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REVIEW ARTICLE

Towards the Utilization of Fly Ash as a Feedstock for Smelter Grade Alumina Production: A Review of the Developments

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Abstract The major commercial technology for the production of smelter grade alumina has conventionally been the Bayer process which converts bauxite ore, an aluminum containing ore which typically contains about 50 % Al_2O_3, into smelter grade alumina that contains over 99.0 % Al_2O_3. Another potential source of aluminum that is receiving renewed attention is coal fly ash (CFA), which is a by-product of coal combustion during electricity generation in power stations. Most coal fly ash found around the world contain typically between 25 and 35 % Al_2O_3, which is substantial to make CFA a potential alternative source of alumina. There has been some considerable research effort, in the last two decades, aimed at extracting aluminum from this semi-waste product. Much emphasis from the different workers has been on the leaching of the contained aluminum, while the purification and recovery of alumina from the liquor solution has received less attention. Notwithstanding that several patents on the processes to recover alumina from CFA exist, limited commercialisation of the processes has been reported. This paper seeks to review and discuss the hydrometallurgical extraction processes that have been formulated and tested by different workers and then assesses the available opportunities and the way forward on the prospects of commercially extracting alumina and other valuable components from this abundant resource.

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Introduction

The depletion of natural ore deposits of the majority of mined minerals makes it imperative for researchers to shift focus to the development of innovative methods that look at the smart use and recovery of metals and other valuable products from alternative and waste resources. To tackle this imminent supply risk challenge there is a need to start viewing wastes as potential resources, and to think about how to use these resources most efficiently thereby reducing the demand on primary resources. The true value of waste is not the cost of discarding it but there is inherent value in the waste that includes the residual content of valuable components, the energy and water used in the primary production process. Maximizing the reuse, recycling, and recovery of valuable materials from waste resources has a major advantage of saving the earth's finite resources and reducing the negative impact that waste has on the environment.

Coal fly ash (CFA), also generally regarded as waste, is the lightweight fraction of the incombustible material or ash formed after combustion of coal in coal-fired power plants. It is typically spherical in shape and ranges from 1 to 150 μm in particle size. This material is driven out of the boilers with flue gases owing to its light weight and gets captured and recovered by gas cleaning devices like electrostatic precipitators before the gases are exhausted to the atmosphere. Generally, the total ash content of the coals used in most power generation plants range between 30 and 40 % and fine CFA can make up to 80 % of the total ash content, this gives a perspective of how much CFA gets

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generated during coal combustion. CFA has been largely regarded as an environmental pollutant with very limited industrial applications. However, the relative abundance of Al_2O_3 in the ash is significant enough to justify an attempt to exploit it commercially and the potential success of such an initiative would vastly boost a lot of economies. The potential presented by developing another alternative source of alumina from CFA would supplement bauxite resources, significantly reduce the volume of ash disposal; realize savings on disposal and landfill costs, and lessen the potential for environmental damage.

Worldwide, it is estimated that coal combustion in power plants provides about 41 % of the electricity generation [1], producing more than 800 million tonnes of CFA per annum of which approximately 500 million tonnes is generated in China, 140 million tonnes in India, 115 million tonnes in the United States & European Union [2], and South Africa produces about 40 million tonnes. In South Africa, Eskom and Sasol are the major producers of CFA. Eskom, according to its 2010 annual report, combusted 122.7 million tonnes of coal and generated a net of 215,940 GWh power with emission of 0.39 kg M Wh^{-1} of particulate matter, most of which is in the form of coal fly ash (CFA).

It is estimated that only 30 % of the CFA produced finds use [3], and the balance is disposed of in controlled landfills or stockpiled in waste containment facilities resulting in serious environmental liability. Despite the environmental pollution it causes and its potential harmful effect on life on earth, fly ash production is still increasing, since many power plants through out the world still rely heavily on coal combustion.

Some of the CFA is used as a raw material in cement production and as partial replacement for cement in concrete [4, 5], in the ceramic manufacturing, in the production of catalysts and catalysts support, and as an adsorbent in pollution abatement [6].

Chemical and mineralogical compositions of CFA are highly variable due to the variability of the sources of the coal, its pre-treatment, and the operational parameters during its combustion in the power generation plants. However, on average it contains between 25 and 30 % Al_2O_3, making it a potential alternative source of alumina for aluminum production after bauxite which contains about 50 % Al_2O_3 [7]. According to the International Aluminium Institute [8], the world's primary aluminum production for year 2014 was about 57.9 million tonnes. The bulk of that aluminum production came from bauxite resources while the balance was produced from other aluminum-containing ores like nepheline syenite in a few plants in Russia and Iran. Therefore, the availability of CFA as a substitute or to augment bauxite will not only have environmental benefits, but also potentially expand the raw materials base for the aluminum industry.

Therefore, in this context, research aimed at developing alternative routes for extracting alumina from CFA is needed. Amenability of CFA to different forms of leaching for aluminum recovery has been successfully demonstrated in concept by a number of workers including sulfuric acid leaching [21, 22, 9], nitric acid leaching [10], alternate alkaline (other than NaOH) leaching [11], and bioleaching [12, 13].

Although research into processing of CFA for metal recovery has been widespread, large-scale production plants dedicated solely to this waste material have not been completely successful. The economics of any new processes developed must compete with others which are already in commercialization that use other mineral feedstocks. Alumina production from bauxite through the Bayer Process is one mature technology that is conventionally used to convert bauxite ore to smelter grade alumina.

Most major economies like China, the United States, and European Union are still heavily dependent on imports of bauxite ore from countries like Australia, Indonesia, Guinea, Brazil, and India as feedstock for smelter grade alumina production. Therefore, the potential usability of CFA as a substitute or to augment bauxite imports as a raw material in aluminum production presents an opportunity that is worth exploring. Although bauxite remains the preferred commercial source of alumina since the Bayer process technology is established and mature, it remains interesting to explore the suitability of CFA as a substitute especially when the opportunity is assessed holistically.
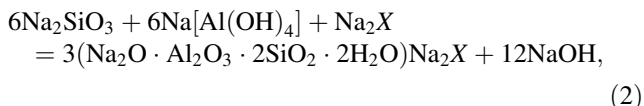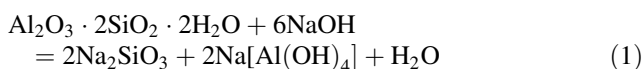
There still remains, however, a plethora of challenges before a comprehensive assessment of the commercial possibilities of using CFA as a viable substitute to bauxite in aluminum production can be achieved. This paper intends to review the knowledge gathered through past and current research on extraction and recovery of alumina from CFA. It also discusses the opportunities arising from the current knowledge and how these can be leveraged in order to assess the suitability of CFA as a substitute for bauxite in aluminum production.

Overview of CFA Processing Methods

Research on aluminum extraction from CFA has mainly focused on hydrometallurgical processes in which leaching plays a pivotal role. Invariably, the methods proposed thus far may be broadly divided into two groups namely alkaline and acid leaching. Some modifications of these two methods have resulted in variations such as bioleaching and the 2-step acid leaching. What has come out clear from early research is that aluminum in CFA cannot be extracted using the conventional and economically proven Bayer

process [10–12, 14, 15]. This difficulty emanates from high silica content of CFA when compared to bauxite. By way of example, the composition of South African CFA and typical bauxite composition are presented in Table 1.

The Bayer process, in brief, involves three stages: leaching, precipitation, and calcination. During leaching the hydrated alumina minerals in ground bauxite ore are dissolved in hot caustic soda solution (NaOH) at high pressure to obtain sodium aluminate solution. During the process, while the silica that is in the form of quartz remains largely insoluble some of the silicates in the form of kaolinite clay minerals are dissolved as shown in the Eqs. (1) and (2) below to form a desilication product, which together with other solid impurities like iron oxides constitute a residual by-product called *red mud*:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + 6NaOH \\ = 2Na_2SiO_3 + 2Na[Al(OH)_4] + H_2O \quad (1)$$

$$6Na_2SiO_3 + 6Na[Al(OH)_4] + Na_2X \\ = 3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)Na_2X + 12NaOH, \quad (2)$$

where X can be SO_4^{2-}, CO_3^{2-}, Cl^-, OH^-.

The red mud is filtered off from the alumina-containing liquid through settling and washed to recycle the original sodium hydroxide, and is eventually stored in holding ponds [16]. Aluminum hydroxide precipitates out of the alumina solution as it is cooled and solidifies into alumina crystals around "seeds" of alumina i.e., particles that have been suspended in the processing tanks to promote crystal growth. The precipitate mixture from the crystallization step is heated to a temperature of about 1050 °C and this causes the aluminum hydroxide to give off moisture in the form of water vapor and decompose chemically into alumina, the final product. Ideally, the particles of alumina produced will be small and fine, roughly the size of sand grains [17].

For bauxites having more than 10 % reactive silica, the Bayer process becomes unfeasible due to the high chemically combined sodium loss through the formation of the insoluble sodium aluminum hydrosilicate (desilication

Table 1 Typical mineralogical compositions of bauxite and CFA [9]

Component	Bauxite (wt%)	Eskom CFA (wt%)
SiO_2	<0.5–10	46–60
Al_2O_3	30–60	26–31
Fe_2O_3	1–30	4–6
TiO_2	<0.5–10	1.3–1.7
CaO	0.1–2.0	3–11
P_2O_5	0.02–1.0	0.3–1.1

product). Therefore, considering the very high silica levels found in CFA, typically 40–60 %, application of this process would virtually be impractical because the removal of silica would have to be done at the expense of extreme soda losses [11, 14, 15]. For this reason, research efforts have been focused on alternative (other than NaOH) alkaline leaching, bioleaching, and more significantly, acid leaching. Advances made in these methods are reviewed in the following sections.

Direct Leaching

Direct Alkaline Leaching

A number of studies have been conducted on alumina extraction of coal fly ash using the alkaline hydrothermal processes. Su et al. [18] prepared ultrafine aluminum hydroxide from fly ash using a two-step alkaline (NaOH) dissolution process. In the process, NaOH was added into an alkaline hydrothermal reaction system as a liquid reactant to extract silica. NaOH and CaO were then used to treat the desilicated fly ash. As NaOH reacts with the SiO_2 present in CFA, the consumption rate of the NaOH becomes relatively high, and the alumina also needs to be separated from the silica in the solution before the precipitation of sodium aluminate happens. A study by Li et al. [19] focused on improving this particular process using a $Ca(OH)_2$ additive. $Ca(OH)_2$ was introduced into the hydrothermal reaction system with NaOH with a view of forming alumina-free minerals, such as calcium silicate ($2CaO \cdot SiO_2$) and calcium metasilicate ($CaO \cdot SiO_2$). The addition of $Ca(OH)_2$ resulted in a reduced usage rate of NaOH and also immobilized the SiO_2; however, the resultant silicate compounds still contained appreciable amounts of aluminum and/or sodium.

