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REVIEW

A mini review on the separation of Al, Fe and Ti elements from coal fly ash leachate

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Abstract
The electricity demand is increasing rapidly with the development of society and technology. Coal-fired thermal power plants have become one of the primary sources of electricity generation for urbanization. However, coal-fired thermal power plants produce a great amount of by-product coal fly ash every year. Coal fly ash disposal in landfills requires a sizable space and has negative environmental impacts. Therefore, it is crucial to develop new technologies and methods to utilize this enormous volume of solid waste in order to protect the environment. In this review, the fundamental physical and chemical characteristics of coal fly ash are introduced, and afterward the disposal policies and utilization ways of coal fly ash are discussed to gain a comprehensive understanding of the various ways this waste. The leaching of valuable metals in coal fly ash and the extraction of metal elements in leachate under different conditions are also summarized. Furthermore, the possibility of coal fly ash to serve as a supplementary source for mineral resources is analyzed, providing a basis for its extensive use as a raw material in the metal industry in China and worldwide.

Keywords Coal fly ash · Waste utilization · Metals extraction

1 Introduction

Coal fly ash (CFA) can be divided into traditional pulverized coal furnace (CF) fly ash and circulating fluidized bed boiler derived (CFB) fly ash. CF fly ash is a common industrial solid waste generated from coal-fired power plants, with an estimated global production of approximately 600–800 million tons per year (Jayaranjan et al. 2014; Xiao et al. 2021). CFB fly ash is solid waste discharged from thermal power plants using circulating fluidized bed boilers and has different characteristics to fly ash produced by pulverized coal boiler units due to the relatively low combustion temperatures used (850–900 °C) (He et al. 2021). By summarizing the basic characteristics and current status of utilization of CFA, a comprehensive understanding of the interrelationships between different applications can be obtained.

1.1 Main characteristics of the CF fly ash and CFB fly ash

CF fly ash usually shows a spherical or spherical structure after drying (Shi et al. 2022) with its physical appearance, ranging from dark brown to light grey (Qiu et al. 2021; Ram and Mohanty 2022), determined by the amount of unburned carbon remaining after the coal combustion process (Gollakota et al. 2019; Yang et al. 2022). The carbon content is generally lower (higher) when the color is lighter (darker). The chemical makeup of CF fly ash is significantly influenced by factors of coal type and combustion conditions, while CF fly ash consists of approximately 90%–99% inorganic components, 1%–9% organic components, and less than 0.5% fluid components (Besari et al. 2022). In addition, Zhang et al. (2018a) proposed that the surface of CF fly ash will form a large amount of mullite and encapsulate the amorphous phase material during coal combustion. In general, the primary

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constituents of CF fly ash include SiO_2 (35 wt%–65 wt%), Al_2O_3 (9 wt%–45 wt%), and Fe_2O_3 (1%–20%) (Wang et al. 2021; Mushtaq et al. 2019). Moreover, CaO, MgO, K_2O, Na_2O, TiO_2 and other oxides (Lee et al. 2017; Shi et al. 2020), as well as Hg, Cr, Ni, Co, Pb, V, As, Se and other trace hazardous elements (Ramanathan et al. 2020) are also included.

Compared to CF fly ash, CFB fly ash has a smaller particle size and a larger specific surface area (Liu et al. 2019). The main chemical components of CFB fly ash exist in the form of oxides, including SiO_2, Al_2O_3, CaO, Fe_2O_3 (0.1 wt%–30 wt%), SO_3 (0.5 wt%–40 wt%), where the chemical composition of SiO_2, Al_2O_3, and CaO varies from 0 to over 50 wt% (Ohenoja et al. 2020). In addition, CFB fly ash contains some trace elements such as chloride, Na, Ti, As, Cd, Cr, Hg, Ni, and Pb etc. (Yang et al. 2019).

CFA is commonly categorized into two different types based on the content of silica, aluminum, and iron. That is, according to the American Society for Testing and Materials (ASTM) C618 standard, when the total percentage of this ingredient is less than 60%, it is named Class C, and more than 70% is defined as Class F. The chemical constituents of CFA from different literature are listed in Table 1.

Improper handling of CFA can lead to serious environmental pollution due to the presence of toxic elements (Wang et al. 2020a). On the other hand, inhaling abandoned or hoarded CFA can also pose health risks to humans, potentially leading to various illnesses (Hong et al. 2021). Moreover, CFA has the potential to adversely impact the environment through groundwater contamination (Almahayni and Vanhoudt 2018). Therefore, making the harmless and environmentally friendly utilization of CFA is crucial. In recent years, the extraction of valent metals in CFA has received a lot of attention. It is one of the ways of high value-added application of CFA with good economic benefits.

1.2 The development strategy for the CFA

CFA is classified as a special waste by regulations, and its treatment in an ordinary landfill is prohibited (Gupta et al. 2020), so to reduce the environmental contamination created by coal-fired power facilities, the waste is separated from the flue gas in the chimney by a dust collector to realize the standardized production of CFA (Asl et al. 2018). However, it has been shown that CFA ponds and landfills leach harmful substances into streams and drinking water (Singh et al. 2016). CFA will have a long-term impact on the ecosystem due to its weathering environment that cannot maintain continuous isolation. As a result, the current waste treatment regulations require the isolation of CFA deposits in the containment system to avoid contaminants from seeping (Bhatt et al. 2019). To lower the leaching rate of heavy metals in the trash during landfill treatment, the Environmental Protection Agency rules additionally promote the disposal of CFA using new methods such as sintering (Biernacki et al. 2008) and geopolymer matrix stabilization (Gupta et al. 2020).

Most nations regulate CFA reuse under the Environmental Protection Agency's (EPA) Coal Combustion Residuals regulation, although there have been occasional failures to establish necessary protections for community and environmental health (SACE, Southern Alliance for Clean Energy 2020). Based on the USEPA's CFA rules, some health and safety simulation experiments are required for projects using CFA over 12,400 tons on land. (SACE, Southern Alliance for Clean Energy 2020). Numerous environmental laws are

Table 1 Chemical composition of different CFAs

No.	Oxide compositions (%)													References
	SiO_2	Al_2O_3	CaO	Fe_2O_3	TiO_2	MgO	K_2O	Na_2O	MnO	SrO	ZnO	Others	LOI	
1	48.68	40.28	2.56	3.02	–	0.56	0.73	–	–	–	–	1.99	2.18	Han et al. (2020)
2	46.90	19.60	5.60	17.45	–	1.40	2.04	1.09	–	–	–	1.84	2.50	Jiang et al. (2020)
	42.78	30.01	12.11	4.97	–	4.77	0.61	0.80	–	–	–	1.71	2.24	
3	45.5	23.1	4.1	4.3	0.8	1.7	0.6	0.1	0.1	–	–	3.3	3.2	Koshy et al. (2019)
4	52.06	20.54	14.07	5.50	–	3.29	0.69	0.94	–	–	–	0.58	0.10	Nikilioć et al. (2016)
5	64.2	28.2	0.06	3.70	–	–	1.34	0.17	0.46	–	–	–	1.74	Mudgal et al. (2019)
6	50.7	36.4	1.4	3.9	–	1.2	2.0	1.0	–	–	–	–	–	Rożek et al. (2018)
7	57.41	28.50	2.14	5.45	0.61	0.54	1.26	0.60	0.43	–	–	1.51	1.55	Samantasinghar and Singh (2018)
8	55.9	27.8	3.95	7.09	2.25	–	1.55	–	–	0.37	–	0.7	0.38	Ahmad et al. (2020)
9	63	22	3.80	7.22	1.3	0.7	1.3	0.2	–	–	–	–	–	Naveed et al. (2019)
10	55.60	29.80	1.59	5.91	1.63	1.08	1.94	0.23	0.05	0.04	0.03	–	–	Das and Raout (2019)
11	52.79	20.95	6.95	7.76	0.85	3.42	0.51	0.09	–	–	–	6.86	–	Wang et al. (2020b)

Note: LOI loss on ignition

supportive of innovative approaches that can effectively minimize CFA production and promote its recycling or use as a more environmentally friendly alternative (Khatri and Rani 2008).

