporized the chlorides of other metals. Aluminum and Ti were selectively separated and recovered by condensation from the vapors. Overall, this method recovered 70 %–80 % Al and 80 % Ti. However, this method can become very expensive if the chlorination of unwanted metals is not suppressed.

Another method for the recovery of Al and Ti involves leaching CFA by acid/alkali leaching followed by precipitation, solvent extraction, or re-crystallization (Matjie et al. 2005; Halina et al. 2007; Li et al. 2011). US Patent No. 4243640 (1981) investigated a process for the recovery of Al from CFA where the ash was subjected to a magnetic separation and subsequently leaching was carried out on the non-magnetic fraction using nitric acid (strength about 30 %–56 %). The leachate was then evaporated and calcinated at 1000 °C for the recovery of Al. The calcinated product contained 90 % alumina along with other impurities like Fe oxides. US Patent No. 4567026 (1986) reported another acid leaching method for the recovery of Al and Ti

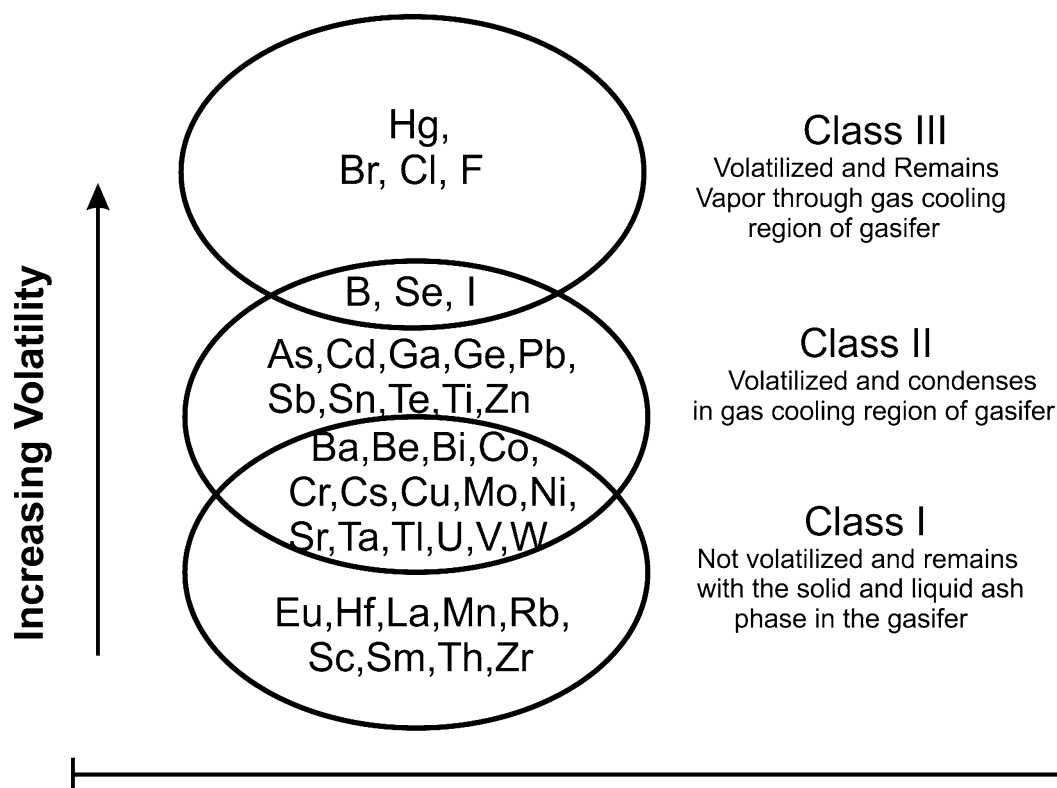


Fig. 2 Relative volatility of trace elements in coal gasification systems (US Patent 0274886A1 2007)

Table 3 Trace element concentrations in fly ash (mg/kg) (National Research Council 2006; USEPA 1999; Meawad et al. 2010)

| Element | Median | Range |
|---------|--------|-------------|
| As | 43.4 | 0.0003–391 |
| Ba | 806.5 | 0.02–10,850 |
| Be | 5 | 0.2–2105 |
| B | 311 | 2.98–2050 |
| Cd | 3.4 | 0.01–79 |
| Cr | 136 | 3.6–437 |
| Co | 35.9 | 4.9–79 |
| Cu | 112 | 0.2–655 |
| F | 29 | 0.04–320 |
| Pb | 56.8 | 0.02–273 |
| Mn | 250 | 24.5–750 |
| Hg | 0.1 | 0.013–49.5 |
| Ni | 77.7 | 0.1–1270 |
| Se | 7.7 | 0.0003–46.5 |
| Sb | 4.6 | 0.2–205 |
| Ag | 3.2 | 0.01–49.5 |
| Sr | 775 | 30–3885 |
| Tl | 9 | 0.15–85 |
| V | 252 | 43.5–5015 |
| Zn | 148 | 0.28–2200 |

from CFA. The process involved separation of magnetic fractions from the ash, followed by leaching the non-magnetic fraction with sulfuric acid, precipitating and removing Ti and Fe oxides from the leach solution by adding a strong base (NaOH), and precipitating and removing Al by contacting the reclaiming solution with CO₂. The precipitated aluminium hydroxide is calcinated to get aluminum oxide. However, direct sulfuric acid leaching yielded a low aluminum extraction (Matjie et al. 2005). Nayak and Panda (2010) also showed that direct sulphuric acid leaching at low concentration did not yield high aluminum recovery.