Alkaline leaching can also be used as a pre-treatment step to help dissolve substances that would otherwise mask alumina from acid attack and render it less soluble. Russ et al. [20] showed that aluminum extraction of 89 % could be achieved by first pre-treating the CFA with an alkaline aqueous solution of pH in the range 11.5–13.5 at a temperature of 120 °C. The residue obtained after filtration was then contacted with aqueous HCl at a temperature of about 80 °C to solubilise the metal species.

Direct Acid Leaching

Several methods of extracting aluminum from CFA by direct acid leaching have been documented [10, 21–23]. A range of acids have been investigated as potential lixiviants, these include nitric acid, hydrochloric acid, and sulfuric acid. The use of acid as lixiviants has been found

to be attractive because silica, the major gangue mineral in CFA, is considered insoluble in acidic medium [23]. In the literature, researchers used varying concentrations of acids under diverse conditions to leach CFA achieving a wide range of extraction efficiencies. Figure 1 shows a summary of the conceptual flow sheet for the direct acid leaching of coal fly using various acids with the subsequent recovery of alumina from solution using the crystallization technique.

What came out clearly from the work of these researchers was that the leaching of aluminum compounds from CFA at low concentration and ambient or even elevated temperature gives low-extraction efficiencies [10, 21, 23]. For instance, in the work of Hill and Raistrick [10] that used HNO_3 with a concentration of 30 % (wt) to leach aluminum in a 3-step process, despite raising the operational temperature to 220 °C, only 27 % extraction of the contained aluminum was achieved. This observation is aligned to the findings of Petruševski et al. [24], who found that aluminum does not readily react with either dilute or concentrated nitric acid unless the acid contains Cl^- ions and Cu^{2+} ion to catalyze the reaction.

In another study involving the use of H_2SO_4, Nayak and Panda [23] showed that extraction efficiency could increase from 2.7 to 41.3 % by increasing the concentration of H_2SO_4 from 1.5 to 18 M. The temperature range used was 150–200 °C while the liquid: solid (acid: ash) ratio was fixed at 1 over a leaching time of 4 h. However, extraction efficiency as high as 84.2 % was achieved when the liquid:solid ratio was increased to 2 and when other variables were held constant. The researchers attributed the low-extraction efficiency at low liquid:solid ratio to the formation of an acid-insoluble calcium sulfate layer which inhibited further dissolution of the metal by impeding mass transfer. In this process, leaching is achieved by proton attack whereby the hydronium ion displaces the metal cation from the ash particle matrix (Eq. 3), rendering the metal soluble [9]:

$$CaO \cdot Al_2O_{3(s)} + 4H_2SO_{4(aq)} \rightarrow Al_2(SO_4)_{3(aq)}$$
$$+ CaSO_{4(s)} + 4H_2O_{(l)}.$$
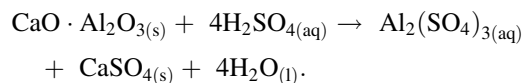
Increasing the liquid:solid ratio increases the solubility of $CaSO_4$ in acid, thus exposing the underlying aluminum to the acid for further dissolution. Their findings confirmed earlier results by Seidel and Zimmels [13] who also achieved poor alumina extraction at low acid concentration. In both cases, the researchers also further attributed this phenomenon to the fact that aluminum in CFA exists in two different phases, namely, the amorphous non-crystalline phase and the crystalline and refractory mullite phase. The crystalline mullite phase is acid-insoluble and aluminum in this phase cannot be easily recovered whilst the non-crystalline amorphous phase is acid-soluble and aluminum can thus be easily recovered by direct acid leaching.

While sulfuric acid has the advantage of being cheaper and also giving satisfactorily high levels of aluminum extraction, there are major problems associated with the crystallization and calcinations of aluminum sulfate. The main drawback however, in all of the proposed acid leaching processes is the co-dissolution of other metals such as iron, magnesium, titanium, sodium, and potassium during the leaching stage and the need to remove these impurities prior to the recovery of alumina. Alternative aluminous material with a low iron content and high silica content indicates that technically, an acid process could be more attractive than an alkaline route; this is confirmed by published process economics on the treatment of clays [25, 26].

The published process evaluations by Margolin and Hyde [26] indicated that a nitric acid-leach process was a possible acid leaching route at high acid concentrations. An

Fig. 1 A block flow diagram of the direct acid leaching process for extracting alumina from CFA [55]
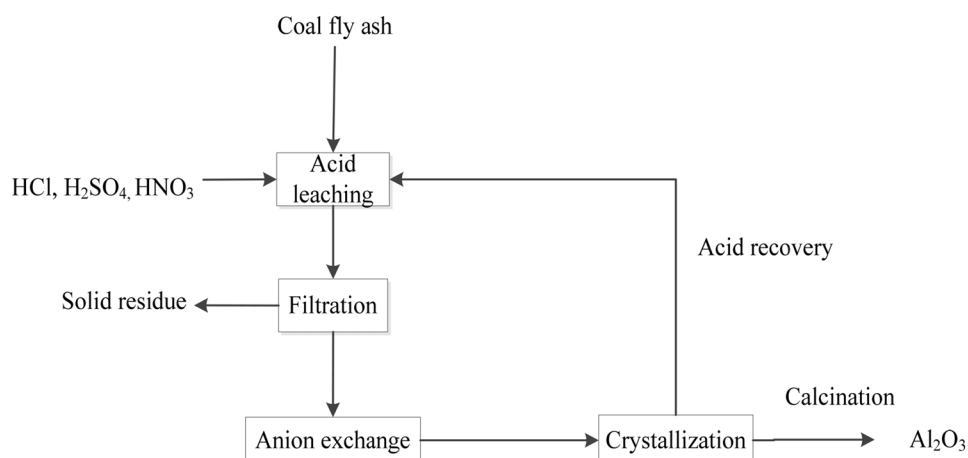
analysis of the various nitric acid routes has, however, shown that the major disadvantages of these routes is the energy-intensive step of crystallization by evaporation and thermal decomposition of aluminum nitrate nonahydrate to alumina. In addition, partial decomposition and loss of nitric acid occurs. The success of such extraction and recovery processes is dependent on the type of acid used, the pre-treatment stages done on the CFA and the subsequent purification stages prior to the recovery of alumina.

Shemi [9] conveniently categorized the processing of CFA using the acid route into two groups: direct and indirect leaching. In direct leaching, there is no prior treatment of the CFA before contacting with the acid, whereas indirect leaching involves prior interventions meant to make the alumina more responsive to acid leaching. While the amorphous phase is reactive and soluble in inorganic acids, the mullite phase is refractory and unresponsive to acid leaching under conditions of low acid concentration [9, 14, 15, 23]. Unfortunately, in typical CFA, it is the mullite phase which contains a larger proportion of the total alumina. The phase composition of typical South African CFA is as presented in Table 2 and shows the relative abundancies of these alumina-bearing phases. As such, a high extraction of aluminum from fly ash requires methods that will attack the refractory glass matrix of the ash particles [11]. The following sub-sections discuss the major breakthroughs that have been made in these areas

Indirect Leaching

The difficulties associated with processing of the mullite phase led to research efforts shifting toward additional interventions to convert mullite into a more soluble phase [9, 14, 27, 28] in what is now generally known as indirect leaching.

Indirect Acid Leaching

The indirect acid leaching process generally involves a thermal pre-treatment of the CFA in order to convert the mullite phase to a product that is easier to leach in the
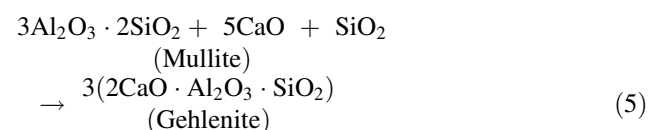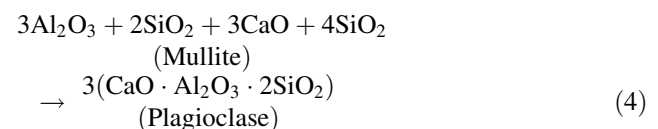
Table 2 Mineralogical analysis of Eskom CFA [9]

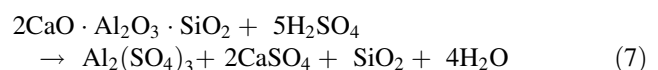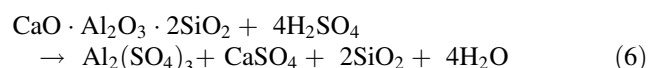| Phase	wt% of phase in CFA	Al_2O_3 content of phase (wt%)
Amorphous	52.9	27.8
Hematite	0.8	–
Magnetite	1.65	–
Mullite	30.68	72.2
Quartz	13.97	–

subsequent processes. A number of studies have shown that low-temperature acid leaching is not suitable in extracting aluminum from coal fly ash as discussed in the preceding section. To improve the reactivity of minerals and the aluminum extraction efficiency, thermal activation is usually performed as a pre-treatment for minerals, followed by acid leaching.

McDowell and Seeley [27] patented a method for improving the recovery of aluminum from CFA by sintering CFA mixed with a $CaSO_4$–$CaCO_3$ flux, prior to leaching as shown in the process block flow diagram, Fig. 2. Sintering was done for 3 h at 1450 °C in order to convert alumina into an acid-soluble phase. The resulting sinter was leached for a total of 6 h in two successive stages to achieve an overall aluminum extraction efficiency of 98 %. In the first leaching stage, aluminum leaches together with iron and titanium in the sinter. The leach liquor from the 1st stage of leaching has its pH adjusted which allows the solvent extraction of iron and titanium. In the second stage, leaching a residue that is deficient of the other metals is leached. The aluminum sulfate, $Al_2(SO_4)_3$ in the leach liquor is reacted with ammonium sulfate, $(NH_4)_2SO_4$ to precipitate an alum, $NH_4Al(SO_4)_2$ which is calcined to produce final alumina product.