China's rapid economic development has caused serious environmental pollution and resource waste, such as heavy metal pollution (Zhou and Wang 2019), sand storms (Li et al. 2018), haze (Sun et al. 2016), etc. With the growing awareness about environmental protection, the Chinese government adopted a series of tough environmental legislation in 2013, 2015, and 2016 to avoid pollution, including the national strategy to reduce air, water, and soil pollution. On the one hand, the act's implementation has imposed a significant burden on the cement sector (Hu et al. 2018), and several small and medium-sized cement manufacturing firms have been compelled to halt operations to comply with new environmental rules. On the other hand, with the demand for stronger environmental rules, it is more necessary to handle the problem of CFA pollution. Therefore, the harmless and efficient use of CFA needs further research.

1.3 CFA utilization

Annually coal consumption in the thermal power industry surpasses 4100 Mt (Chen et al. 2022a), resulting in annual CFA output of roughly 620 Mt (Mushtaq et al. 2019; Luo et al. 2019). The according quantity of CFA produced is projected to expand more as power consumption rises. CFA, being the major solid waste product from coal-fired power stations, accounts for a considerable fraction

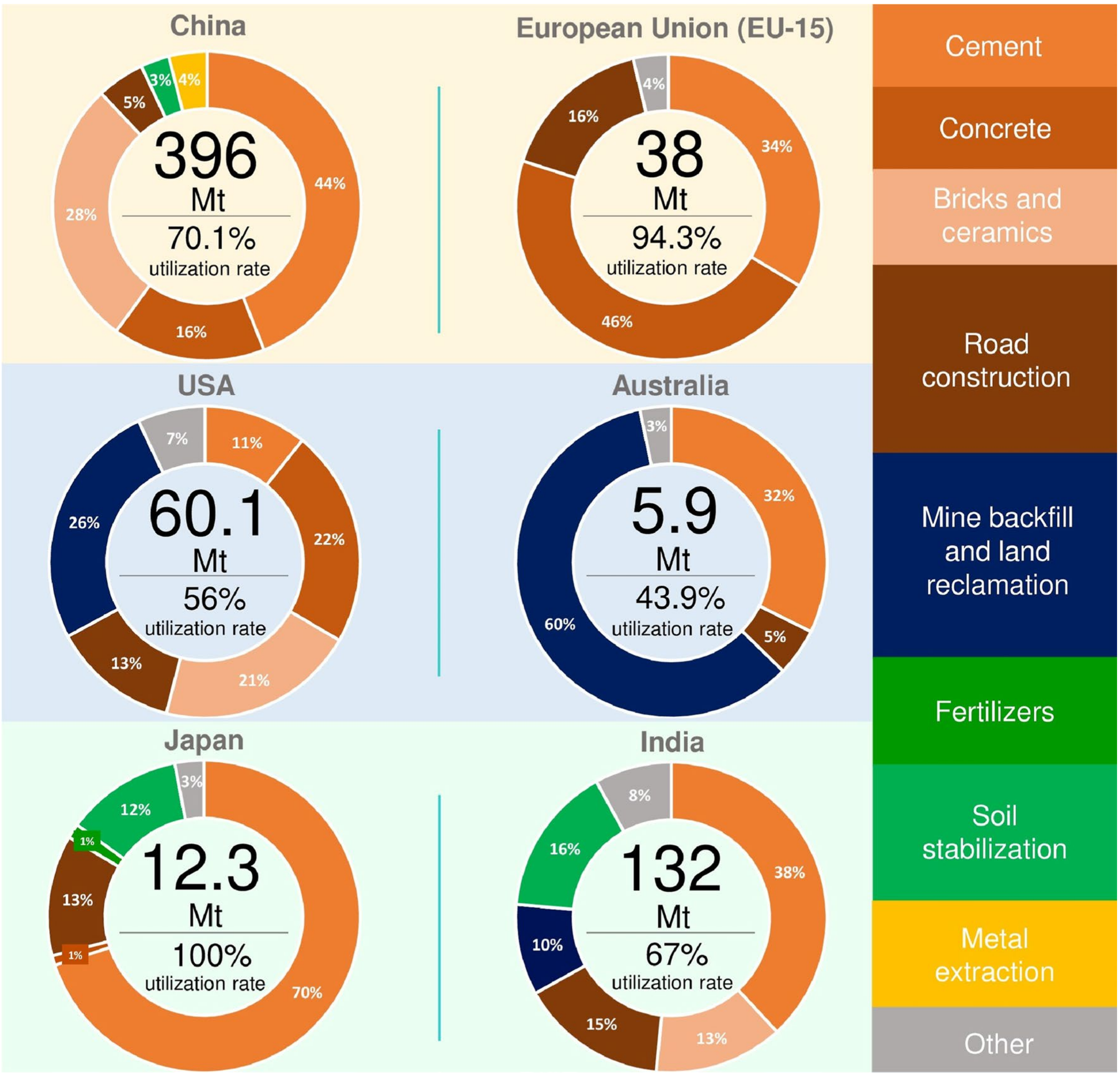

Fig. 1 Indicators for the generation and disposal of CFA in various countries. Adapted with permission (Valeev et al. 2022)

of solid waste released globally today, giving it a high potential for utilization (Yao et al. 2015). However, the degree of comprehensive coal fly ash utilization remains at a "low-grade" level for quite a while. In this regard, the coal fly ash use rate for China was 70.1%, India was 43.9%, and the US was 56% (Fig. 1) (Valeev et al. 2022).

In recent years, there has been growing global attention towards the comprehensive utilization of CFA, leading to an increase in the utilization rate of coal fly ash. One application is the inclusion of CFA as an additive to different kinds of construction supplies to boost their strength (Teixeira et al. 2022), including sintering bricks (Gupta et al. 2019), concrete (Ragipani et al. 2021), cement (Teixeira et al. 2019), and mine backfilling (Cavusoglu et al. 2021). At present, new ways of using CFA with high additional value utilization are being developed gradually. For instance, CFA can be utilized as a potential resource since it includes iron ore (Nyarko-Appiah et al. 2022), mullite (Chen et al. 2022b), and quartz (Ma et al. 2021). Recovery of useful substances from CFA can save production expenses, safeguard mineral resources, reduce contamination, and preserve the ecosystem (Huang et al. 2020). As a result, it is critical to extract high additional value components from CFA to achieve efficient use of resources.