In contrast, CFA was treated pelletized with lime and calcinated, leaching with sulfuric acid that yielded better recovery. US Patent No. 4254088 (1981) discusses a process where the CFA was sintered with a mixture of NaCl and Na₂CO₃ at a temperature 700–900 °C. After sintering, 90 % of the aluminum CFA was in the acid soluble fraction. Recently, Matjie et al. (2005) discussed this calcinated technique at high temperature to decompose mullite phases, and then the calcinated CFA was leached in sulfuric acid to produce a solution containing Fe, Al and Ti species. The selective recovery of Al and Ti was carried out using various extraction methods, solvent extraction was more efficient than others and recovered 99.4 % of

Table 4 Recovery of major and trace elements, their extraction methods and recovery efficiency from coal fly ash

| References | Element | Method | Chemical reagent/others | Recovery efficiency |
|------------------------------|------------|---|--|---|
| Burnet et al. (1977) | Al | High-temperature chlorination | Carbon, chlorine | Not known |
| Mehrotra (1982a, b) | Al, Ti | High-temperature chlorination | Carbon, carbon monoxide, chlorine | 25 % Al, 25 % of Ti |
| US Pat. No. 4159310 (1979) | Al, Ti | High-temperature chlorination | Carbon monoxide, chlorine, H ₂ SO ₄ | 70 %–80 % Al, 80 % Ti |
| US Pat. No. 4243640 (1981) | Al | Magnetic separation, acid leaching, calcination | HNO ₃ | Up to 90 % Al |
| US Patent No. 4567026 (1986) | Al, Ti | Magnetic separation, leaching, calcination | H ₂ SO ₄ , NaOH, CO ₂ | Not known |
| US Patent No. 4254088 (1981) | Al, Ti | Salt-soda sintering, leaching | NaCl, Na ₂ CO ₃ , HNO ₃ /H ₂ SO ₄ | 90 % Al |
| Matjie et al. (2005) | Al, Ti | Calcination, leaching, solvent extraction | CaO, H ₂ SO ₄ | 99.4 % Al ₂ O ₃ , 97 % TiO ₂ |
| US Pat. No. 4539187 (1985) | Al, Ti | Acid leaching | Fluorosilicic acid, HF | Not known |
| Wu et al. (2012) | Al | Pressure acid-leaching | H ₂ SO ₄ | 82.4 % Al |
| US Pat. No. 4130627 (1978) | Al, Fe | Alkaline leaching, electrolysis | NaOH, HCl/HF | 65 % Fe, 89 % Al |
| Padil and Sohn (1985) | Al | Lime-soda sintering | CaCO ₃ , NaCO ₃ | 50 %–60 % alumina |
| Lu et al. (2003) | Al | Lime-soda sintering | Limestone, NaHCO ₃ | 70 % alumina |
| Bai et al. (2010) | Al | Lime-soda sintering | Lime, NaCO ₃ , NaOH | 90 % alumina |
| US Pat No. 4397822A (1983) | | Lime-soda sintering | CaCO ₃ , NaCO ₃ , Sulfur, carbon | 90 % alumina |
| US Pat No. 0119426A1 (2010) | Si, Al | Leaching, calcination | NaOH, CO ₂ , CaO, H ₂ SO ₄ | Not known |
| US Pat No. 7871583B2 (2011) | Si, Al | Leaching, calcination | NaOH, CO ₂ , CaO, H ₂ SO ₄ | Not known |
| US Pat No. 5231018 (1993) | Al, Ti | Bioleaching | C and N source, GIN-1, growth medium | Not known |
| US Pat No. 5278069 (1994) | Al, Ti | Bioleaching, acid precipitation | <i>Thiobacillus thiooxidans</i> | Not known |
| US. Pat No. 4539187 (1985) | Si | Acid leaching | SiF ₄ , HF | Not known |
| US Pat. No 0287827A1 (2010) | Si | Acid leaching | HF, coal, S | Not known |
| US Pat. No. 0119426A1 (2010) | Si | Alkaline leaching, carbonation | NaOH, H ₂ SO ₄ , CaO, CO ₂ | >98.5 % SiO ₂ (purity) |
| US Pat. No. 7871583B2 (2011) | Si | Alkaline leaching, carbonation | NaOH, H ₂ SO ₄ , CaO, CO ₂ | >98.5 % SiO ₂ (purity) |
| US Pat. No 4814150 (1989) | V | Leaching, precipitation | NaOH, H ₂ SO ₄ , ammonium salt | 80 %–90 % |
| US Pat. No. 4966761 (1990) | V | Leaching, solvent extraction | NaOH, resin, HCl, NH ₄ Cl, quaternary amine | Up to 93.4 % V |
| US Pat. No. 7498007B2 (2009) | V | Acidic leaching | Calcium hydroxide, quick lime, acid | >98 % |
| Xiang-yang et al. (2010) | V | Acid leaching | H ₂ SO ₄ | 95 % |
| Vitolo et al. (2000) | V | Combustion, acid leaching | H ₂ SO ₄ , NaClO ₃ | 83 % |
| US Pat. No. 6652819B2 (2003) | V | Combustion, acid leaching | H ₂ SO ₄ | Not known |
| US Pat No. 4475993 (1984) | Ga, others | Alkali halite melt, electrolysis | Aluminium trichloride | 69 % of Ga |
| US Pat No. 4643110 (1987) | Ga, Ge | Sublimation | | Not known |
| US Pat No. 4678647 (1986) | Ga, Ge | Sublimation | | Up to 90 % Ga |
| US Pat No. 4757772 (1988) | Ge, Ga | Sublimation | | Not known |
| US Pat No. 4678647 (1986) | Ge, Ga | Sublimation | | Up to 90 % Ga |