In the studies by Matjie et al. [14] shown in Fig. 3, pellets containing CFA, fine coal, and CaO in a ratio of 5:4:1, respectively, were produced. Sintering was then done at 1000–1100 °C for times ranging from 30 to 180 min. Possible compounds that form after sintering include plagioclase and gehlenite [9] according to the following reactions:

$$3Al_2O_3 + 2SiO_2 + 3CaO + 4SiO_2 \atop \text{(Mullite)}$$
$$\rightarrow 3(CaO \cdot Al_2O_3 \cdot 2SiO_2) \atop \text{(Plagioclase)} \qquad (4)$$

$$3Al_2O_3 \cdot 2SiO_2 + 5CaO + SiO_2 \atop \text{(Mullite)}$$
$$\rightarrow 3(2CaO \cdot Al_2O_3 \cdot SiO_2) \atop \text{(Gehlenite)} \qquad (5)$$

Subsequent leaching of the sintered pellets using 6.12 M H_2SO_4 at 80 °C yielded an aluminum extraction efficiency of 85 % over a comparatively shorter period of 4 h. Possible reactions that take place in post-sinter leaching include the following [9]:

$$CaO \cdot Al_2O_3 \cdot 2SiO_2 + 4H_2SO_4$$
$$\rightarrow Al_2(SO_4)_3 + CaSO_4 + 2SiO_2 + 4H_2O \qquad (6)$$

$$2CaO \cdot Al_2O_3 \cdot SiO_2 + 5H_2SO_4$$
$$\rightarrow Al_2(SO_4)_3 + 2CaSO_4 + SiO_2 + 4H_2O \qquad (7)$$

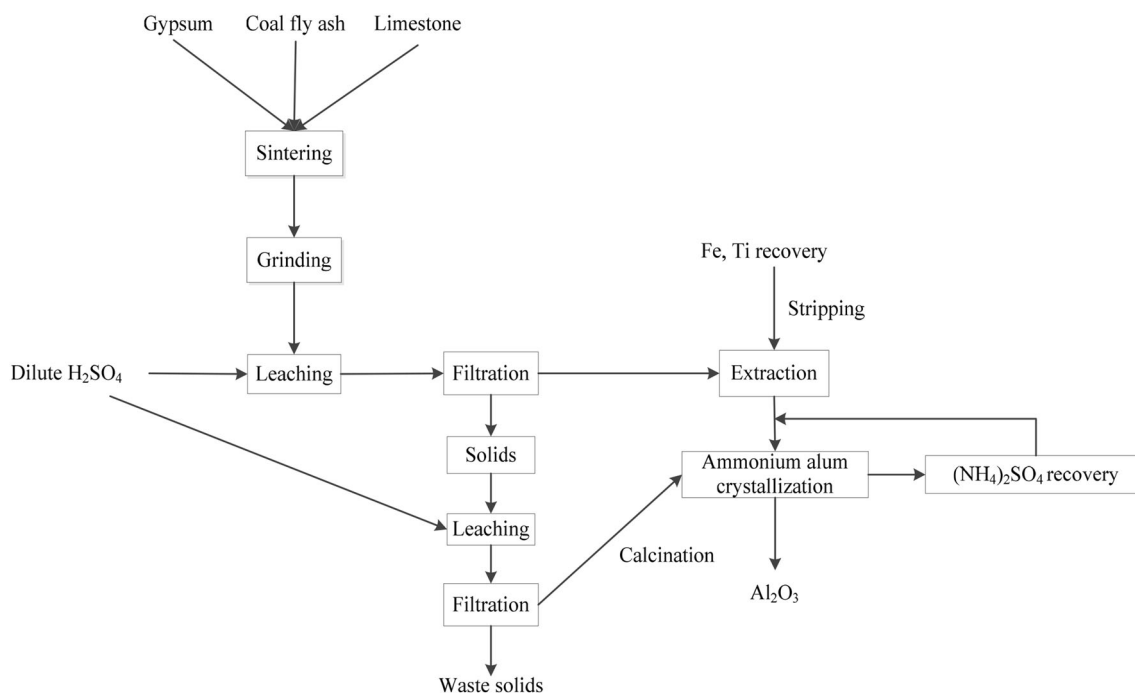This lime sinter process gave an aluminum extraction efficiency of about 85 % [14]. The authors did not,

Fig. 2 A block flow diagram of the $CaSO_4$-$CaCO_3$ sinter process for extracting alumina from CFA (Bai et al. [56])

however, give an indication of the optimum sintering conditions.

Although thermal activation through sintering leads to a significant increase in the extraction rate of aluminum, the energy required to achieve the thermal activation is very high. In this regard, research on the application of effective additives to reduce the reaction temperature will play a significant role in the economic extraction of alumina from the fly ash [29].

Two-Step Acid Leaching

The sintering process is based on the concept that the recovery of minerals from fly ash requires methods that will thermally attack the refractory glass matrix of the ash particles to break the crystalline mullite phase ($3Al_2O_3 \cdot 2SiO_2$) and that acidic leaching is most effective when used on sintered ash particles [11, 14]. While this is true, however, it is important to remember that not all the alumina is contained in the mullite phase. Heating both phases may therefore not be necessary as the amorphous phase in CFA is acid-soluble and thus, does not necessarily need heat application to achieve metal dissolution. Taking this into account, Shemi [9] postulated separating leaching into a pre-sinter and post-sinter leaching stages to come up with what has become known as the 2-step acid leaching process or leach-sinter-leach process [28].

In this method, Shemi [9] proposed that the different alumina phases i.e., amorphous and mullite, when leached

separately would yield a higher combined alumina extraction and minimize reagent consumption and process costs. The acid-soluble amorphous phase could be leached directly without prior chemical pre-treatment and the residue from this first step, predominantly made up of mullite, would then be subjected to sintering prior to a second acid leaching stage. Figure 4 is the block flow diagram of the proposed acid leach-sinter-acid leach process for extracting alumina from CFA.

A combined aluminum extraction efficiency of 88.2 % was achieved after the 2-step leaching process [9, 28]. In the first step, aluminum contained in the amorphous phase was extracted by direct leaching with 6 M H_2SO_4 solution giving maximum extraction efficiency of 89.3 % after about 10 h of leaching at 82 °C. Residue from the first leach stage was sintered for 180 min at 1050 °C to convert the mullite phase into an acid-soluble plagioclase phase. The sintered product was subjected to a second stage of leaching with 6 M H_2SO_4 solution at 82 °C to achieve 84.3 % aluminum extraction efficiency. The combined aluminum extraction efficiency of 88.2 % was significantly higher than the 85.2 % obtained from conventional lime sinter method done in a single step.

What remains to be investigated is whether the leach-sinter-leach process has any significant advantage over the lime-sinter-leach processes. From an energy savings standpoint, one can argue that the lime-sinter-leach process would require less energy than the leach-sinter-leach method because the feedstock is sintered dry and then

Fig. 3 A block flow diagram of the lime-sinter-acid leach process for extracting alumina from CFA [after 14]

Coal fly ash

H_2O → Pelletization ← Lime and coal

↓

Sintering

↓

Post-sinter leaching ← H_2SO_4

↓

Construction industry ← Lightweight aggregate ← Filtration

↓ Leach liquor

Primene JMT → Solvent extraction → Loaded organic phase – Fe and Ti

↓ ↓

Purified leach liquor   Selective stripping

↓

Crystallization

↓

Pure $AlNH_4(SO_4)_3$

↓ Calcination

Al_2O_3

Coal fly ash

↓

Pre-sinter leaching

↓

Filtration

Leach residue

Lime and coal

H_2O → Pelletization ←

↓

Sintering   Leach liquor

↓

H_2SO_4 → Post-sinter leaching

↓

Lightweight aggregate ← Filtration
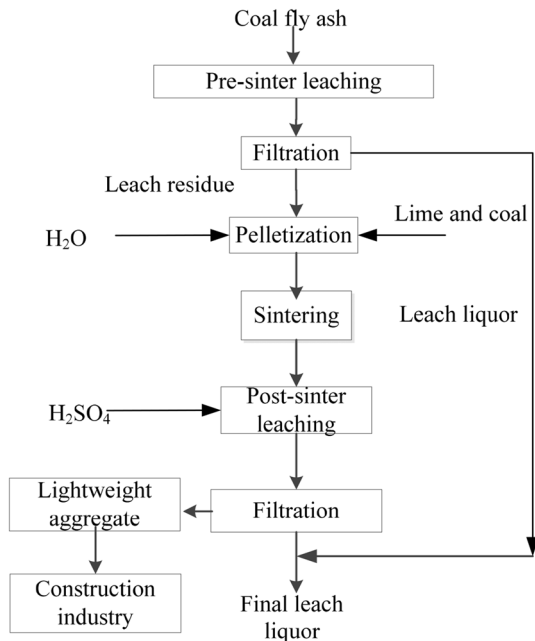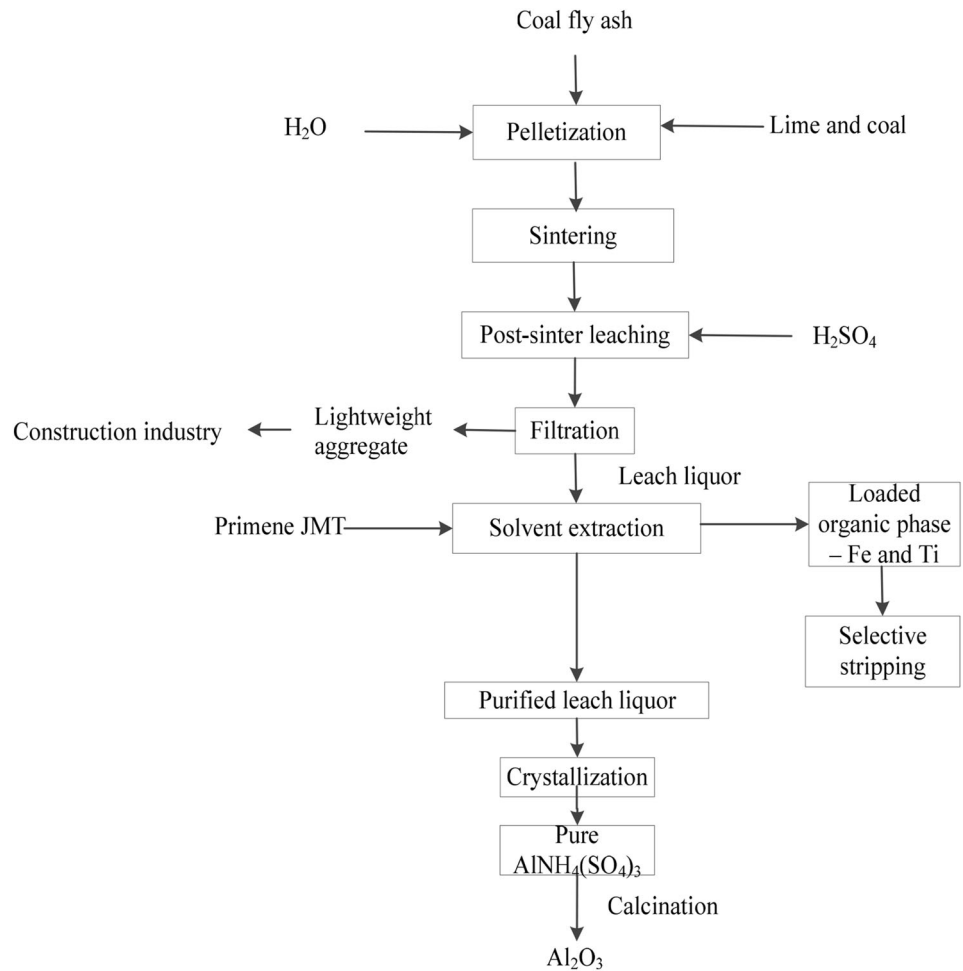
↓ ↓