1.4 Separation technology of elements in the CFA leachate

The composition of CFA varies from different origins. CFA can be divided into high alumina fly ash, high iron fly ash and common fly ash. The Fe_3O_4 content of high iron CFA can reach 49 wt%, which is a good raw material for iron extraction (You et al. 2019). Fe, a major component in CFA, can adversely affect the selective recovery of target metals. It is important to remove iron for the recovery of valuable metals. Ti is an associated element in the leaching of valuable metals. It is a waste of resources if Ti is not recovered.

The extraction of Al, Fe, Ti and other valuable metals from CFA has been extensively studied. The whole extraction process is carried out in two steps: firstly, the CFA leachate is obtained and then the metal, oxide or hydroxide is extracted from the CFA leachate (Shi et al. 2020). CFA leachate can be extracted from CFA using the acids (Shi et al. 2020), alkali (Su et al. 2011), alkaline-acid combination (Ma et al. 2019), or ammonium methods (Xu et al. 2021), where all of these methods have been extensively investigated. Electrolytic (Shi et al. 2021), precipitation (Zhang et al. 2018b), extraction (Wang et al. 2020b) or biological (Fan et al. 2019) methods are commonly used for the extraction of metals, oxides, or hydroxides from CFA leachate. For example, iron in CFA leachate can be extracted by adding oxalic acid (Hu et al. 2017), microorganisms (Kim et al. 2004) or P507 (Wang et al. 2020c). Then, carbonization (Cao et al. 2021), electrolysis (Shi et al. 2020) or pyrolysis method (Bai et al. 2011) can be applied to extract aluminum from leachate. At the same time, Ti is extracted mainly by hydrolysis with the addition of strong bases, ammonia, $NaCO_3$ and other reaction products (Ma et al. 2021). However, the extraction of Al, Fe and Ti from CFA leachate is a complex and lengthy process, which consumes a lot of energy and causes secondary pollution.

The increase in global CFA production is a serious environmental issue, and improper disposal can cause severe damage to public health and the natural environment. In recent years, the recovery of valuable metals from CFA becomes very valuable as mineral resources decline and demand continues to increase, and is currently a challenging topic for international research.

2 Results and discussion

2.1 CFA as an alternative to bauxites at China alumina refineries

China emits around 50 Mt of high-alumina CFA yearly, the alumina levels of which can exceed 50 wt%. Long-lasting hoarding has resulted in the squandering of aluminum resources (Wang et al. 2019). At the moment, bauxite is the primary raw material source for alumina manufacturing (Chen et al. 2022c). China's alumina manufacturing capacity has topped 50% of global total output, but due to a severe scarcity of bauxite resources and a relatively low proportion of high-quality ore, the yearly import of bauxite has overtaken the output (Chao et al. 2022). Fine-grained CFA can be used as a raw material for the production of the aluminum industry, and is widely and inexpensive (Valeev et al. 2022). Therefore, as a result, making rational use of current bauxite resources and aggressively exploring possible alternative bauxite mineral resources is important for the long-term development of China's alumina sector.

2.2 Composition of CFA and CFA leachate

Table 1 displays the concentration of some major oxides found in CFA. However, it does not provide information on the lower mass proportion elements such as La, Ce, Nd, Ga, and Li. Nonetheless, it is worth noting that these elements are often present in CFA, even though they are not specifically mentioned in the table.

As presented in Table 2, the research on leaching targets included common metals and rare elements. Aluminum, iron extraction from CFA is a common practice due to their economic value and their significant proportion in CFA (Wang et al. 2020c). Regarding titanium, lanthanum, cerium, neodymium, gallium, lithium, and other elements, despite their

Table 2 Some examples of research on the extraction of valuable components from CFA

No.	Metal	Extraction method	Results	References
1	Al, Fe	1. Mixed with Na_2CO_3, calcined at 800 °C for 2 h; 2. Leached using HCl solution	The concentrations of Al and Fe are 34.2 and 30.7 g/L, and the leaching of Al is > 90%	Yan et al. (2016)
2	Fe, Mg	1. Leaching with 2 M HCl after water washing for $MgFe_2O_4$ enrichment; 2. Fe and Mg were leached from $MgFe_2O_4$ by the reduction method	According to the leaching effect, the leaching effect of Na_2S on Fe and Mg is poor, whereas $Na_2S_2O_4$ performs best at 100 °C and FeS_2 performs best at 200 °C. The reductants had no discernible effect on leaching Mg	Choo et al. (2016)
3	La, Ce, Nd	1. Leaching with HCl solution	Significant effects are observed from the temperature of the leaching, the duration of the leaching, the dose of acid, and also the ratio of liquid to solid. La leaches at rates of 71.9%, 66.0%, and 61.9% respectively, more readily than Ce and Nd	Cao et al. (2018)
4	Ga	1. It is calcined for 1.5 h at a temperature of 1050 °C; 2. Using HCl solution (8 M) at 80 °C by leaching	Leaching temperature > concentration of HCl > leaching time > solid/liquid ratio. Ga leaches at a rate of 46.4%	Fan et al. (2012)
5	Li	1. Mixed with K_2CO_3 and Na_2CO_3 and calcined at 800 °C; 2. Leaching with HCl solution following MW irradiation	HCl extracts Li more effectively better than H_2SO_4. The combination of Na_2CO_3 (30%) and K_2CO_3 (70%) activates CFA more efficiently as a solo activator, Li leach rates can be as high as 93.0%	Dong et al. (2019)
		1. Mixed with Na_2CO_3 and $CaCO_3$, the mixture was then calcined for 1.5 h at a temperature of 1050 °C; 2. Li was leached with Na_2CO_3 solution for 2 h at a temperature of 140 °C	At a liquid-to-solid ratio of 100:1, Li leaching can be as high as 70%	Hou et al. (2015)
6	Al, Ti	1. A mixture of H_2SO_4 and NH_4HSO_4 as the leaching agent; 2. Microwave-assisted baking at 280 °C for 60 min, 1.2 times the theoretical amount of reagent	60 °C, L/S: 5 g H_2O to 1 g baked ash, leaching for 30 min, 82.4% and 55.6% of Al and Ti were leached	Ma et al. (2021)
7	Al, Li	The mixture of CFA and $Na_2S_2O_7$ was mechanically activated, followed by addition of $Na_2S_2O_8$ for pressurized leaching	At a molar ratio of $Na_2S_2O_7/Al_2O_3$ of 3:1, ball milling for 60 min, a molar ratio of $Na_2S_2O_8/Al_2O_3$ of 8:1, a liquid-to-solid ratio of 4:1, and a reaction time of 120 min at 200 °C, the leaching yields of aluminum and lithium reached 95.58% and 71.59%, and the lithium leaching rate could reach 95.45% at an elevated temperature of 230 °C	Fang et al. (2023)
8	Fe, Ti	HAFA was mixed with 15 M H_2SO_4 solution at a liquid–solid ratio of 33.33 mL/g. The reaction was carried out at 180 °C for 60 min. At the end of the reaction, it was diluted, filtered, washed, and the residue was dried for 24 h at 105 °C	During sulfuric acid leaching, titanium was more difficult to leach, and the content of TiO_2 decreased from 2.30 to 2.25%, while the content of Fe_2O_3 decreased from 1.50 to 0.86%	Yang et al. (2021)

relatively low percentage in CFA, their extraction is worthwhile due to their rarity and high value in various applications (Rezaei et al. 2022). The target components in CFA can be leached or eliminated, but other elements will always be leached. This phenomenon has little influence on the overall removal of elements in CFA but has a substantial impact on the purity of the extracted target elements. As a result, in the case of valuable element extraction, a suitable leaching agent or a feasible and efficient leaching method, if we want to achieve a high selectivity for the target element, is needed.