Table 4 continued

| References | Element | Method | Chemical reagent/others | Recovery efficiency |
|-----------------------------|----------------|---|---|---|
| Arroyo et al. (2014) | Ge, Ga | Acid, alkaline, complexant leaching | Oxalic acid, sulfuric acid | Up to 90 % Ge; up to 82 % Ga |
| Gutiérrez et al. (1997) | Ga | Acid leaching | HCl, Amberlite LA-2 | 83 % of Ga |
| Fang and Gesser (1996) | Ga | Acid leaching, flotation | HCl | Up to 80 % of Ga |
| Arroyo et al. (2009) | Ge | Water leaching, solvent extraction | Water, catechol, NaOH | 95 % Ge |
| Font et al. (2005) | Ge | Water leaching | | 86 % of Ge |
| Mok et al. (1984) | Mo | Acid digestion, solvent extraction | HCl, HNO ₃ , dithiocarbamate | Not known |
| Ogata et al. (2011) | Mo | Acid/alkaline leaching | HCl, NaOH, gibbsite | 90 % of Mo |
| US Pat. No. 3857920 (1974) | Li | Leaching | Water, CO ₂ | 80 %–90 % of Li ₂ CO ₃ |
| Wang et al. (2007) | Se | Leaching | HNO ₃ , NaOH | 55 %–69 % at pH 12 |
| Sparton Res Inc. (2007) | U | Acid leaching, ion-exchange | H ₂ SO ₄ , resin | Not known |
| Maslov et al. (2010) | U, Ra | Acid leaching | HNO ₃ , HF | U (99 %), Ra (97 %) |
| US Pat No. 6827837B2 (2004) | Au, Pt group | Combustion, acid digestion, precipitation | HNO ₃ , HCl | Not known |
| US Pat No. 0056548A1 (2005) | Au, Pt group | Combustion, acid digestion, precipitation | HNO ₃ , HCl | Not known |
| US Pat No. 4649031 (1987) | REEs | Sieving, aqueous alkali/acid digestion | Na ₂ CO ₃ , HCl, HNO ₃ | Not known |
| US Pat No. 0287653A1 (2013) | REEs | Acid leaching, Ion-exchange | HNO ₃ , tributyl phosphate, kerosene | Not known |
| US Pat No. 8968688B2 (2015) | REEs | Acid leaching, Ion-exchange | HNO ₃ , tributyl phosphate, kerosene | Not known |
| Narukawa et al. (2007) | Cr | Alkaline leaching | NaOH | Not known |
| Huang et al. (2011) | Pb, Zn | Alkaline leaching | NH ₄ OH/NaOH | Not known |
| Okada et al. (2007) | Zn, Pb | Acid leaching | CH ₃ COOH | 97 % Zn, 98 % Pb |
| Hong et al. (2000) | Cr, Cu, Pb, Zn | Leaching | Chelating agents (EDTA) | 20 %–50 % Cr, 60 %–95 % Cu 60 %–100 % Pb, 50 %–100 % Zn |
| US Pat. No. 5278069 (1994) | Co, others | Bioextraction | <i>Thiobacillus thiooxidans</i> | Not known |

Al₂O₃ and 97 % of TiO₂. US Patent No. 4539187 (1985) also used an acid treatment where CFA was reacted with concentrated fluorosilicic acid and hydrogen fluoride at high temperature to form aqueous silicon fluoride vapor and fluoride and fluorosilicate of Al and Fe. Separated the Al and Fe bearing fluorides and fluorosilicate from aqueous silicon vapor, hydrolyzed and then recovered the substantial amount of pure Fe and Al following electroplating process. Recently, Wu et al. (2012) demonstrated pressure acid-leaching method, wherein the high extraction (82.4 %) of Al was obtained by diminishing CFA size (74 μm) and increasing acid concentrations (50 %). However in this method, the non-target metals readily leached into the acid, resulting in impurities. In addition, acid

leaching had limited application due to its highly corrosive nature, besides this process required high cost, acid resistant equipment, and air-tight processing to protect the work environment.

Recovery of alumina by alkaline leaching is less problematic than techniques using acid leaching. US Patent No. 4130627 (1978) describes the alkaline leaching method where in the process takes place in an aqueous alkali solution of approximately pH 13, using NaOH, to form an aqueous CFA blend. The blend was agitated on a hotplate at temperatures of about 90 °C, and filtered to recover an alkaline solid. The filtrate was then contacted with hydrochloric or hydrofluoric acid to form soluble salts of various metals. Iron and aluminum were then selectively

precipitated and recovered. This process recovered 65 % by weight of Fe and about 89 % of Al. However, this process has some disadvantages, such as being complex, time consuming, requiring larger quantities of processing materials, and high facility costs. This problem can be dealt with lime-soda sinter process, where a mixture of CFA, calcium carbonate, and sodium carbonate was sintered at high temperature to form a soluble sodium and calcium aluminate (Padil and Sohn 1985). Lu et al. (2003) reported this process where the CFA was mixed with limestone, sintered at 1260 °C, and then dissolved in sodium carbonate solution at 80 °C. This process obtained 99.9 % purity of alumina, and its recovery efficiency was 70 %. Recently, Bai et al. (2010) also used a lime-soda sintering method for the recovery of aluminum from an alkali desilicated CFA. The final Al extraction efficiency was 90 %. This process extracted Al from nearly 88 %–92 % at temperatures below 85 °C, while Al was not fully released from the sintered ash when the temperature was greater than 85 °C. US Patent No. 4397822A (1983) demonstrated an improvement method which added a small amount of sulfur and carbon to the lime-CFA sinter mixture before sintering to lower the optimum sinter temperature. This method recovered almost 90 % of alumina from CFA, and the results indicate that the addition of a combination of S and C, either elementally or as coal refuse, produces a higher recovery of alumina from CFA and at lower sintering temperatures, resulting in an energy savings. Recently, two US Patent Nos. 0119426A1 (2010) and 7871583B2 (2011) released a method for the recovery of alumina from high Si containing CFA, where CFA is leached with highly concentrated NaOH (>40 %). Silica is first removed from the CFA in the form of Na₂SiO₃, followed by separation of the residues having Al:Si ≥ 2. Subsequently the product was calcinated at 900–1100 °C to get pure alumina.

Besides acid/alkaline leaching, bioleaching also is used for the recovery of metals from CFA. This is discussed by in US Patent No. 5231018 (1993), where the CFA is suspended in an aqueous saline solution having pH ranging from 5 to 8, and then forming a reactive mixture by adding a pure culture a gram-positive bacteria (GIN-1), genus *Rhodococcus*. The mixture is then incubated for a period of time sufficient for the formation of microorganism cells/metal oxide adsorbate agglomerates, which separate from the reaction mixture. In this process, incubation reaction time was adjusted to selectively recover TiO₂ and Al₂O₃ from CFA. In another biochemical study, US Patent No. 5278069 (1994) used *Thiobacillus thiooxidans* strain in an acidic media for the recovery of metals from CFA. The metals were selectively recovered by precipitating the solution by adjusting the pH. Aluminum was mostly precipitated at pH 3.1–4.7, while Ti was precipitated at pH

1.5–3.1. These results indicate that bioleaching is one of the most cost-effective methods for the removal of metals from CFA; however, the percentage of metal recovery and their purity have not been reported.

3.2 Silica

Silica is used for various purposes, such as semi-conductors, soda-lime glass, high temperature thermal protection fabrics, glasses (including borosilicate glass and lead glass), and contact lenses and medical devices (Lukkassen and Meidell 2007). Coal fly ash is enriched with silica.