Construction industry   Final leach liquor

Fig. 4 A block flow diagram of the acid leach-sinter-acid leach process for extracting alumina from CFA proposed by [9]

leached by acid to solubilize the aluminum carrying phases. In the leach-sinter-leach process, the feedstock is first contacted with acid to leach the amorphous phase and the resultant slurry would need to be filtered and dried before sintering the residue for the conversion of the mullite phase. Both the dewatering and the sintering processes are energy intensive. However, according to Shemi [9], this 2-step leach-sinter-leach (LSL) process could offer several advantages including reducing weight of feedstock to the sintering process after eliminating the amorphous phase thus, saving on sintering energy. Secondly, in the absence of the amorphous phase, the available specific surface area for mullite reaction during sintering would increase, thus enhancing the process kinetics. In addition, the $CaSO_4$ produced from stage 1 (Eq. 2) could be used as flux in the sintering process and in so doing reducing costs of running the process as well as the amount of waste product. Apart from the increase in extraction efficiency, the leach-sinter-leach process presents potential savings on disposal and containment costs of calcium sulfate.
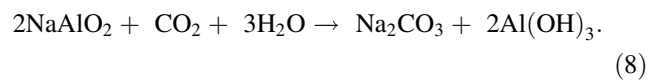
Indirect Alkaline Leaching

The work by Murtha [11] centered on sintering of CFA-CaCO$_3$-Sulfur-Carbon mixture at about 1200 °C to achieve a calcium sulfo-aluminate clinker. The clinker was contacted with 3 wt% Na$_2$CO$_3$ at 65 °C, causing the dissolution of the contained aluminum resulting in a reported 90 % alumina recovery.

Another indirect alkaline leaching process investigated by a number of workers is the lime sinter process. In this process, shown in Fig. 5, the fly ash is mixed and reacted with lime (added as limestone) at elevated temperature >1100 °C to form calcium aluminate (12CaO·7Al$_2$O$_3$) and di-calcium silicate (2CaO·SiO$_2$). When the sinter is cooed to temperatures below 500 °C auto disintegration of the sinter occurs, where the sinter matrix shatters into fine powder, this is believed to happen due to the phase transformations that happen during cooling which result in the increase in the volume or swelling of the sinter, this eliminates the need to mill the sinter before leaching. The calcium aluminate (12CaO·7Al$_2$O$_3$) formed is soluble in Na$_2$CO$_3$ which is used as a leaching reagent while di-calcium silicate (2CaO·SiO$_2$)

is insoluble in the same solution. The other common leaching agents that can be used include dilute alkaline solutions such as NaOH solutions and water [30]. After leaching, the aluminum in the pregnant liquor is in the form of NaAlO$_2$ while most of the silica remains in the solid state in the form of 2CaO·SiO$_2$. However, some amounts of silica co-dissolve in the solution causing contamination of the NaAlO$_2$ liquor and this necessitates a desilicating stage. Desilication is achieved by mixing the pregnant liquor with Ca(OH)$_2$ at 70 °C to form calcium aluminosilicates which have very low solubilities in the alkaline solution.

The purified NaAlO$_2$-rich solution is carbonized by contacting the solution with bubbling CO$_2$ this subsequently causes precipitation of Al(OH)$_3$ as shown in Eq. 2. which is then calcined to form the final alumina. The equations below show how these reactions occur

$$2NaAlO_2 + CO_2 + 3H_2O \rightarrow Na_2CO_3 + 2Al(OH)_3. \tag{8}$$

The above reaction (Eq. 7) re-generates the Na$_2$CO$_3$ which is recycled to the leaching stage. The calcination reaction (Eq. 8) then forms the final alumina product.
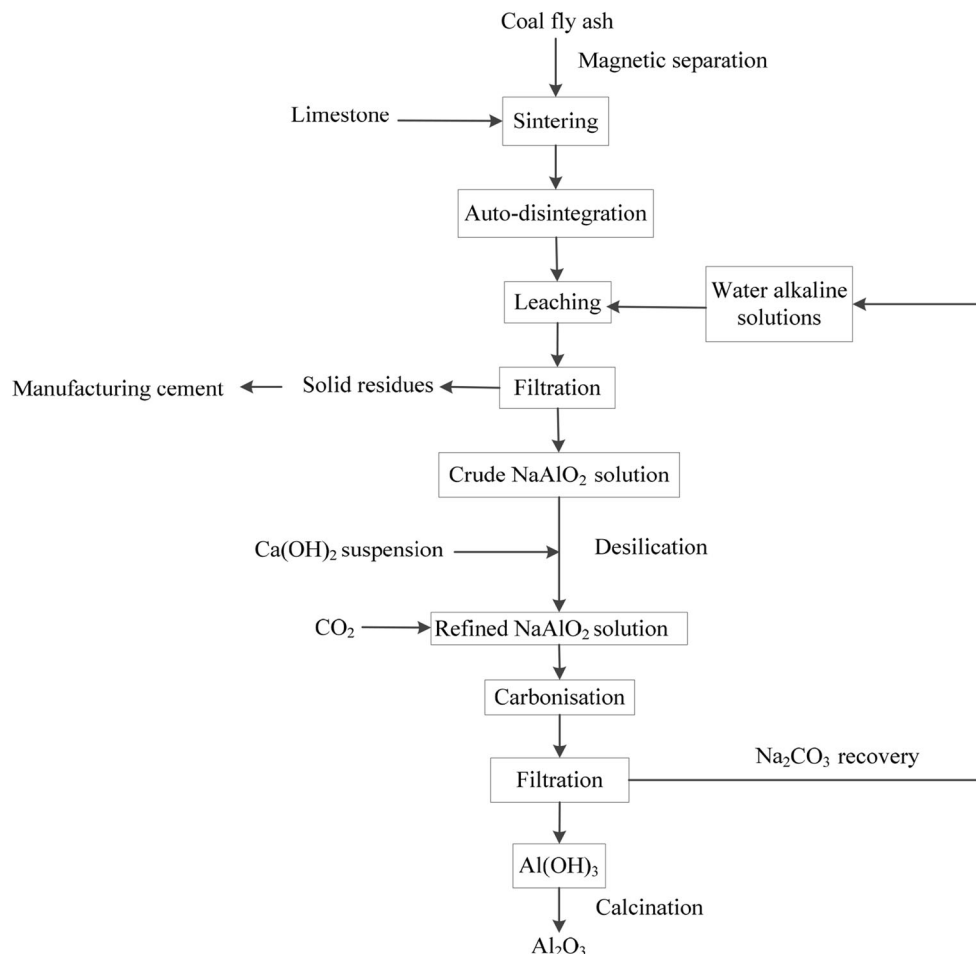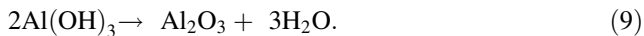

Fig. 5 A block flow diagram of the lime-sinter-alkaline leach process for extracting alumina from CFA

$$2Al(OH)_3 \rightarrow \ Al_2O_3 + \ 3H_2O. \tag{9}$$

The solid residues from the leaching step are sintered and mixed with gypsum during grinding to prepare cement.

In another processes by Bai et al. [31], fly ash is calcined with soda and lime at 1200 C, and the silica is converted into stable calcium silicate (2CaO·SiO$_2$), thus separating the silica from the alumina The desilicated coal fly ash could then be used as a substitute for bauxite in the Bayer process, allowing for dissolution using sodium hydroxide. Due to the addition of a large amount of limestone in the sintering process, a considerable amount of calcium silicate residue is generated and this can be used for cement production.

Wang et al. [32, 33] studied the extraction of SiO$_2$ from fly ash by alkali leaching, and then Al$_2$O$_3$ was extracted from desilicated fly ash using the alkali lime sintering process. The process of pre-desilication followed by sintering was developed to reduce the silica content and the consumption of sintering reagents. The process resulted in a high recovery of both silica and alumina and the silica could be re-used as silica white and calcium silicate.

Despite these successes, alkali sintering is energy intensive [11, 22, 34].

Bioleaching

The use of bacterial microorganisms to enhance aluminum recoveries in the processing of CFA has received considerable attention in the past. The motivation to pursue this technology is perhaps derived from the successes it has achieved in the processing of refractory ores of gold, silver, copper, uranium etc. In recent years, bioleaching of kaolin using organic acids and fermented medium from *Aspergillus niger* cultivation as the leaching agent [35], bio beneficiation of bauxite to remove iron and calcium for abrasives and refractory applications [36], and bioleaching of aluminum from low grade bauxite using Bacillus polyxyma, *Aspergillus niger*, and *Penicillium notatum* has been documented [37]. In general, bioleaching involves contacting the feedstock material with a bacterial microorganism culture in order to oxidize insoluble sulfide metal species, rendering them soluble in inorganic lixiviants. These microorganisms are mostly indigenously associated with several oxide mineral deposits and secrete exopolysaccharides, several proteins, enzymes, and organic acids such as citric, acetic, formic, and oxalic acids formed during their metabolism of carbohydrate substrates. The organic acids usually have dual effect of increasing metal dissolution by lowering the pH and increasing the load of soluble metals by complexation/chelating into soluble organic–metallic complexes [38].

Fass et al. [12] patented a method for facilitating the extraction of metals from CFA using at least one strain of *Thiobacillus thiooxidans*. The bacteria was cultured in seawater with an original pH of about 3 until the pH dropped to about 1.2–1.5 over an incubation period of 5 days. Washed CFA was then contacted with the bacterial culture to leach Al, Ti, Fe, Co, etc. over a period of 31 days. The researchers reported an aluminum extraction of about 20 % over that period.