The common processes used to leach target metals from CFA are acid leaching or activation by roasting of CFA mixed with alkalis. Yang et al.(2021) conducted leaching experiments on high-alumina fly ash using sulfuric acid at room temperature, and it was found that the leaching effect of Fe and Ti was poor, and Ti was more difficult to leach. Ma et al. (2021) used a mixture of H_2SO_4 and NH_4HSO_4 as a leaching agent, along with microwave-assisted roasting, and the leaching rates of Al and Ti were 82.4% and 55.6%, respectively, under the optimal conditions. Fang et al. (2023) mechanically activated the mixture of CFA and $Na_2S_2O_7$ and then added $Na_2S_2O_8$ for pressurized leaching, and the leaching rate of Al was 95.58%, which reached a high level. CFA was mixed with Na_2CO_3, calcined at 800 °C for 2 h, and then leached with hydrochloric acid at concentrations of 34.2 and 30.7 g/L for aluminum and iron, respectively (Yan et al. 2016).

A great deal of research has been carried out on different processes for the extraction of metals and significant results have been obtained, while some special methods exist. Using the above documented processes and methods it is possible to leach one or more elements simultaneously and then extract them with good economic benefits.

2.3 Developing technologies to extract valuable metals from CFA leachate

A giant quantity of CFA containing heavy metals will reason significant environmental harm. CFA provides advantages for both the economy and the environment when it is used to extract titanium, iron, and alumina. Acid, alkali, and other techniques are commonly employed for the extraction of valuable components from CFA. Electrolysis, precipitation, extraction and biological methods are used to extract valuable metals from CFA leachate.

2.3.1 Electrolytic method

The electrochemical method is a kind of hydrometallurgy. Electrochemical methods are considered to be a promising method to combine with renewable resources to achieve a sustainable recovery process for metals (Kim et al. 2021). Electrodeposition is a simple and widely used method for modulating product nucleation, growth, morphology and composition during the electrolysis process (Hussein et al. 2020; Shi et al. 2022). The electrodeposition method enables the separation and recovery of the desired metals from multicomponent mixed solutions by setting key parameters according to the reduction potential of the component metals (Liu et al. 2017). During electrolysis, the anode loses electrons and an oxidation reaction occurs, and the cathode gains electrons and a reduction reaction occurs. The equation of the reaction occurring in an acidic solution is as follows:

Anode reactions:

$$2H_2O = O_2 + 4H^+ + 4e^- \tag{1}$$

Cathode reactions:

$$2H^+ + 2e^- = H_2 \tag{2}$$

$$M^{2+} + 2e^- = M \tag{3}$$

Chemical reactions:

$$M^{2+} + 2OH^- = M(OH)_2 \tag{4}$$

Alumina, iron, and titanium were simultaneously separated from CFA at the same time using an electrolysis–hydrolysis process (Shi et al. 2022). The techniques for this study involved two steps: leaching of the target elements from the CFA, followed by successive extraction of Ti, Fe, and Al_2O_3 from the leachate.

2.3.1.1 Obtaining leachate from coal fly ash In this first stage, CFA leachate is obtained from CFA, including the baking process and leaching processes (Shi et al. 2020). The reaction equation during the baking process can be represented as follows:

$$\begin{aligned} &9H_2SO_4(l) + 3Al_2O_3 \cdot 2SiO_2(s) \\ &= 3Al_2\left(SO_4\right)_3(s) + 2SiO_2(s) + 9H_2O(q) \end{aligned} \tag{5}$$

$$3H_2SO_4(l) + Al_2O_3(s) = Al_2\left(SO_4\right)_3(s) + 3H_2O(q) \tag{6}$$

$$3H_2SO_4(l) + Fe_2O_3(s) = Fe_2\left(SO_4\right)_3(s) + 3H_2O(q) \tag{7}$$

$$H_2SO_4(l) + TiO_2(s) = TiOSO_4(s) + H_2O(q) \tag{8}$$

$$H_2SO_4(l) + CaO(s) = CaSO_4(s) + H_2O(q) \tag{9}$$

After baking, all the clinkers are dissolved in varying quantities of deionized H_2O for 10 min at 95 °C and 400 rpm for the leaching procedure. Filtration is used to separate the leachate and CFA residue to produce leachates of varying concentrations. The produced soluble compounds ($Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, and $Ti(SO_4)_2$) and a slightly soluble component ($CaSO_4$) were ionized during this leaching process, as Eqs. (10)–(13) states.

$$Al_2(SO_4)_3(s) = 2Al^{3+} + 3SO_4^{2-} \tag{10}$$

$$Fe_2(SO_4)_3(s) = 2Fe^{3+} + 3SO_4^{2-} \tag{11}$$

$$Ti(SO_4)_2(s) + 3H_2O = Ti(OH)_3^+ + 2SO_4^{2-} + 3H^+ \tag{12}$$

$$CaSO_4(s) = Ca^{2+} + SO_4^{2-} \tag{13}$$

2.3.1.2 Sequential extraction of titanium, iron, and alumina from coal fly ash leachate

The method for extracting alumina from CFA by electrolysis–hydrolysis is proposed. $Ti(OH)_4$, Fe, and $Al(OH)_3$ were extracted successively from the coal fly ash extract, consisting of two electrolysis phases. The separation of $Ti(OH)_4$ and Fe from the CFA leachate is the initial phase of the electrolysis process. During electrolysis, Fe can be produced at the cathode, as Eq. (14) shows.

$$Fe^{3+} + 3e^- = Fe \tag{14}$$

Hydrolysis can produce $Ti(OH)_4$, as Eq. (15) shows.

$$Ti(OH)_3^+ + H_2O = Ti(OH)_4 \downarrow + H^+ \tag{15}$$

Following the elimination of titanium and iron in the initial phase of electrolysis, the leachate of coal fly ash was diluted to an Al^{3+} concentration of 0.05–0.40 M in the next phase of electrolysis to obtain $Al(OH)_3$ on the cathode (Eq. (16)).

$$Al^{3+} + 3H_2O = Al(OH)_3 \downarrow + 3H^+ \tag{16}$$

This task involves two electrolysis phases, as illustrated in Fig. 2. The initial stage of electrolysis involved a hydrolysis procedure to recover heat and form the leachate containing $Ti(OH)_4$ precipitate. During this stage, Fe was removed from the cathode. In the subsequent phase of electrolysis, following the preceding process, $Al(OH)_3$ was recovered from the cleaned coal fly ash leachate. The focus of this research is on the electrolysis–hydrolysis process (red part in Fig. 2) and the mechanics of the electrolysis–hydrolysis process are depicted in Fig. 3.