Several methods have been developed for the recovery of silica such as acid or alkali leaching, followed by separation and purification using different techniques. US Patent No. 4539187 (1985) describes a method where CFA is reacted with fluorosilicic acid and hydrogen fluoride at a high temperature to form fluorides of Fe, Al and Si. The fluoride mixture is distilled, separating the aqueous and gaseous silicon fluoride from the mixtures, hydrolyzing the silicon fluorides vapor, and recovering silicon dioxide in high purity form. Recently, US Patent No. 0287827A1 (2010) released a method where a mixture of coal and CFA is reacted with hydrogen fluoride in water to produce a liquid stream containing silicon fluoride and metal fluorides, and a solid stream containing unreacted coal and S compounds. Sulfur compounds are reacted with metallic nitrates dissolved in the water, which separated the aqueous solution of nitrate, S and metallic ions from the solid coal, and the solid coal is then washed with water. Subsequently, silicon fluoride and metal fluorides are contacted with metallic nitrates in an aqueous mixture to form solid silicon dioxide, and solid silicon dioxide is separated from the aqueous mixture. This process has recovered high purity silica from CFA. However, acid leaching is not always appropriate because it needs better acid resistant and airtight processing equipment and it causes environmental pollution. This problem can be solved by using alkaline leaching methods. US Patent Nos. 0119426A1 (2010) and 7871583B2 (2011) released an alkaline leaching method for the recovery of silica from CFA, where Si is leached using NaOH in the form of Na₂SiO₃ solution. The solution is vaporized to obtain Na₂SiO₃, and pure silica (>98.5 %) is produced by carbonation.

4 Recovery of trace elements

There are a number of methods have been developed for the recovery of trace elements from CFA (Table 4), which are discussed below.

4.1 Vanadium

Vanadium (V) is mainly used in ferrous and non-ferrous alloys due to its tensile strength, hardness, and fatigue resistance (Moskalyk and Alfantazi 2003; Navarro et al., 2007). In addition, V is used in vanadium redox batteries. Although, V is extracted from various sources, V-enriched coal and carbonaceous residues such as CFA are one of the most important sources (Dai et al. 2015a).

Numerous methods have been used to extract V from carbonaceous residues. The most common method is wet treatment where the residue is subjected to multi-stage leaching, followed by precipitation via pH adjustment and oxidation/reduction (European Patent No. JP-A-H08-325651 1996; H10-251025 1998). US Patent No. 4814150 (1989) created a process where the combustion residue is reacted with sodium hydroxide in the presence of an oxidizer, dried at 100–250 °C, and leached with water to selectively extract V. Vanadium is precipitated from the alkaline extract by adding H₂SO₄ (up to pH 2) and an ammonium salt. The precipitated ammonium polyvanadate is calcinated to get vanadium pentoxide, which yields 80 %–90 % of V. US Patent No. 4966761 (1990) discusses a process in which CFA is mixed with water to prepare a slurry, carbon is skimmed off followed by alkaline pressure leaching and solvent extraction for the recovery of V (up to 93.4 %). US Patent No. 7498007B2 (2009) uses an acid solution to recover V. The extraction is carried out by precipitating vanadium pentoxide as a result of increasing pH by adding calcium hydroxide, quick lime, or calcium carbonate to the acid solution. After V is precipitated, the solid is separated by filtration or centrifugation. The percentage of V recovery from the acidic solution was ≥ 98 %. Recently, Xiang-yang et al. (2010) also described an acid leaching process using large volumes of sulfuric acid, extracting V up to 95.8 % from the leachate; however, no purification of V was attempted. Wet treatment techniques using acid/alkali leaching still have problems since they need a relatively large amount of expensive reagents, and they deal with complicated, troublesome repetition of steps, including conversion of solid CFA to a solution, isolating V from other metals and reconversion of V the solution into a solid. In addition, this technique may be unsuitable for CFA samples containing a high carbonaceous fraction and a low concentration of V because leaching V may not be efficient. To cope with this problem, dry treatment techniques have been developed (US Patent Nos. 4420464 1983, 4816236 1989). In these methods, the carbon is removed by combusting the V-containing residue at a controlled temperature, and then the residue is leached with a strong alkali/acid to recover the vanadium. Vitolo et al. (2000) used this method for the recovery of V from a fly ash at temperatures of 650–1150 °C, followed by an

acid leaching and oxidative precipitation of vanadium pentoxide. Overall, this process yielded 83 % V. US Patent No. 6652819B2 (2003) also employed this method for the recovery of V from carbonaceous residues. The method involves a preliminary combustion of the residue at temperatures of 500–690 °C, followed by leaching with H₂SO₄ at a pH range of 1.5–4, and selective precipitation V by adjusting the pH in the range of 4.5–7.5, and separating the V ion as a tetravalent vanadium compound.

4.2 Gallium and germanium

Gallium (Ga) is used for the manufacture of high technology optical devices such as semiconductors, DVD's, laser diodes, and other electronic devices (Moskalyk 2004). Germanium (Ge) is used in the manufacture of photovoltaic cells, fiber optics and as a catalyst for polyethylene terephthalate production (Butterman and Jogerson 2005). Germanium and gallium in the Earth's crust are mainly associated with Zn and its mineral phases. Thus, they are typically recovered from by-products of Zn mineral processing. Germanium and Ga are also enriched in coals (Gluskoter et al. 1977; Harvey et al. 1983; Dai et al. 2012a, b; Seredin 2012; Dai et al. 2014b; Qin et al. 2015a, b; Dai et al. 2015b). Thus, coal fly ash is a promising alternative resource of those elements (Fang and Gesser 1996; Zhang et al. 1999; Arroyo et al. 2014; Dai et al. 2014a, b). After combustion in a coal burning power plant, both elements condense from the vapor phase onto the surface of the CFA, thus are enriched in CFA relative to the feed coal (Font et al. 2005; Querol et al. 1995).