In a related study, Seidel et al. [13] investigated the effects of CFA composition on the growth of bacterial load and subsequent bioleaching of Al and Fe. The CFA was pre-treated with HCl in order to get rid of CaO, and therefore, inhibit the formation of undesirable CaSO$_4$ [13]. Aluminum extraction of about 25 % was achieved over a 3-week leaching period.

It is clear that CFA bioleaching suffers the disadvantages of slow kinetics and poor extraction. Therefore, despite the known advantages such as low capital and energy costs, no commercial considerations have been reported for this extraction route.

Leaching Processes Summary

Table 3 shows a summary of some of the studies conducted on processing of CFA for alumina recovery. It shows the leaching reagents, conditions as well as extraction efficiencies.

Leach Liquor Purification and Alumina Recovery

In order to evaluate the processes to be considered in the purification of the CFA leach liquor and the eventual alumina recovery, the specific requirement for the composition of the smelter grade alumina should be kept in view. The purification objective is, therefore, to develop a process that can produce a solution that when further solidified through crystallization and calcination can generate a product that is comparable to the typical composition of the smelter grade alumina as shown in Table 4.

Table 4 suggests that the amount of calcium, iron, and titanium should be very low in the final composition of the smelter grade alumina. Since the CFA contains a significant amount of iron, calcium, and to a certain extent, relatively high titanium, there is therefore the need to purify the leach solution before alumina can be recovered by crystallization, calcined, and subsequently sent to the smelter. Of these three impurity metals, calcium is relatively simple to remove, mainly because calcium sulfate has a very low solubility in acids. This low solubility can be exploited to aid in the removal of calcium from CFA leach solutions. Iron and titanium on the other hand are more difficult to remove and as such most processes for the purification of coal fly ash leach liquor tend to focus on the

Table 3 Processes for leaching aluminum from CFA

Leaching method	Process conditions	Al extraction efficiency (%wt)	Salient aspects	References
Sinter alkaline	Sintering CFA-CaCO$_3$-S-C mixture at 1200 °C	Up to 90	High-extraction efficiency	[11]
	Leaching with dilute Na$_2$CO$_3$ at 65 °C		High energy costs for alkali sintering	
Direct acid	Leaching with 30 % (wt) HNO$_3$ at 220 °C	Up to 27	Low-extraction efficiency	[10]
			High leaching temperature	
	Leaching with 18 M H$_2$SO$_4$ at acid:CFA ratio of 2	Up to 84.2	High-extraction efficiency	[23]
	Temperature up to 200 °C		High acid consumption	
			High leaching temperature	
Indirect acid leaching	Contacting CFA with aqueous alkaline solution at 120 °C and pH 12.5	Up to 89	High-extraction efficiency	[20]
	Filtration and leaching residue from step 1 with 20 % (wt) HCl at about 80 °C		Low-to-medium temperature processes	
			High reagent consumption	
	Sintering CFA mixed with a CaSO$_4$-CaCO$_3$ flux for 3 h at 1450 °C	Up to 98	High-extraction efficiency	[27]
	Leaching the sinter with 2 M H$_2$SO$_4$ for about 6 h		High reagent consumption	
	Sintering a 5:4:1 mixture of CFA, fine coal and CaO respectively for up to 3 h at 1100 °C	Up to 85	High-extraction efficiency	[14]
	Leaching the sinter for 4 h with 6.12 M H$_2$SO$_4$ at 80 °C		Potentially high energy consumption	
2-step Indirect acid leaching	Direct leaching with 6 M H$_2$SO$_4$ solution for 10 h at 82 °C	Up to 88.2 overall	High-extraction efficiency	[9]
	Sintering the residue for 3 h at 1050 °C		Potentially low energy consumption	
	Leaching the with 6 M H$_2$SO$_4$ solution at 82 °C		Reduced amount of waste	
Bioleaching	Using *Thiobacillus thiooxidans* to reduce the pH of seawater to about 1.3 over a 5-day incubation period	Up to 20	Low-extraction efficiency	[12]
	Leaching CFA with the solution over 31 days		Slow kinetics	
	Pre-treating CFA with HCl at pH 4 over 24 h agitation	Up to 25	Low-extraction efficiency	[13]
	Leaching the CFA with *Thiobacillus thiooxidans* culture with a cell load of 5 × 10^8 cell/ml for 21 days		Slow kinetics	

iron and titanium removal. The purification process must be able to selectively separate the titanium and iron from aluminum. If possible, it should also be able to recover valuable metals such as titanium if present in solution in reasonable amounts. The processes that have been applied in the downstream processing of CFA leach liquors have involved mostly crystallization or precipitation processes and solvent extraction.

Crystallization Processes

Crystallization methods have been investigated for the direct recovery of alumina from CFA leach solutions. Matjie et al. [14] employed the crystallization technique with the addition of (NH$_4$)$_2$SO$_4$ to a CFA leach solution produced from the sulfuric acid leaching of coal fly ash. The addition of ammonium sulfate produced white crystals of Al$_2$ (NH)$_4$SO$_4$ at a pH of 1.5:

$$Al_2(SO_4)_3 + (NH_4)_2SO_4 + 40 \ H_2O \rightleftharpoons 2Al(NH_4)(SO_4)_2 \cdot 20H_2O \quad (10)$$
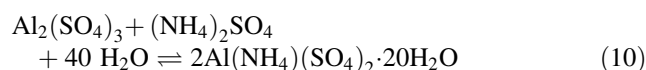
After calcination of the crystals, white alumina was formed giving a product with 97 wt% Al$_2$O$_3$, 0.59 wt% CaO, 0.8 wt% SiO$_2$, and 0.4 wt% MgO with iron and titanium oxides making up the balance of 1.21 wt%. Due to the high levels of impurities in the calcined product, this alumina would not be suitable as feed material in the electrolysis plant for the production of Al. Thus, crystallization on its own as a method of purification was found not to be adequate.

Li et al. [21] reported a possibility of 87 % alumina extraction from acid leaching of coal fly ash. Crystallization was then applied to recover the aluminum sulfate which was subsequently sintered. The product powder was then re-digested and recrystallized to produce purer metallurgical grade alumina.

Table 4 Composition of Smelter Grade Alumina [57]

Compound	wt%
Al_2O_3	98.3 Min
Na_2O	0.310 Max
SiO_2	0.013 Max
CaO	0.016 Max
Fe_2O_3	0.014 Max
TiO_2	0.002 Max
ZnO	0.010 Max
P_2O_5	0.0004 Max
Ga_2O_3	0.015 Max
V_2O_5	0.005 Max
SO_3	0.200 Max
Other specs	
Loss on ignition (300–1000 °C)	1.00 % Max
Alpha Al_2O_3 content	12 % Max
Specific surface area (m^2/g)	60–80
	Min–Max
Particle size distribution	−45 µm-12.0 % Max
	+45 µm-88.0 % Max
Angle of repose	30–35°
Moisture content	0.7 %
Bulk density (kg/m^3)	Loose: 0.92–0.98 Min–Max
	Packed: 1.08–1.16 Min–Max

It has been postulated by Charlot [39] that impurities of Ti^{4+}, Fe^{3+}, and Al^{3+} ions in aqueous solution can be selectively precipitated as metal hydroxides at pH of 2, 3, and 3.5, respectively. Matjie et al. [14] obtained an aluminum extraction of 85 % following the sulfuric acid leaching of coal fly ash. In the purification process, selective hydroxide precipitation using NaOH was applied to remove metal hydroxides, firstly, Ti(IV) ions at a pH of 2, followed by Fe(III) at a pH of 3. The solid precipitates formed were dried, calcined, and characterized by XRF and XRD. Following the titanium and iron removal, alumina was recovered from solution at a pH of 3.5. Matjie et al. [14] also looked at the recovery of alumina from the coal fly ash leach liquor via a sodium aluminate process. The coal fly ash leach liquor was firstly purified by removing iron and titanium ions using NaOH at a pH of 13. This process resulted in the formation of a sodium aluminate which was then reacted with carbon dioxide gas to produce a gibbsite an $Al(OH)_3$ precipitate that was dried and calcined.

The solid products produced using the selective precipitation process, however, contained unacceptable level of impurities such as silica, calcium, phosphorus, titanium, and iron. This implies that selective precipitation is also not an effective method for the production of smelter grade alumina. The major drawback of using sodium hydroxide as a precipitating agent is the reagents costs unless the sodium hydroxide is regenerated as practiced in the Bayer process. In the event that the impurity levels of the leach liquors are high, excessive consumption of the reagent will occur rendering the process unviable.

Solvent Extraction Processes

Solvent extraction is a separation technique by which a solute is transferred from one liquid phase to another immiscible or partially miscible liquid phase. In hydrometallurgy, the aqueous phase contains the metal which is to be concentrated into the organic phase. Solvent extraction is a method that has been more successful at purifying CFA leach solutions compared to purification by precipitation [14]. While most reports indicate that it is possible to extract aluminum from the leach solutions, the desired purity of aluminum can at most be achieved by the prior removal of iron which is also strongly extracted by most solvent extraction systems [40].

The direct extraction of aluminum by solvent extraction has been examined [41, 42]. Preston [42], investigated the ability of carboxylic acids in a xylene diluent to recover aluminum and other metals from nitrate solutions. Research has also focused on the solvent extraction of impurity metals as a means of purifying leach solutions prior to crystallization [14]. Organo phosphates such as bis-(2-ethyl-hexl) phosphoric acid (D2EHPA) and tributyl phosphoric acid (TBP) are popular because of their commercial availability and lower price. Da Silva et al. [43] showed that D2EPHA in *n*-dodecane was able to extract iron and titanium in sulfuric acid solution with the possibility of recycling the reagents used. However, the selective removal of iron and titanium from aluminum-containing leach solutions was not possible with D2EHPA due to co-extraction of aluminum [14, 41]. Organo-phosphate extractants are also difficult to strip, requiring expensive stripping agents such as fluorine and hydrogen peroxide to improve the stripping kinetics [43, 44] hence, their use in the purification of CFA leach solutions is limited.

Although amines are more expensive, they have been shown to be better at removing iron from sulfate leach solutions than extractants such as carboxylic acids and phosphates in terms of selectivity, extraction yield, and stripping [45]. Primary amines have shown the best promise of extracting impurities from CFA sulfate solutions. Seeley et al. [46], used Primene JMT-T in toluene to purify CFA leach solutions. Alguacil et al. [47] used the primary amine Primene 81R to extract iron (III) from aluminum sulfate solutions in the presence of various impurities such

as Ca, Mg, and Ti. Good extractions were obtained with H_2SO_4 concentrations of up to 0.1 M with an iron distribution ratio of 100. At hydrogen ion concentration greater than 0.1 M the distribution ratio diminished exponentially. Hence, pH adjustment must be exercised for the effective use of the Primene 81R.