This research involves two stages of electrolysis, and the results of these two phases were evaluated at the cathode. During electrolysis, Fe and Al_2O_3 were produced at the cathode. The cathode reaction is primarily responsible for the formation of iron and alumina precipitates. The primary molecules and ions in the coal fly ash leachate were Al^{3+}, Fe^{3+}, $Ti(OH)_3^+$, and H_2O, according to the findings of iron speciation at various pH levels.

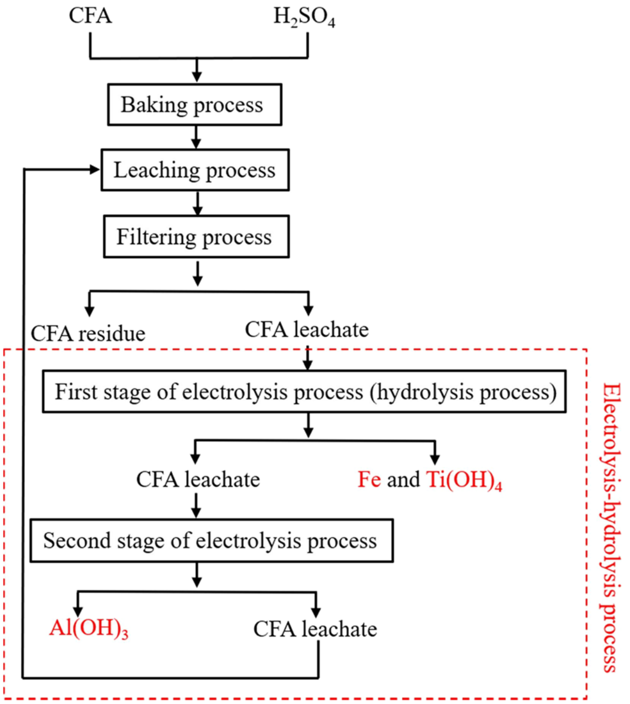

Fig. 2 Flowchart for extraction of titanium, iron, and alumina from CFA (Shi et al. 2022)

The stated electrolysis–hydrolysis process offers significant advantages over existing technologies. Firstly, the stated electrolysis–hydrolysis technique mentioned above allows for the simultaneous recovery of Fe, $Ti(OH)_4$, and $Al(OH)_3$ from the same solution. Secondly, this approach may create Fe and $Al(OH)_3$ selectively by altering the charge sequence of ions during the electrolysis process without the need for additives. Thirdly, the stated technique efficiently recovers heat from titanium. Additionally, the stated approach is non-polluting and does not emit hazardous gases. Furthermore, this technology allows for the simultaneous extraction of Fe, $Ti(OH)_4$, and $Al(OH)_3$ from CFA leachate at a single location. Nieto et al. (2019) discovered that the cost of electricity generated by photovoltaic power is decreasing, further reducing the overall cost of implementing this technology. As a result, this research offers an alternative and effective approach for extracting Ti, Al_2O_3, and Fe from CFA leachates.

2.3.2 Precipitation method

The precipitation method, being a more traditional and extensively studied approach, is relatively simple to operate. However, it requires the use of significant amounts of strong acids and bases during the production process, necessitating equipment with high corrosion resistance. Over the years, research

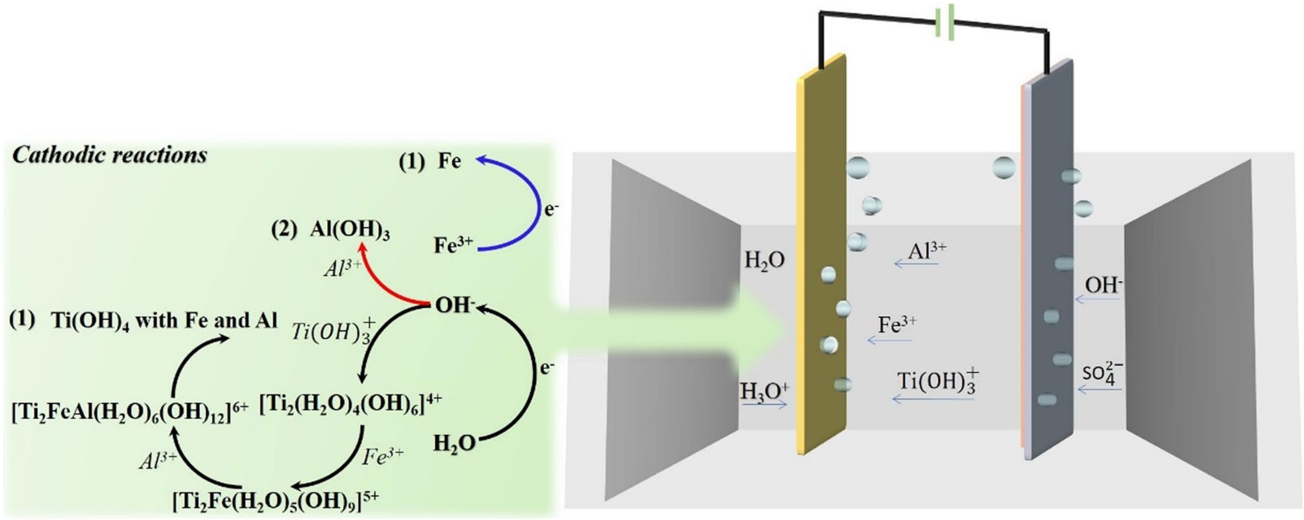

Fig. 3 Proposed mechanism of the electrolysis–hydrolysis process. Adapted with permission (Shi et al. 2022)

efforts have aimed not only at enhancing the yield of valuable elements but also at continuously optimizing operating conditions and the utilization of agents in order to minimize environmental impact and improve overall efficiency.

Wang et al. (2014) proposed a new technology for NH_4HSO_4 mixed roasting to extract Al_2O_3 from coal fly ash (Fig. 4). This process includes baking, aluminum precipitation, alkali dissolution of aluminum residue, carbonization decomposition, and calcination. Under the optimal conditions, the extraction rate of Al_2O_3 reaches more than 90%, and 99% of α-Al_2O_3 products are finally obtained. Equations (17)–(23) shows the baking process principle of this method.