Several techniques have been developed for the recovery of Ge and Ga from CFA. Alkali halite melt is one of the methods, and is discussed in US Patent No. 4475993 (1984). In this method, the CFA is reacted with aluminium trichloride to form a soluble compound of trace metals in the melt. Gallium was recovered from the melt by electrolysis. However, this process is uneconomical and recovered a moderate percentage (69 %) of Ga. Another method of Ga and Ge extraction is sublimation, which is discussed in several US Patents (Nos. 4757772 1988, 4757770 1988, and 4643110 1987). The steps include heating the CFA in an oxidizing atmosphere to vaporize the Ge and Ga, then treating the oxides in a reducing atmosphere to reduce oxides to suboxides, which subsequently precipitate on the surface of sand particles, and recovery of the products from the sand particles using a cold liquid solution. This method has problems involving other volatile compounds such as As and S. To cope with this problem, US Patent No. 4678647 (1986) introduced a method where CFA is pelletized and treated in the presence of an oxidizing gas at a temperature of about 900 °C. This treatment removes As and S from the CFA, so that they

will not remain in the concentrated Ga and Ge fractions. Then, the oxides are treated in the presence of a reducing gas at the same temperature range to reduce the oxides to suboxides. Recover of Ga suboxides is done by condensation at a lower temperature (nearly 700–800 °C) and dissolving the condensed material using an acidic solution. The recovery rate of Ga for this method is up to 90 %. This method can be more economical and more efficient than the alkali halite method.

Other techniques for the recovery of Ga and Ge include using water/acid/alkali leaching of CFA, followed by separation/purification by using precipitation, distillation, ion flotation, adsorption into activated carbon, and solvent extraction (Meawad et al. 2010). Arroyo (2014) optimized Ge and Ga recovery from CFA using different extractants in a wide range of extraction conditions (acid, alkaline, complexant, reducing and oxidizing). High extraction yields of Ge (up to 90 %) and Ga (up to 82 %) were made using weak oxalic acid and sulfuric acid solution, respectively within 1–2 h extraction period. Gutiérrez et al. (1997) discuss the recovery of Ga from CFA by 6 M hydrochloric acid in contact with Amberlite LA-2. Iron is precipitated with sodium hydroxide, while 83 % of Ga remains in solution, which is extracted selectively with LIX 54. Fang and Gesser (1996) studied the recovery of Ga from CFA involving a of two stage acid leaching with hydrochloric acid, followed by removal of silica and calcium, reduction of iron, extraction of Ga by foam floatation (polyurethane foam) and finally purification. This method showed that better extraction of Ga occurs at higher acid concentrations, low temperatures, short extraction times and smaller particle size. However, acid leaching is costly, requires better acid resistant equipment, and better environmental protection. Arroyo et al. (2009) discussed a water leaching process for extracting Ge from CFA, followed by solvent extraction. In this process, Ge complexation achieved with catechol, then extraction of the Ge-catechol complex with an organic reagent such as trioctylamine diluted in an organic solvent, and finally, stripping Ge from the organic extract by NaOH. This process extracted 95 % of the Ge from the leachate. In another study, Font et al. (2005) invented a low cost and environment friendly process for the recovery of Ge, where the CFA is leached in water at different ash/water ratios and temperatures. Results showed that temperature is the most important parameter in the extraction process, maximum content (up to 86 %) of the Ge extracted at 90 °C. For the recovery of Ge from solution, Hernandez-Exposito et al. (2006) developed an ion flotation method using different complexing agents (pyrogallol, catechol, hydroquinone and resorcin) at pH range of 4–7. It was found that using dodecyl amine as a surfactant, and pyrogallol or catechol as a complexing agent at pH values of 4–7, 100 % of the Ge

could be recovered in 30 min. Torralvo and Fernández-pereira (2011) also reported that catechol as complexing agent for the recovery of Ge from leachates.

All the above methods were tested on bulk CFA; however, Ge and Ga are mainly concentrated in the finer fractions. This was examined in US Patent No. 4686031 (1987), where the process is mainly subjected to size classified CFA, and then extraction by various treatments. It was found that fine fraction, isolating 30 % of the finest particles while avoiding substantial rupturing of cenospheres and plerosphere, provided the best recovery.

4.3 Molybdenum

Molybdenum (Mo) is used to produce high tensile strength steel. It is also used as a biocatalyst for plants and animals and it is widely used in the manufacture of super alloys, lubricants, and electronic products. Coal fly ash can provide an alternative source for Mo recovery since some coals are enriched with Mo (Dai et al. 2015a, b). Mok et al. (1984) extracted Mo from CFA using the steps, digestion of CFA using concentrated HCl and HNO₃, diluting the solution using HCl, and selectively extracting Mo from the solution using dithiocarbamate. Ogata et al. (2011) disclosed a method for the recovery of Mo from CFA where the CFA is leached at pH levels 2, 7 and 11, and then adjusted with hydrochloric acid or sodium hydroxide solution. Subsequently, gibbsite (GB), an amorphous aluminium oxide, is used for the adsorption of Mo from elutes from the solutions. A greater concentration of Mo was eluted under acidic conditions onto GB400 (gibbsite calcinated at 400 °C) at pH 2 than from neutral or basic eluates. Recovery of Mo from eluates was 90 % using GB400. The main adsorption mechanism was ion exchange with a number of the hydroxyl groups in GB.

4.4 Lithium

There are a number of applications used for lithium carbonate, including as an additive in aluminum smelting, production of glasses, enamels, and ceramics, and production of electronic grade crystals. Its pure form is used in lithium ion batteries. Lithium has been found enriched in coal deposits (Qin et al. 2015b). US Patent No. 3857920 (1974) describes a method for the recovery of lithium carbonate from slurries resulting from the dispersion of CFA in water. In this method, CFA slurry is treated with carbon dioxide to convert the lithium carbonate to the more soluble lithium bicarbonate. The resulting bicarbonate solution is then filtered to remove insoluble material. The filtrate containing lithium bicarbonate is decarbonated either by vacuum treatment, heat, or preferably by aeration of the solution to precipitate lithium carbonate in the

aqueous medium. The precipitated lithium carbonate is then filtered from the aqueous solution. This method is inexpensive and it recovered 80 %–90 % of the lithium carbonate.

4.5 Selenium

Selenium (Se) is mainly used in glassmaking and for pigments. It is also used for making semiconductors and in photocells. Selenium is commercially extracted as a byproduct in the refining of metal sulfide ores, most often during copper production. It can also be extracted from CFA since some coals are enriched in Se (Dai et al. 2014a, b; 2015b, c). Wang et al. (2007) studied the leaching of selenium from bituminous and sub-bituminous coal ash with respect to pH. Very low concentrations of selenium were released at a pH range from 3 to 4, while the amount increased with increasing pH above 4, and the maximum amount of Se (55 %–69 % of the total) was leached at pH 12. Iwashita et al. (2005) also reported that leaching of Se increased when pH was raised. However, recovery of this element is not attempted in these literatures.