Li et al. [45] examined the removal of iron from industrial grade aluminum sulfate using the primary amine N-1923 and got good extraction and selectivity at pH above 1.2. Matjie et al. [14] used a primary amine, Primene JMT to remove iron and titanium from CFA leach solution. The pH of the solution was adjusted using ammonium hydroxide solution. It was found that the amine extractant was very selective for the removal of silica, iron, and titanium impurities while leaving the aluminum ions in the raffinate in the form of aluminum ammonium sulfate crystals. An alumina product with a purity >99.4 % was produced on calcination. This product was found to adhere to the specifications for the production of aluminum via the commercial Hall–Heroult process.

Ajgaonkar and Dhadke [48] used Cyanex 302 in chloroform to separate iron (III) and aluminum (III) from other elements, iron (III) was extracted at pH 2.0–2.5, whereas the extraction of aluminum (III) occured in the pH range 3.0–4.0. Iron (III) was stripped from the organic phase with 1.0 M and aluminum (III) with 2.0 M hydrochloric acid. Both metals were separated from multicomponent mixtures. An extraction efficiency of more than 99 % for each metal was reported in all the tests undertaken.

Notable successes have been the research by Dougill et al. [49] and Matjie et al. [14] who generated alumina of as close purity as that required by alumina smelters. A process developed by Dougill et al. [49] involved leaching ash with 60 % HNO_3 at 115 °C to dissolve aluminum. This was recovered as crude aluminum nitrate by cooling the pregnant leach liquor to cause crystallization. Iron was removed from the crude aluminum nitrate by selective precipitation by ammonia and the solution was then neutralized with ammonia and hydrolyzed at 200 °C to form filterable aluminum monohydrate. This was calcined to produce cell-grade alumina. The filtrate contained ammonium nitrate, which was recovered as co-product fertilizer by evaporation.

Matjie et al. [14] went as far as extracting alumina of over 99 % purity. This was achieved by crystallization of the purified liquor solution after recovering titanium and iron by solvent extraction. The authors reported that ammonium sulfate was then added to the purified liquor to precipitate aluminum ions as aluminum ammonium sulfate. The resulting crystals were calcined to produce alumina.

Future Prospects of CFA in the Aluminum & Metals Industry

In this paper, a review of various chemical processes that have been formulated or at least tested on a laboratory scale by various researchers for the extraction and recovery of alumina from coal fly ash has been presented. In general, the various processes use either an alkaline or acidic leach to extract the aluminum from the sinter residue. After the solution is isolated from the insoluble residue, it is treated to recover the alumina in pure form by solvent extraction, ion exchange, crystallization, or precipitation. The most successful of the processes conceptually utilize a sinter-leach process where a high temperature solid-state reaction is used to modify the alumina-silicate matrix and make it more amenable to leaching, thereby improving the overall extraction of the aluminum.

In order to establish the overall techno-economic feasibility of the developed processes a thorough economic assessment of the different routes needs to be conducted so as to compare them to the existing and well-established Bayer process. At the current state of knowledge, the scarce economic modeling and analysis of the CFA-to-Alumina plants suggests that commercial viability has not yet been achieved.

Economic considerations of CFA to Alumina Plants

The economic viability studies of the CFA to Alumina plants at commercial scale have not been reported in literature. Economic viability of the plants can only be fully assessed when detailed knowledge of the capital as well as operational costs of running the plant have been understood comprehensively and this is beyond the scope of this article. The section below is a high-level discussion of some of the key cost drivers that could well explain why aluminum extraction from CFA technologies has not seen aggressive uptake at commercial scale.

(1) *Capital Expenditure (Capex)* Numerous flowsheets including those that have been developed to full scale plants are substantially big plants with typically 8–12 major processing units in a plant. These unit operations include pelletising, sintering, leaching, filtration, solvent extraction, precipitation, desilication, filtration, seeding, and calcination. Capex and costs of installing plants of such size are considerably high and with the potential revenue from alumina sales as low as USD 250/tonne CFA processed [50]. It is unlikely that investment will have an acceptable payback period or give positive net present value (NPV).

(2) *Materials of Construction* Another very important aspect to consider that has a huge bearing on the Capex and choice of a processing route is the costs associated with materials of construction of the processing equipment and transfer equipment required for different flowsheets or routes. For example, in a typical Bayer process plant, tanks, pipes, and valves are made of mild steel because of the less corrosive nature of the leaching reagents and reaction products of the process, mild steel is not very expensive and can last for many years under those conditions hence, a plant made from mild steel will have relatively low capital and maintenance costs. To the contrary, in acid extraction routes the key area of concern is corrosivity of the leaching reagents, especially of hydrochloric acid. Hydrochloric acid was found to be the most suitable leaching agent, in concept, in the extraction of alumina from clay sources however, because of cost of corrosion the plant that uses HCL was found to be uneconomic. The Orbite process uses glass-lined reactors and valves and pipes made with high performance, chemically resistant polymers. Other plants using CFA as the source of aluminum have used glass tanks and expensive nickel-containing alloys.

(3) *Reagent costs* the absence of a pre-concentration stage before leaching in most flowsheets developed to recover alumina from CFA means that the entire feedstock needs to be contacted with the leaching reagent. This bulk leaching results in consumption of huge amounts of leaching reagent per tonne of CFA processed. The cost of acid or alkali alone could typically be close to the value of the Al_2O_3 produced. Additional reagents are also required for the downstream purification stages of the process which include solvent extraction and/or crystallization/precipitation. The reagents for these processes are costly and their aggregated costs considering volumes of leachates/solutions generated and requiring purification may be prohibitive in the absence of recycling.

(4) *Energy costs* The most successful processes to recover alumina from CFA as seen in Table 5 utilize a sinter-leach process where a high temperature solid-state reaction at $T > 1100$ °C is used to modify the alumina-silicate matrix and make it more amenable to leaching to improve the overall extraction of the aluminum. The energy expended in sintering the entire feedstock has significant impact on the process costs owing to the exorbitant cost of energy globally. Significant energy is also required for calcining, which is another common denominator process in all flowsheets. Dewatering by filtration which is used to separate leach residue from the liquor and precipitates from the liquid is also another energy-intensive operation and most flowsheets have at least two filtration stages.

(5) *Logistics expenses* The logistics costs for hauling the coal fly ash from source-to-plant represents a major cost in the event that the processing plant is not located in close proximity to the source of ash. CFA is a light (low density) but bulky material and hauling it by road or rail is potentially very expensive. A plausible transportation mode might be overland conveyance if distances involved are not long.

(6) *Other operational costs* Other costs that attend to such big and extensive plants are

- high plant maintenance costs
- high labor costs
- high utility costs.

(7) *Process Optimisation Costs* the huge variability of the feedstocks of coal fly ash from different sources means that the processing plants will have to be re-adjusted when a new feed with different properties needs to be processed and this could require major changes to the plant whose cost can be inhibitive.

(8) *Environmental Impact Assessment costs* Since recovery of alumina from CFA is still a relatively new area, understanding the environmental impacts of this metal recovery route and all the associated waste streams requires further investigations as there is little data comparing metal extraction from virgin materials to the recovery from CFA. Hence, the uptake and entry of this new technology in countries with stringent environmental legislations will come at a huge cost.

The key to a sustainable business model for CFA beneficiation is in developing process that can generate other valuable by-products that can offset some of the operational costs of the alumina production process. Thus, processes that generate, besides alumina, other valuable by-products and allow for the reuse of treatment chemicals and minimize the waste production so that safe disposal can be sustained should generally be the focus of any future research and development.

Evaluation of Process Routes

The evaluation and selection criteria of a preferred process route/s and the commercial success will depend on the specific details around the following factors: mineralogy of the feedstock; achievable recoveries; size of process plant, i.e., pre-concentration of the CFA feedstock to reduce

Table 5 Existing large commercial scale alumina producing plants that use CFA as the feedstock (after [2])

Name of plant (location)	Recovery Process	Year commissioned	Production Capacity (tonnes/year)	Product/s
Inner Mongolia Melic Sea Ordos Al. Co. Ltd (Etuke banner, Erdos city, China)	Lime-sinter-low temperature Bayer process	2013	400,000	Alumina
Inner Mongolia Datang International Recycling Resource Development Co. Ltd (Tuoketuo county, Hohhot city, China)	Pre-desilication—lime-soda sinter process	2012	240,000	Alumina
			200,000	Calcium silicate
Inner Mongolia Datang International Recycling Resource Development Co. Ltd (Tuoketuo county, Hohhot city, China)	Pre-desilication—lime-soda sinter process	2015	500,000	Alumina
			560,000	Calcium silicate
			100,000	Zeolite 4A
Inner Mongolia Datang International Recycling Resource Development Co. Ltd (Zhungeer banner, Erdos city, China)	Pre-desilication—lime-soda sinter process	2015	500,000	Alumina
			469,000	Calcium silicate
Inner Mongolia Kaiyuan Ecological Aluminium Co. Ltd (Zhungeer banner, Erdos city, China)	Ammonium sulfate sinter	2015 or later	1000,000	Alumina
			300,000	Si rich product
Huadian Inner Mongolia Energy Co, Ltd (Zhungeer banner, Erdos city, China)	Ammonium sulfate sinter	2013 or later	550,000	Alumina
Inner Mongolia Erdos Electrical Metallurgical Co. Ltd (Etuoke banner, Erdos city, China)	Acid leach followed by Bayer process	2015 or later	1000,000	Alumina
			510,000	Silica white
			770,000	Sodium silicate
Inner Mongolia Tongsheng Electric Power Co. Ltd (Qingshuihe county, Hohhot city, China)	Activation followed by water leach	2015 or later	1,000,000	Alumina
Shenhua Group Co. Ltd, (Zhungeer banner, Erdos city, China)	Acid leach process	2013	1000,000	Alumina
China Coal Pingshuo Coal Industry Co. Ltd (Shuozhou city, Shanxi province, China)	Pre-desilication—lime-soda sinter process	2013	100,000	Alumina
			40,000	Silica white
China Coal Pingshuo Coal Industry Co. Ltd (Baicheng city, Jilin province, China)	Alkali sinter-acid leach process		200,000	Alumina
			200,000	Silica white

material flow is key; process conditions; associated process costs, i.e., reagent costs, energy costs & materials of construction; feasibility of recovering other valuable metals; and utilization of residual bulk materials and environmental liability associated with process waste streams.