High aluminum CFA mixed with NH_4HSO_4 at 400 °C:

$$3Al_2O_3 \cdot 2SiO_2 + 12NH_4HSO_4 = 6NH_4Al\left(SO_4\right)_2 + \ 6NH_3 \uparrow + 9H_2O + 2SiO_2 \tag{17}$$

$$3Al_2O_3 \cdot 2SiO_2 + 9NH_4HSO_4 = 3Al_2\left(SO_4\right)_3 + 9NH_3 \uparrow + 9H_2O + 2SiO_2 \tag{18}$$

$$Fe_2O_3 + 4NH_4HSO_4 = 2NH_4Fe\left(SO_4\right)_2 + 2NH_3 \uparrow + 3H_2O \tag{19}$$

$$Fe_2O_3 + 3NH_4HSO_4 = Fe_2\left(SO_4\right)_3 + 3NH_3 \uparrow + 3H_2O \tag{20}$$

The sintered clinker was leached with water and heated, and then NH_4HCO_3 was added to precipitate Al and Fe in the leaching solution:

$$NH_4HCO_3 = NH_4^+ + OH^- + CO_2 \tag{21}$$

$$Al^{3+} + 3OH^- = \ Al(OH)_3 \downarrow \tag{22}$$

$$Fe^{3+} + \ 3OH^- = \ Fe(OH)_3 \downarrow \tag{23}$$

In the precipitation method, the separation of Fe and Al in NaOH solution with different solubility, and then the Al_2O_3 product was achieved through carbon fraction and calcination. However, iron presents a significant challenge as a strong interfering contaminant, as it can adversely affect the quality of the α-Al_2O_3 product. Therefore, efficient separation of iron from aluminum is crucial to ensure high-quality α-Al_2O_3 production. To separate aluminum and iron, the dissolution of $Al(OH)_3$ in NaOH solution can be employed. The dose of NaOH (solid) can be estimated based on the Al concentration in the mixture of $Al(OH)_3$ and $Fe(OH)_3$ precipitation. The alkali dissolution process was examined at a mass ratio of 1:1–1:5 of $Al(OH)_3$ to NaOH. Heat the sodium hydroxide (solid) and 250 mL deionized water mixture to a temperature range of 25–99 °C. When the temperature is reached and maintained constant, the mixture of precipitates is added to the NaOH solution. Continuous stirring is applied during this period, followed by filtration of the mixture. The resulting filtrate is the $NaAl(OH)_4$ solution, while the residue consists of the deposit of $Fe(OH)_3$.

In this process, the following reaction could occur, as shown in Eq. (24):

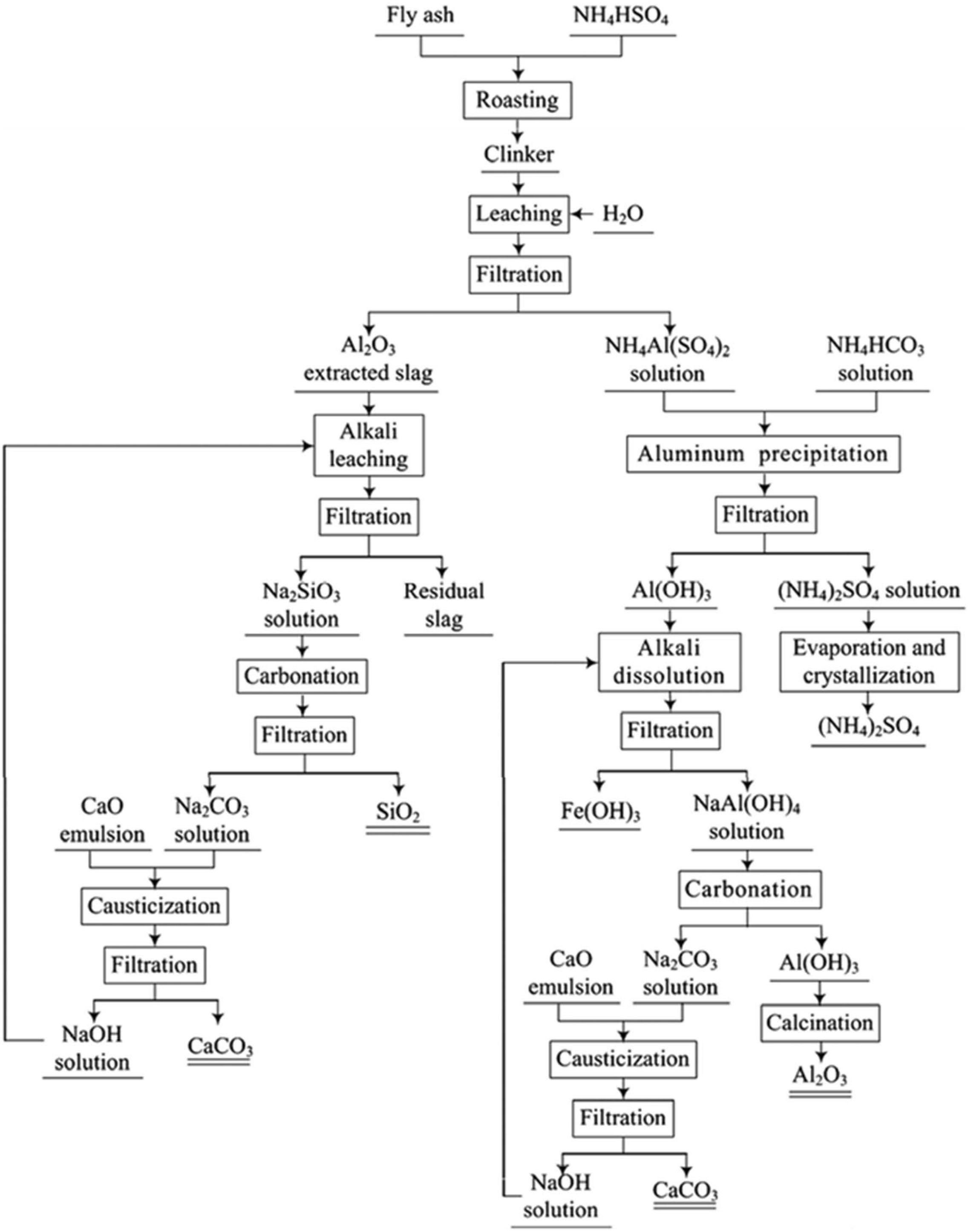

Fig. 4 Flowsheet of ammonium hydrogen sulfates inter process (Wang et al. 2014)

$$Al(OH)_3 + NaOH = NaAl(OH)_4 \quad (24)$$

Single-factor tests were conducted to establish three crucial parameters, including temperature, the ratio by mass of $Al(OH)_3$ to NaOH, and heat preservation time.

By heating the $NaAl(OH)_4$ solution, the temperature is reached 25–99 °C. CO_2 at a gas flow rate of 20–100 mL/min was injected into the solution at the chosen temperature. The solution in this reaction undergoes agitation and is then filtered under air pressure. The resulting filter cake consists of

$Al(OH)_3$ precipitation, while the filtrate is a Na_2CO_3 solution that may be subjected to causticization by the addition of CaO. The following Eqs. (25) and (26) describe the chemical reactions occurred during this process:

$$2NaOH + CO_2 = Na_2CO_3 + H_2O \tag{25}$$

$$NaAl(OH)_4 = Al(OH)_3 \downarrow +NaOH \tag{26}$$

Carbonation breakdown required two critical steps. The first was the neutralization reaction between NaOH with CO_2, and the second step was the $Al(OH)_3$ precipitation procedure. Single-factor tests were used to investigate three essential parameters: temperature, CO_2 gas flow rate, and holding time.

The carbonated solution was further utilized by adding it to lime milk for recycling. However, the ammonium hydrogen sulfate baking method has low energy consumption and cost, but the process is relatively complex. During the baking process, the release of NH_3 occurs, and the material recycling efficiency is low.