4.6 Radioactive elements

Radioactive elements have many industrial and scientific applications, despite the obvious dangers if they are not handled properly. Radioactive elements are used as tracers in the medical field, the generation of electricity in nuclear power plants and in the production of nuclear weapons. Coal contains significant amounts of radioactive elements such as uranium (U) (Dai et al. 2015a, c). Thus, CFA can be alternative source of these elements. Sparton Resources Inc. (2007) reported the extraction of U from CFA. This process included acid leaching (H_2SO_4) and formation of yellowcake by passing the filtered leachate solution through a standard ion exchange resin, stripping the resin and precipitating a U compound. This process is essentially similar to the U extraction method used by the primary U ore processing plants. However, this work is preliminary and requires further work to improve recovery.

Maslov et al. (2010) discussed a method for recovering U from brown coal ash of Mangolia where the ash is leached with an acid mixture (8 M HNO_3 + 10 % HF). The acid mixture leached U and Ra as high as 99 % and 97 %, respectively. The extraction of U from the solution and its purification for the removal of accompanying elements were carried out using an anion exchanger (Dowex 2X8) with a 2 M HCl solution as the eluate. After leaching, the CFA contained neither natural radioactive elements nor their decay products, thereby allowing for the use of the ash as a building material.

4.7 Gold, silver and platinum group of elements

Precious metals such as gold (Au) and silver (Ag) have many application in industry, jewelry and medicine (Guerra and Calligaro 2003; Drake and Hazelwood 2005; Eisler 2003). Some Au compounds are used as anti-inflammatory drugs in the treatment of rheumatoid arthritis and Ag compounds are used in the treatment of infections. Gold is also found in electronic apparatus and Ag is used in photography, industry and for hard solder.

US Patent Nos. 6827837B2 (2004) and 0056548A1 (2005) released a method for the recovering of gold and one and more platinum group elements, such as platinum, rhodium, ruthenium, osmium and iridium, from CFA. In this method an ash formed by the combustion of a pre-selected coal is mixed with the ash contains gold and one more platinum group of elements, an inquant containing gold and one or more platinum group elements, and fluxing agent to form a 'charge'. The 'charge' is then heated in a furnace to a preselected temperature and forming a molten charge including a molten inquant; absorbing a portion of the gold and more platinum group elements of the ash into the molten inquant. Casting a dore bar (which contains gold and one or more platinum group elements) by discharging the molten inquant. Digesting the dore bar in an electrowinning process where the dore bar is introduced as an anode in an acidic bath and an electrical potential is maintained between the cathode and anode, then precipitating and dissolving trace elements in the electrolytic solution producing an anode slime. The digestion of anode slimes is done using 30 % solution of HNO_3 . The digestion is filtered and rinsed then the liquid rinsed portion containing Ag in solution is washed with HCl and filtered. The residue is mixed with aqua regia, forming a solution containing gold, platinum and palladium. Gold may then be removed by solvent extraction. Rhodium and other metals may be removed by precipitation by the treatment of the solution with potassium hydroxide and sodium borohydride. Palladium in solution may be removed by precipitation by treatment with ammonium hydroxide, NH_4OH , and HCl as the complex $\text{PdCl}_2(\text{NH}_3)_2$. Alternatively, Pd in solution is removed by precipitation with DiMethyl Glyxime, followed by filtration and reduction and ashing of the residue. Platinum in solution is removed by any of the accepted methods including precipitation as impure $(\text{NH}_4)_2\text{PtCl}_6$ after treatment with NH_4Cl , or leaching H_2PdCl_4 from solution. An organic solvent such as DiMethyl Glyoxime is used to extract gold, after treatment with NH_4Cl , the solution should also be treated with ethanol and hydrogen peroxide. The solution is filtered and the residue, including $(\text{NH}_4)_2\text{PtCl}_6$, subjected to reduction and burning leaving an impure platinum sponge. The platinum sponge can be purified by redissolving in aqua-regia. This method

is very complex, and a recovery and purity level is not mentioned.

4.8 Rare earth elements (REEs)

Rare earth elements include light REEs (Sc, La, Ce, Pr, Nd, and Pm), medium REEs (Sm, Eu and Gd) and heavy REEs (Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), which are mainly used in various industrial purposes such as fuel cells, green energy devices, hi-capacity batteries, magnets for wind generation (Chen 2011; Hoenderdal et al. 2013; Franus et al. 2015). REEs have been recovered from bauxite residue (Borra et al. 2015) and electronic wastes (Anonymous 2015). It has also been recognized that some coals (Seredin 1996; Dai et al. 2014a, b) and CFA (Ketris and Yudovich 2009; Blissett et al. 2014; Dai et al. 2012a, b; Dai et al. 2014a, b; Franus et al. 2015) are enriched with REE; thus, recently sparking interest in evaluating of this product as a potential alternative source of REEs (Seredin et al. 2013).

There are several methods developed for recovery of rare elements from CFA, the chlorination method is favored due to selectivity and high reactivity. The necessary apparatus required for this process is very expensive. This technique can be used to recover only certain rare elements where other complex recovery processes are not suitable. From this standpoint, US Patent No. 4649031 (1987) reported a non-destructive digestion process for the recovery of rare elements, including Lanthanides and Actinides and group V and VI elements that are adsorbed onto the surfaces of coal combustion residues. This technique includes: (1) reducing the grain size of the combustion residues from 0.1 to 1 mm, (2) digestion of the residues with water, (3) digestion of the residues with a dilute aqueous alkali solution (1.5 %–8 %), (4) digestion of the residue with a dilute aqueous acid solution (0.5 %–5 %) at a temperature below the boiling point of water, (5) separating the solid and liquid phases after each digestion, (6) and isolating the rare metals from the liquid phases. This study shows that the mild digestion agents used dissolve an unexpectedly high proportion of rare metals present in the byproducts and that increasing the heat and residence time lowers the availability of the metals. This process is not appropriate for the recovery of individual elements from the mixed solution.