The different processing routes developed by various workers as outlined in this paper were conveniently grouped into two broad categories of acid leaching processes: (i) direct acid leaching and (ii) indirect acid leaching, i.e., which includes a sintering stage and alkaline leaching processes—(i) direct alkaline leaching and (ii) indirect alkaline leaching, i.e., that includes a sintering stage.

In general, direct acid leaching (DAL) routes were found to require high concentrations of acids and high leaching temperatures to achieve low to moderate recoveries typically less than 30 %, the high acid concentration means the reagent consumption would be high in DAL routes and high temperatures translate to high energy consumption. On the other hand, the indirect acid leaching routes with sintering step were found to have high recoveries >85 %, lower

leaching temperatures, high reagent consumption, and high overall energy consumption because of the sintering stage. The main advantage of acid leaching is that SiO_2 which is very high in CFA (about 50 %) remains largely insoluble in the acid medium and that in general the mineral acids especially sulfuric acid is relatively cheap. The main disadvantage of acid leaching route is the serious corrosion it causes to the process equipment necessitating protection of equipment with expensive lining increasing the capex and maintenance costs. It was also observed from literature that acid routes experience more difficulties in achieving high-quality alumina because of contamination of the leach liquors with co-dissolved ions like Fe, Ti, and Co and challenges presented by removing FeO and CaO. Crystallization and calcination of $Al_2(SO_4)_3$ and $Al(NO_3)_3$, the salts from sulfuric and nitric acid leaching was reported to be more difficult and more energy intensive compared to crystallization and calcination of gibbsite $Al(OH)_3$ which is the main salt from alkaline leaching processes. Acid leaching routes could also not effectively recycle the leaching medium making reagent consumption very high.

The direct alkaline leaching routes were found to generally take place at higher leaching temperatures and also associated with high reagent consumption because SiO_2 dissolves in most alkaline mediums and because of the excessive SiO_2 in the leach liquor an additional desilication stage is required which increases the unit operations. However, the desilication stage has an advantage in that it drastically reduces the total material flow into subsequent stages allowing for smaller reactors/equipment to be used and the product of desilication i.e., silica white and calcium silicate can be sold as a by-product. The quality of alumina that has been achieved with alkaline processing route has also been reported to be significantly higher than that achieved from acid leaching routes. The energy associated with sintering, as in indirect acid leaching, increases the energy costs of the indirect alkaline processing routes. An interesting observation was made by Murtha [11] that the product from the lime-sintering stage disintegrated automatically when the sinter was cooled to temperatures below 500 °C, practically eliminating any need for milling the sinter before leaching with Na_2CO_3. The other main attractions of the alkaline processing routes have been the ease with which the leaching reagent is recycled or regenerated which lowers the overall reagents costs and that alkaline mediums are not corrosive hence process and transfer equipment can be made from cheaper materials like mild steel.

An affirmative route selection cannot be completed in the absence of an accurate economic evaluation of the different process routes or flowsheets which was outside the scope of this current review. However, from the qualitative considerations outlined above, the indirect alkaline leaching routes appear to outweigh the other routes in terms of merits and presents the more attractive route to process the CFA. The preferred process routes, however, still has to contend with the more establish Bayer process which might remain viable for the forseeable future considering that the global reserves of Bauxite have been reported to be so abundant that they could last over 100 years at the current rate of consumption [51].

Current Status of CFA to Alumina Plants

Countries like China and Canada have nevertheless made huge strides in the last 10 years or so in developing and setting up the few large scale plants available today to produce alumina from CFA. In China, the recovery of alumina from CFA has been aggressively undertaken on the back of the preferential policies and subsidies issued by the state [2]. The plants in China are expected to scale up alumina production from CFA to over six million tonnes per annum over the next few years. In Canada, the research on exploiting CFA to produce alumina culminated in Orbite Aluminae Inc. successfully designing, building, and

commissioning a pilot plant in 2013. The pilot plant also has capabilities of producing other high value metals like the rare earths with minimum recoveries of 88 % for aluminum and 96 % for a range of rare earths being achieved by the plant [52]. In the US, the US Bureau of Mines has published several patents of different processes that exploit CFA to produce alumina and some of these patents have successfully gone through pilot scale trials.

Opportunities for a Sustainable CFA Value Chain

Researchers have recently been focusing on developing processes that can also recover strategic metals such as vanadium, titanium, germanium, gallium, rare earth elements, and scandium which are in CFA feedstocks in varying proportions. These metals are used in sectors such as automotive industry, catalysts, batteries, optics, electronics, and clean energy applications.

The amount of metal value in fly ash can vary greatly depending on the source of the coal. British Geological Society analyzed a set of data from 11 coal ash samples and the data were used to generate the value of different metals in the ash, as shown in Fig. 6. The more commonly found ashes around the world are typically richer in aluminum and when aluminum is the sole target for metal recovery only about US$250/tonne CFA processed can be realized [50]. The data from Fig. 6 indicate that scandium (Sc)- and germanium (Ge)-enriched coals may present the highest extractable value from the derivative ashes and show that more scandium (Sc)-enriched ashes can reach over US $40,000 per tonne of fly ash, and even the lowest scandium seen in these samples was worth nearly US $5000 per tonne of fly ash. The maximum germanium levels are at almost US $3500 per tonne of fly ash. The return from Sc and Ge is of an order of magnitude higher than the return that can be realized from alumina revenue per tonne of CFA processed. Some types of coal that are rich in dysprosium (Dy) and yttrium (Y) may realize US $245 and US $210 per tonne of CFA from these metals and these trace elements give a return similar to alumina.

Fly ash has also been found to contain appreciable amounts of rare earth metals to make it a potential source of these metals as well. The increasing demand of rare earth elements globally has stimulated research in the US on identifying coal deposits and seams that have high rare elements (REE) content i.e., >1000 ppm, so that these elements could be extracted from the fly ash after the coal has been used. The Orbite plant has been reported to give a positive return on investment as a result of a range of rare earths metals that have also been produced as by-product of aluminum extraction processes [52].

Therefore, in assessing the mineralogy of the CFA going forward it is advisable to perform a full chemical analysis

scan to ascertain all the components present, those elements that are present in trace amounts may be missed completely by conventional chemical analysis yet they carry higher monetary value per unit weight of fly ash processed.

CFA has also been found to be a potential raw material for other valuable products which are not metals. It can potentially be applied 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, and as an adsorbent for gases and waste water processes [6].

Dougill et al. [49] successfully produced ammonium nitrate fertilizer as a by-product of the nitric acid leaching of coal fly ash to produce alumina. The work by [53] also resulted in the production of saleable inorganic chemical by-products such as carbon, magnetite (Fe_3O_4), alumina (Al_2O_3), iron oxide (Fe_2O_3), iron chloride ($FeCl_3$), and cenospheres (hollow microspheres). Recent work by Xiao et al. [54] has also resulted in the by-production of silicon carbide. Some of the value adding uses of CFA are shown in Table 6.

The capability to fully utilize all the components in coal fly ash can support movement toward an increasingly sustainable CFA value chain. The ultimate goal should be to cleverly segregate the different materials within the ash and utilize each component to its highest value, whether that is metal recovery, functional materials for higher value applications, construction, chemicals industry, or commodity uses. This approach to the use of CFA resources has a scope for creating new industrial synergies that can enhance many economies.

Conclusions

This review dealt with a variety of studies by different workers on extraction of alumina from CFA. The studies were motivated by the fact CFA has been found to contain significant amounts of alumina which if effectively extracted can be a potential source of alumina in the aluminum industry. However, unlike bauxite, CFA cannot be processed via the well-established Bayer process because of the high silica content of CFA. In the review, the processes were conveniently grouped into two broad categories which are (1) Acid leaching processes (a) direct acid leaching (b) indirect acid leaching i.e., that includes a sintering stage and (2) Alkaline leaching processes (a) direct alkaline leaching (b) indirect alkaline leaching i.e., that includes a sintering stage. Pre-treatment of the feedstock and particularly sintering after mixing with lime, was found to significantly enhance dissolution of aluminum during both acid and alkaline leaching. The acid-insoluble mullite phase of CFA gets transformed into soluble phases like plagioclase and gehlenite during the sintering process. As way of reducing the amount of contamination from impurity elements after acid leaching solution purification has been achieved using solvent extraction and selective precipitation techniques while desilication is used in alkaline leaching to purify the leach liquor. Recovery of alumina from the purified solutions has been done by crystallization of aluminum salts followed by calcination to get a high-quality alumina product, which in certain cases analyses >99.4 % Al_2O_3 which is the required smelter grade alumina content. The indirect alkaline leaching routes on doing a qualitative evaluation of routes emerged as the most promising CFA processing route in comparison to acid leaching routes. The preferred process routes, however, still have to contend with the more establish Bayer process which might remain viable for the forseeable future considering that the global reserves of Bauxite have been reported to be so abundant that they could last over 100 years at the current rate of consumption. Notwithstanding the above, a few plants in China have been established to produce alumina from CFA on the back of the respective government issuing incentives for the establishment of the plants rather than on their economic viability. There still remains a possibility after full life-

Fig. 6 Ash Metal Value based on 11 different coal samples (London Metal Exchange prices as at September 2014, after [50])
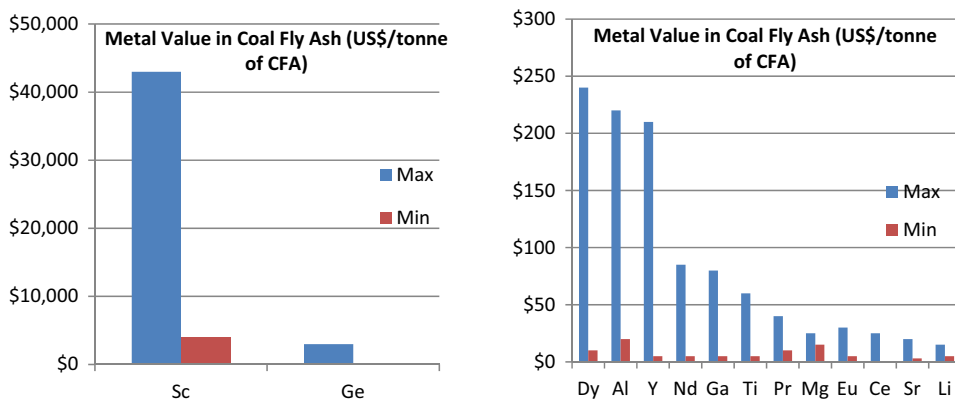
Table 6 Value added utilization of CFA

CFA Use	Description
Construction Industry	Concrete additive, concrete blocks, oil well cement, fly ash fire bricks
Ceramic manufacture	High wear-resistant ceramic tiles, light weight refractories, glass ceramics
Agriculture	Soil pH buffer
Cenospheres	Light weight composite materials, photo-catalysis, electromagnetic shields
Geotechnical field	Grouting, structural fill, infill, soil amendment
Adsorbent	Water purification & treatment, zeolite production
Catalysis	Heterogenous catalyst support

cycle assessments that these ventures could be economically viable in the long term.