It is a brand-new processing method that has been designed and thoroughly studied to extract Al and Ti from CFA (Ma et al. 2021). In this study, the roasting process used earlier was modified to microwave heating method, and H_2SO_4 and NH_4HSO_4 solutions were used as extractants. Compared to conventional acidic baking procedures, this approach improved the Al and Ti extraction efficiencies while reducing energy use and gas emissions. The proposed flowchart for the method of extracting Al and Ti from CFA in this work is shown in Fig. 5. The first stage of the process facilitated the transfer of Al and Ti to the aqueous solution with the aid of a microwave and water leaching. To break down the CFA during the baking process, a solution of H_2SO_4 and NH_4HSO_4 was chosen. After cooling at a low pH, Al^{3+} was then preferentially precipitated from the leach liquor by alum ($NH_4Al(SO_4)_2 \cdot 12H_2O$) precipitation. The iron in solution is reduced from Fe^{3+} to Fe^{2+} using iron powder, and TiO^{2+} is precipitated by a neutralization reaction.

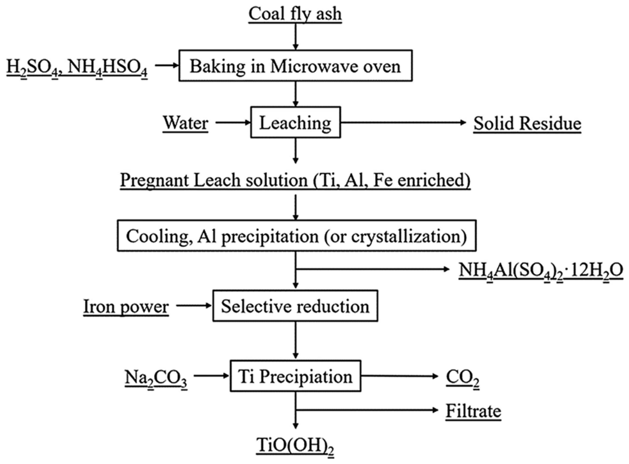

Fig. 5 Proposed flowchart for recovering Al and Ti from CFA (Ma et al. 2021)

Al^{3+}, TiO^{2+}, and certain contaminants including Na^+, Ca^{2+}, and Fe^{3+} were present in the final leach solution. Due to the strong temperature dependence of the water solubility of $NH_4Al(SO_4)_2 \cdot 12H_2O$, the recovery of Al^{3+} from the leaching solution can be achieved through alum precipitation using $NH_4Al(SO_4)_2$. This precipitation process can be carried out under low pH conditions. The relevant reactions involved in this process are described by Eqs. (27) and (28).

$$Fe + Fe^{3+} = 2Fe^{2+} \tag{27}$$

$$TiO^{2+} = 2OH^- = TiO(OH)_2(s) \tag{28}$$

The major goal of the conventional extraction procedure is to recover aluminum from CFA by decomposing the stable mullite phase using acid or alkali techniques (Valeev et al. 2022). Despite having considerable economic importance, the presence of iron and silicon compounds in CFA has typically been ignored in recent studies. Alkali desilication, carbonation, and acid leaching were combined to create a cascade extraction process (Zhao et al. 2023) that can effectively separate and recover all aluminum, silicon, and iron compounds from CFA. Activation of aluminum, acidic leaching, and Fe/Al deposition make up the four main components of the cascade extraction process used by the CFA, resulting in the simultaneous recovery of various resources (Fig. 6). Prior to adding $Ca(OH)_2$ to the dedicated unit's supernatant to produce $CaSiO_3$, alkali leaching was employed to disilicate the raw CFA. The objective was to release silicon species and the corresponding reaction is shown in Eq. (29).

$$Na_2SiO_3 + Ca(OH)_2 = CaSiO_3 \downarrow +NaOH \tag{29}$$

The desilication supernatant is treated with $Ca(OH)_2$, and the $CaSiO_3$ crystals are recovered in such a way that lye consumption and waste liquor outflow are reduced. To convert mullite to the nepheline phase, the dedicated CFA was activated by carbonate calcination, increasing the acid-leaching dissolving efficiencies of Al_2O_3 and Fe_2O_3 to 90.4% and 92.3%, respectively. Additionally, acid leaching transformed the silicious components in activated CFA into 93.9% pure silicic acid. $Fe(OH)_3$ and $Al(OH)_3$ products with purities of 70.6% and 90.8% were produced using stepwise precipitation. The produced $CaSiO_3$, silica gel, $Fe(OH)_3$, and $Al(OH)_3$ can all be used again as flame retardants, and the recovered $Al(OH)_3$ can be transformed into $NaAlO_2$ for the removal of chloride from saline wastewater. Without producing solid waste, the cascade

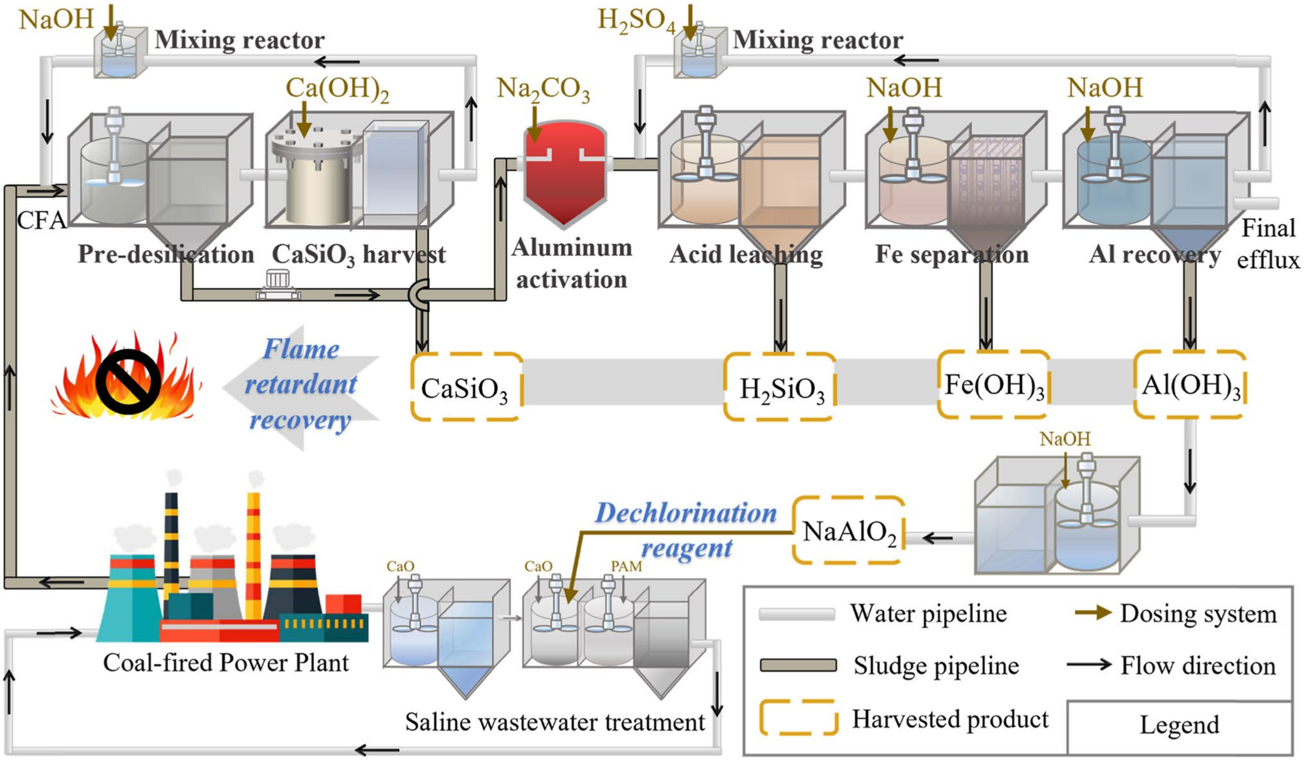

Fig. 6 Schematic diagram of cascade extraction process for comprehensive utilization and resource recovery of CFA. Adapted with permission (Zhao et al. 2023)

extraction of CFA is both ecologically friendly and economically advantageous.