Recently, US Patent No. 0287653A1 (2013) demonstrated the recovery of REEs from CFA. In this method, first the CFA was treated with a mineral acid (HNO_3) at 90 °C to form a more concentrated mineral acid solution. This solution is mixed with an organic solution (tributyl phosphate and kerosene) that includes the rare earth salts. The organic solution is mixed with water to form an aqueous solution. REEs substantially recovered from the

aqueous solution by using ion exchange process. In a continuation-in-part of the above patent, US Patent No. 0139871 (2015) was carried out using the same method, but here the CFA was sorted into a substantially magnetic and non-magnetic fraction. This indicates magnetic treatment can maximize efficiency of extracting REEs from CFA. However, extraction efficiency of these methods is not reported. Furthermore, ion exchange method can remove other metals from the solution. This method needs to be optimized to improve the yields for REEs.

4.9 Other trace elements (Pb, Cr, Cd, and Cu)

Coal fly ash also contains considerable amounts of trace and rare elements, and some of them can be hazardous (Izquierdo and Querol 2012). There are many studies which focused on the extraction of trace metals from CFA, some employing hydrometallurgical techniques using various lixiviants: inorganic acids such as sulfuric acid, hydrochloric acid, nitric acid, organic acid such as acetic acid, citric acid, oxalic acid, alkaline reagents such as sodium and ammonium hydroxide, chelating reagents such as ethylenediaminetetraacetate (EDTA) and diethylenetriaminepentaacetate (DTPA) (Hong et al. 2000; Zhang and Itoh 2006).

Narukawa et al. (2007) studied Cr extraction from an Australian CFA using 0.01 M NaOH. However, this process did not leach Cr(III) from the CFA. Huang et al. (2011) discussed the alkaline leaching by ammonium or sodium hydroxide, where only Pb and Zn are recovered while other metals remained in the solid residues. However, this process can extract other heavy metals such as Cu and Cd if the leaching process is conducted together with subsequent leaching using acidic lixiviants. Okada et al. (2007) reported that in acidic leaching using acetic acid recovered 97 % of Zn and 98 % of Pb from CFA, while the same CFA in alkaline leaching using 3 M NaOH recovered 81 % Pb and 35.5 % Zn. Consequently, acid leaching is more effective under hydrothermal conditions. This was studied by Zhang and Itoh (2006) for CFA using five types of acids and hydrochloric acid was found to be the most effective for metal extraction from the CFA. Compared to room conditions (standard temperatures and pressures), it was determined that hydrothermal treatment accelerated the dissolution of the CFA and resulted in better leaching of metals such as Cr, Cd, and Pb. Even more effective leaching can be done using chelating agents. Hong et al. (2000) studied the extraction of heavy metals from CFA using acid and chelating agents such as nitritriacetic acid (NTA) and ethylenediaminetetraacetate (EDTA), or diethylenetriaminepentaacetate (DTPA). The results showed that chelating agents provide good leaching efficiency and after the treatment the CFA's were successfully detoxified

to meet landfilling guidelines. Using 3.0 % EDTA or DTPA, 20 %–50 % Cr, 60 %–95 % Cu, 60 %–100 % Pb, and 50 %–100 % Zn were extracted from CFA. However, these agents are not biodegradable and it is difficult to recover the metals from the leachate due to their strong chelating properties.

Recovery of metals from CFA using bioextractants has been studied by many authors (Seidel et al. 2001; Ishigaki et al. 2005; Sierra-Alvarez 2009). This process is important at an industrial scale. In this process, chemolithoautotrophic bacteria such as *Thiobacillus* species and Heterotrophic fungi such as *Aspergillus* and *Penicillium* species are used to leach the metals. The leached metals can then be recovered and the residues may be safely utilized. US Patent No. 5278069 (1994) discusses the bioextraction process using strains of *Rhodococcus* and *Thiobacillus thiooxidans* for the removal of Co along with other metals (Al, Ti and Fe) from CFA. After extraction, the metals were recovered in a series of precipitation steps by controlling pH. This technique is relatively inexpensive and requires low energy inputs when compared with conventional technologies (Krebs et al. 1997). However it is a slow process requires sufficient amounts of cell culture and is not selective toward specific metals (Groudev et al. 1982).

5 Recovery of other materials

5.1 Magnetic materials

Magnetite or other magnetic material is used by the steel industry for cleaning coal prior to combustion. One potential source of magnetite is CFA which can contain economically recoverable amounts of magnetic material. After removal of magnetic material from CFA, the remaining product can be useful for refractory and ceramic manufacturing since it contains appreciable amounts of Al_2O_3 and SiO_2 (Rao et al. 1999). The characteristics of magnetic material in CFA vary depending on the coal source and operating conditions of the coal boiler (Zyryanov et al. 2011). The basic principle behind magnetic separation deals with the fact that materials having different magnetic moments experience varying forces in the presence of a magnetic field gradient. Thus, applying an external magnetic field can extract those materials with similar magnetic properties (Yavuz et al. 2009).

There are many wet or dry magnetic separation methods for the recovery of magnetic materials from CFA. The dry process uses a rotating magnetic drum and initial separation produces middling and tailings which are discarded and a crude iron oxide fraction which must be further refined by passing it through another magnetic unit. The

wet process involves pumping CFA slurry into a magnetic drum where the magnetic iron oxides and associated materials are collected and then the material is passed through a similar unit for further refining. In most of the plants using wet magnetic separation, the advantage is that the slurry can be directly fed into the feed tank. Prakash et al. (2001) demonstrated the use of a selective magnetic coating for the removal of iron from Talcher (India) CFA. They used sodium hexametaphosphate (NaHMP) as a dispersing solution, followed by sodium oleate for the separation of iron from the slurry. The recovery rate for Fe was around 92 %. The wet/dry magnetic separation processes are documented by numerous US Patents (Nos. 4191336 1980; 4319988 1982; 5047145 1991; 5227047 1993). However, these methods are not cost-effective if the ash contains less than 2 % magnetite. In order to improve the process or more recovery, CFA containing sufficient amount of magnetic material (>2 %) need to be selected. Groppo and Honaker (2009) studied the economic recovery of magnetite material from CFA.

US Patent No. 3769054 (1993) released another method for the recovery of magnetic materials from CFA. In this method CFA is dry processed in an air classifier and then separated by magnetic separation. This process is expensive, and the recovered portion of magnetite often contains undesirable impurities. To resolve these problems, US Patent No. 4191336 (1980) provides an improved process for the recovery of high purity magnetite from CFA. This process involves making a water slurry of the CFA and then passing the concentrated slurry through the magnetic separators; magnetite is contained in the separated material. The separated magnetite is then pulverized to a size where 95 % of the magnetite will pass through a 325 mesh sieve. The crushed magnetite is passed through a third separator followed by purification and drying.