References

1. World Coal Organisation (2014) http://www.worldcoal.org/coal/uses-of-coal/coal-electricity/
2. Yao ZT, Xia MS, Sarker PK, Chen T (2014) A review of the alumina recovery from coal fly ash, with a focus in China. Fuel 120:75–85
3. Montes-Hernandez G, Pérez-López R, Renard F, Nieto JM, Charlet L (2009) Mineral sequestration of CO_2 by aqueous carbonation of coal combustion fly-ash. J Hazard Mater 161(2–3):1347–1354
4. Heidrich C, Feuerborn H-J, Weir A (2013) Coal combustion products: a global perspective. In: 2013 World of coal ash (WOCA) conference, Lexington, Ky, vol 1, p 17
5. Manz OE (1997) Worldwide production of coal ash and utilization in concrete and other products. Fuel 76(8):691–696
6. Blissett RS, Rowson NA (2012) A review of the multi-component utilisation of coal fly ash. Fuel 97:1–23
7. Authier-Martin M, Forté G, Ostap S, See J (2001) The mineralogy of bauxite for producing smelter-grade alumina. JOM 53(12):36–40
8. Primary aluminium production (2016) World aluminium-International aluminium institute, 20 Jan 2016. www.world-aluminium.org
9. Shemi A (2012) Extraction of aluminium from coal fly ash using a two-step acid leach process. MSc thesis, University of the Witwatersrand
10. Hill RO, Raistrick B (1981) Process of extraction of aluminium values from coal ash. US Patent 4,243,640
11. Murtha MJ (1983). Process for the recovery of alumina from fly ash. US Patent US 43,97,822
12. Fass R, Geva J, Hasharon R, Shalita ZP, White MD, Lezion R, Fleming JC, Ziona N (1994) Bioleaching method for the extraction of metals from coal fly ash using *Thiobacillus*, US Patent 5,278,069
13. Seidel A, Zimmels Y, Armon R (2001) Mechanism of bioleaching of coal fly ash by thiobacillus thiooxidans. Chem Eng J 83:123–130
14. Matjie RH, Bunt JR, Van Heerden JHP (2005) Extraction of alumina from coal fly ash generated from a selected low rank bituminous South African coal. Miner Eng 18:299–310
15. Shcherban S, Raizman V, Pevzner I (1995) Technologies of coal fly ash processing into metallurgical and silicate chemical products. Kazakh Politechnical University, Alma-Ata
16. The KI, Fulford GD (1992) Desilication of Bayer process solutions. US Patent US 5,118,484
17. Habashi F (1995) Bayer's process for alumina production: a historical perspective. Bull Hist Chem 17–18:15–19
18. Su SQ, Yang J, Ma HW (2011) Preparation of ultrafine aluminum hydroxide from coal fly ash by alkali dissolution process. Integr Ferroelectr 128(1):155–162
19. Li H, Hui J, Wang C, Bao W, Sun Z (2014) Extraction of alumina from coal fly ash by mixed-alkaline hydrothermal method. Hydrometallurgy 147–148:183–187
20. Russ JJ, Russ JS, Heagy RT (1978) Process for Recovering mineral values from fly ash. US Patent 4,130,627
21. Li L, Wu Y, Liu Y, Zhai Y (2011) Extraction of alumina from coal fly ash with sulphuric acid leaching method. Chin J Process Eng 11(2):254–258
22. Wu C, Yu H, Zhang H (2012) Extraction of aluminum by pressure acid-leaching method from coal fly ash. Trans Nonferrous Met Soc China 22:2282–2288
23. Nayak N, Panda CR (2010) Aluminium extraction and leaching characteristics of Talcher Thermal Power Station fly ash with sulphuric acid. Fuel 89:53–58
24. Petruševski VM, Bukleski M, Stojanovska M (2010) Reaction of aluminium with diluted nitric acid containing dissolved sodium chloride on the nature of gaseous products. Chemistry 19(3):233–238
25. Johnson PW, Peters FA, Kirby RC (1964) Methods for producing alumina from clay: an evaluation of the nitric acid process. U.S Bureau of Mines, Providence **6431**
26. Margolin SW, Hyde RW (1974) The ADL nitric acid process for recovery of alumina from aluminium-bearing minerals. In: Forberg H., ed., Light metals proceedings 103rd AIME annual meeting, vol. 2, pp. 469–484
27. McDowell WJ, Seeley FG (1981) Recovery of aluminum and other metal values from fly ash. US Patent 4,252,777
28. Shemi A, Ndlovu S, Sibanda V, van Dyk LD (2015) Extraction of alumina from coal fly ash using an acid leach-sinter-acid leach technique. Hydrometallurgy 157:348–355
29. Guo Y, Li Y, Cheng F, Wang M, Wang X (2013) Role of additives in improved thermal activation of coal fly ash for alumina extraction. Fuel Process Technol 110:114–121
30. Padilla R, Sohn HY (1985) Sodium aluminate leaching and desilication in lime-soda sinter process for alumina from coal wastes. Metall Mater Trans B 16(4):707–713
31. Bai GH, Teng W, Wang XG (2010) Alkali desilicated coal fly ash as substitute of bauxite in lime-soda sintering process for aluminium production. Trans Nonferrous Met Soc China 20(Supplement 1):s169–s175
32. Wang J, Zhai Y, Shen X (2008) Study on extracting silica from fly ash by alkali leaching. J Light Met 12:23–25
33. Wang MW, Yang J, Ma HW, Shen J, Li JH, Guo F (2012) Extraction of aluminum hydroxide from coal fly ash by pre-desilication and calcination methods. Adv Mater Res 396–398:706–710
34. Tang Y, Chen FL (2008) Extraction alumina from fly ash by soda-lime sintering method. Min Metall Eng 28(6):73–75

35. Mesquita LMS, Rodrigues T, Gomes SS (1996) Bleaching of Brazilian Kaolins using organic acids and fermented medium. Miner Eng 9(9):965–971

36. Anand P, Modak JM, Natarajan KA (1996) Bio beneficiation of bauxite using bacillus polymyxa: calcium and iron removal. Int J Miner Process 48:51–60

37. Ghorbani Y, Oliazadeh M, Shahvedi A, Roohi R, Pirayehgar A (2007) Use of some isolated fungi in biological leaching of aluminium from low grade bauxite. Afr J Biotechnol 6(11):1284–1288

38. Vasan SS, Jayant Modak M, Natarajan KA (2001) Some recent advances in the bioprocess of bauxite. Int J Miner Process 62:173–186

39. Charlot G (1983) Les Reactions Chimiques en Solution Aqueuse, et al. Characterization ions, 7th edn. Masson, New York

40. Schrotterová D, Nekovář P (1999) Extraction of iron (III) from aqueous sulfate solutions by Primene JMT. Chem Papers 53(6):412–416

41. Mohapatra D, Kim H, Chul-Woo N, Kyung-H (2007) Liquid–liquid Extraction of aluminium (III) from mixed sulphates solutions using sodium salts of Cyanex 272 and D2EHPA. Sep Purif Technol 56:311–318

42. Preston JS (1985) The solvent extraction of base metals by mixtures of carboxylic acids and non-chelating oximes. Mintek Report No M234; Council for Mineral Technology: Randburg

43. Da Silva GC, Dias Silva, da Cunha JWS, Dweck J, Afonso JC (2007) Liquid-liquid extraction (LLE) of iron and titanium by bis-(20ethyl-hexyl) phosphate acid (D2EHPA). Miner Eng 21:416–419

44. Seyfi S, Abdi M (2008) Extraction of titanium (IV) from acidic media by tri-n-butyl phosphate in kerosene. Miner Eng 2:116–118

45. Li M, He Z, Zhou L (2010) Removal of Iron from Industrial Grade Aluminium Sulphate by primary amine extraction system. Hydrometallurgy 106:170–174

46. Seeley FG, McDowell WJ, Felker LK, Kelmers AD, Egan BZ (1981) Determination of extraction equilibria for several metals in the development of a process designed to recover aluminium and other metals from coal combustion ash. Hydrometallurgy 6:277–290

47. Agluacil FJ, Amer S, Luis A (1987) The application of Primene 81R for the purification of concentrated aluminium sulphate solutions from leaching clay minerals. Hydrometallurgy 18:75–92

48. Ajgankar HS, Dhadke PM (1997) Solvent extraction of iron (III) and aluminium (III) from other elements with cyanex 302. Talanta 44:563–570

49. Dougill SB, Monhemius AJ, Rogers PS (1985) Alumina production from colliery wastes. In: Symposium of extraction metallurgy'85, Sept. 9–12, 1985, London, p. 149

50. Tolhurst L (2015) Commercial recovery of metals from coal fly ash. The MMTA's International Minor Metals Conference, Toronto 27–29 April

51. Li W (2013) Refining alumina from fly ash. In: Proceedings of the International Committee for Study Of Bauxite, Alumina and Aluminium, ICSOBA conference, Krasnoyarsk, Russian Federation, pp. 408–410

52. Baudreault R, Fournier J, Primeau D (2013) Processes for treating fly ashes. Orbite, Canadian Patent, CA 286,230,7A1

53. Ashworth RA, Rodriguez LA, Padilla AA, Spake NB, Berry WW, Schmeda RA (1987) Method for the recovery of minerals and production of by-products from coal ash. US 4,652,433 A

54. Xiao J, Li F, Zhong O, Bao H, Wang B, Huang J, Zhang Y (2015) Separation of aluminum and silica from coal gangue by elevated temperature acid leaching for the preparation of alumina and SiC. Hydrometallurgy 155:118–124

55. Ayres RU, Ayres LW (1995) Coal ash: sources and possible uses. In: Material-cycle optimisation in the production of major finished materials. INSEAD's Center for the Management of Environmental Resources, BRE2-CT93-0894, Fontainebleau, 1995

56. Bai GH, Teng W, Wang XG, Xu P (2010) Processing and kinetics studies on the alumina enrichment of coal fly ash by fractionating silicon dioxide as nano-particles. Fuel Process Technol 91:175–184

57. Archer AM (1983) Considerations in the selection of alumina for smelter operations. Essential readings in light metals. In: Adkins, John EM (eds) Aluminium reduction technologies. Wiley, New York