2.3.3 Extraction method

The extraction method is to add a second solution to the original solution so that the solute in the original solution into another solution due to the difference in solubility, thus concentrating the original solution. The key to using solvent extraction is to select a suitable extraction agent. Acid dissolution is the extraction of Al_2O_3 from CFA compared with the pre-silica-alkali lime sintering method, which greatly reduces the discharge of waste residue.

Ding and Zhang (2017) used hydrochloric acid to leach CFA with the relevant reactions of Eqs. (30) and (31)

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O \tag{30}$$

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O \tag{31}$$

Selecting the extractants to separate the ferric chloride and aluminum chloride. P204-kerosene extractant, P204 is extractant, kerosene is diluent, V_{p204}: $V_{kerosene} = 3:2$, the ratio of organic phase to the aqueous phase is 1:1, extraction time is 20 min, medium speed stirring, the extraction rate of iron can reach 94% (the concentration of hydrochloric acid is 0.1 mol/L). Extraction conditions: at normal temperature, the concentration of hydrochloric acid concentration is 3 mol/L, and iron concentration of 5 g/L for extraction. Then an aluminum chloride solution is obtained, which can react with concentrated ammonia water, as Eq. (32) shows:

$$AlCl_3 + 3NH_3 \cdot H_2O_3 = NH_3Cl + Al(OH)_3 \downarrow \tag{32}$$

The obtained aluminum hydroxide precipitation was subjected to multiple washes to remove the ammonium chloride solution. Then, the ammonium chloride was decomposed at a high temperature to recycle the hydrochloric acid. Aluminum hydroxide was then roasted to obtain alumina. The individual products can be recovered separately and HCl can be reused in this method. This study presents a new technology for alumina production through CFA extraction.

2.3.4 Biological method

Bioleaching technology, which utilizes acids produced by microbial metabolism, prevents the generation of more solid waste during the extraction process and plays an important role in the cost-effective recovery of valuable metals from CFAs. In bioprocessing, bacterial microorganisms are used as catalysts to promote leaching of metals either directly or indirectly. The process is usually applied to low-grade sulfides because the microorganisms utilize the low solubility metal sulfates as an energy source to metabolically generate H_2SO_4, which can be used in the leaching of metals (Rasoulnia et al. 2021). Seidel et al. (2001) pointed out that most bacterial microorganisms usually colonize at low pH, and therefore, the slow growth of bacteria in alkaline species such as CFA results in low leaching efficiency of the target elements. However, additional energy can be provided by the addition of monomeric sulfur to improve leaching efficiency (Seidel et al. 2001). Seidel et al.(2001) performed batch experiments in which Fe and Al_2O_3 were extracted by suspending 10% CFA in a sulfur-containing thiobacillus oxidans inoculum and incubated for 21 days, with recoveries as high as 25% and 22%, respectively. It was found that the precipitation of $CaSO_4$ interfered with the attachment of the cells to the sulfur particles, thus slowing down the growth rate of the cells. Pretreatment of CFA with HCl to remove CaO had no significant effect, resulting in, low alumina selectivity and slow leaching kinetics. Fan et al. (2019) first activated CFA using Na_2CO_3 roasted at 850 °C for 2 h. CFA was then mixed with pyrite (sulfur source) and pH adjusted to 1.5–2.5 with H_2SO_4. Mesophilic thiobacillus ferrooxidans was used as a source of pyrite oxidation, resulting in the production of H_2SO_4 and Fe^{3+}(Eqs. (33)–(35)). After 12 d and 8 d of incubation, aluminum and cerium recoveries were 91.2% and 63.4%, respectively.

$$FeS_2 + 2Fe^{3+} = 3Fe^{2+} + 2S \tag{33}$$

$$2S + 3O_2 + 2H_2O = 2SO_4^{2-} + 4H^+ \tag{34}$$

$$4Fe^{2+} + O_2 + 4H^+ = 2Fe^{3+} + 2H_2O \tag{35}$$

3 Future research prospects

(1) Extraction techniques for elements in CFA leachate

CFA is a potential supplementary source of bauxite. The low and diverse content of most of the elements and the difficulty of extracting multiple elements simultaneously from the leachate pose some challenges for extraction. Therefore, a method that can extract multiple elements simultaneously needs to be investigated further.

(2) Efficiency, sustainability and environmental benefits of different methods of extracting valuable metals

CFA stacking can pose a serious threat to the environment and human health, as well as being a waste of resources. The extraction of valuable metals in CFA which has good environmental and economic benefits. Electrolysis is a cleaner method of extraction, and the use of wind and solar power to provide electricity makes the cost lower. It has good prospects for development. Biological methods also offer good environmental benefits, but have a long production cycle and should focus on the cultivation of more efficient bacteria in the future. Both chemical and extraction methods require secondary treatment of the extracted solution, which is more harmful and costly. Cleaner and more efficient additives are needed in the future.

4 Conclusions

CFA, a major solid waste generated by coal-fired power plants, poses a serious threat to the environment. The extraction of valuable metals can alleviate the resource crisis and environmental pollution. This study aims to introduce the basic physical and chemical properties of CFA, discuss its disposal policy, especially the recovery methods of valuable metals. Among the methods of CFA valence metals recovery, the precipitation method is more traditional and straightforward to operate but uses large quantities of strong acids and bases in the production process and requires high corrosion protection of the equipment. The extraction method offers high efficiency and easy product separation but involves a longer process and requires secondary treatment of the extracted solution. The electrolysis method, on the other hand, offers a clean, non-polluting, and cost-effective option, enabling the extraction of target elements from complex solutions. However, effective separation of target elements becomes challenging when their deposition potentials are similar. The biological method is also a method with good environmental benefits, but it has stringent system requirements and a long reaction cycle. It limits its industrial application. This study provides solutions to environmental problems that are important for the sustainable clean utilization of CFA and promoting a more sustainable future.

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Author contributions XZ: funding acquisition, project administration, review and editing. FJ: investigation, resources, methodology, software, visualization, formal analysis, validation, conceptualization, writing—original draft, formal analysis. RW: writing—original draft, formal analysis. SY: review and editing, project administration, supervision.

YS: data curation, validation, visualization, funding acquisition, review and editing.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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