5.2 Cenospheres

Cenospheres are composed mainly of silica, alumina and iron oxides, and have unique properties such as sphericity, inert, lower density than water, and they are waterproof making them useful in a variety of applications. Generally, cenospheres make up 1 %–3 % by weight of the total CFA produced. They have valuable industrial applications, such as oil well drilling, ceramics, plastic, paint, coatings, polymer fillers, building products, buoyancy, and as low dielectric constant substrates (Huo et al. 2009; Wang et al. 2011). Cenospheres are used for water purification such as the removal of excess fluoride from drinking water. In this process, magnesia loaded cenospheres are produced using a relatively simple wet impregnation method with magnesium chloride (Xu et al. 2011). Cenospheres are used as a carrier because of their low weight, sphericity, non-

toxicity, and high strength. They are ideal for incorporation into materials such as silicone rubber in order to increase the conductivity. In addition, they enhance the rubber's suitability as an electromagnetic wave absorbing material, which can be used in electronic and radar applications (Pang et al. 2011).

There are several methods for the separation of cenospheres from CFA. Traditionally, cenospheres were removed from CFA via float-sink in settling lagoons. This simple procedure allows potentially toxic elements to be leached and requires a large space and significant time (Hirajima et al. 2010). Alternatively, a triboelectric separation system was used (Gurupira et al. 2001) but this technique requires that the spheres have a specific gravity ≤ 1 . Some solid silica particles with specific gravity of ≥ 1 may contain gas bubbles which over their specific gravity so that they mimic cenospheres during this process, rendering it less effective and attractive. Other studies that have looked at the extraction of cenospheres on a wet basis. In US Patent No. 4121945 (1978), CFA is mixed with water to form a slurry then a frothing agent is added and cenospheres lighter than water are skimmed. US Patent No. 4652433 (1987) looked at another method where CFA is separated into fine and coarse fractions and the coarse fraction is then mixed with water, subsequently the cenospheres are removed by skimming. These methods have some disadvantages. Wet processing caused environmental problems and imposed space restrictions. In addition, these methods only collect cenospheres with specific gravity ≤ 1.0 ; those that float on water. Also, these processes are not suitable for CFA that contains 10 % or more lime because high Ca bearing CFA (such as ASTM C618 Class C fly ash) has cementations properties when mixed with water and when pozzolanic reactions occur the material may harden. When using these wet methods many cenospheres can be trapped in agglomerated and/or hardened masses before flotation occurs. This problem was solved by a few recent US Patents (No. 0190327A1 2008, No. 8074804B2 2011, and No. 0050519A1 2012) where cenospheres were separated from CFA in a dry state by using air as the fluid media for the separation. In one of the processes, CFA is separated into narrow particle size fractions, followed by density separation using a fluidized bed of air, preferable in the absence of water by dry screening, and then an optional further particle size separation. The advantages of this technique are that it can yield nearly 100 % cenospheres and it avoids agglomeration of ash having high Ca content.

5.3 Unburned carbon

Unburned carbon in CFA can be used during activated carbon preparation or carbon black, and can be used as a supplementary fuel. It can also be useful in the

manufacture of graphite (Cabiellas et al. 2008; Cameán and Garcia 2011). Removal of unburned carbon from coal ash makes it a more valuable cement additive. There are numerous methods for the recovery of unburned carbon from CFA (Hwang et al. 2002). Electrostatic separation is one of them, has been used by many authors (Gray et al. 2002; Soong et al. 2002). This method operates in a controlled electrode potential condition following the principle of bipolar charging of dry particles either by particle-particle contact or by particle-wall collision under turbulent conditions. This process separates the positively charged carbon particles from the negatively charged ash particles. This technology has been successfully commercialized.

One of the most promising methods for recovering unburned carbon from CFA is froth flotation. This method relies on the ability of air bubbles to selectively adhere to the surface of a particular mineral surface. Since carbon is hydrophobic in nature, other particles that are hydrophilic attached to the air bubbles and become positively buoyant and float on the slurry (Ucurum 2009). This process has been commercialized in the US for CFA beneficiation with reported carbon grade recoveries of up to 70 % (Baltrus et al. 2001).

A similar technology for froth flotation uses oil agglomeration, which involves wetting hydrophobic particles by adding oil to the aqueous slurry. Subsequently, the vessel can be agitated which allows the oil coated particles to collide with each other and form agglomerates. The oil/carbon agglomerates being less dense than the ash suspension rise to the top of the vessel (Mehrotra et al. 1983). US Patent No. 546363 (1995) removes carbon adding floating reagent-mixture of fuel oil and petroleum sulfonate (10:1) and has recovered 44 % after 1 min of flotation while fuel oil flotation after 20 min recovered only 38 %. Gray et al. (2001) used this method with cyclohexane as the solvent, and achieved high carbon recoveries (55 %–57 %). There are other studies reporting similar carbon purities in their agglomerates using vegetable oil as their solvent (Alonso et al. 1999). US Patent No. 6068131 (2000) describes this type of removal using a conditioning agent such as biodegradable soil.

6 Conclusions

Coal fly ash has been explored as an alternative source of various valuable elements and minerals. Recovery of these components from CFA not only provides alternative resources, but also reduces disposal cost and protects the environment. This paper has reviewed a number of hydrometallurgical methods developed for the recovery of those products from CFA and highlighted suitability and effective technique for their extraction based on US Patents

and journal literature. By applying those techniques, it was found that the recovery of major elements such as Fe, Al and Si and trace elements such as Ge and Ga from CFA are satisfactory. However, for other trace and rare earth elements further research is needed to develop adequate results in terms of selective recovery and purification. Mineral matter such as cenospheres, unburned carbon and magnetic materials also significantly extracted from CFA.

Most of these methods were studied at lab-scale, their commercialization utilization is largely limited, and therefore further development in large scale is required to scale up to commercial production levels. In addition, economic viability and environmental impact evaluation of each method should be focused in the future work. This would be helpful to choosing correct method and to ensure that any operations don't result in a greater environmental footprint than mining of primary resources. Quality of raw ash obtained in parallel with the metal recovery processes needs to be assessed.

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