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Review

Methodological Review of Methods and Technology for Utilization of Spent Carbon Cathode in Aluminum Electrolysis

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Abstract: Spent carbon cathode (SCC) is one of the major hazardous solid wastes generated during the overhaul of electrolysis cells in the aluminum production process. SCC is not only rich in carbon resources but also contains soluble fluoride and cyanide, which gives it both recycling value and significant leaching toxicity. In this study, we explore the properties, emissions, and disposal strategies for SCC. Pyrometallurgy involves processes such as vacuum distillation, molten salt roasting, and high-temperature roasting. Hydrometallurgy describes various methods used to separate valuable components from leachate and prepare products. Collaborative disposal plays a positive role in treating SCC alongside other solid wastes. High-value utilization provides an approach to make full use of high-purity carbon-based materials. Finally, we analyze and summarize future prospects for the disposal of SCC. This study aims to contribute to the large-scale treatment and resource utilization of SCC while promoting circular economy principles and green development initiatives.

Keywords: aluminum electrolysis; spent carbon cathode; detoxification; resource utilization

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1. Introduction

Aluminum constitutes 8% of the Earth's crust, making it the third most abundant element after oxygen and silicon [1]. Aluminum has many unique properties, including excellent electrical conductivity, thermal conductivity, ductility, high reflectivity, and corrosion resistance [2]. Statistics indicate that aluminum has become the second most consumed metal in China [3].

Currently, the production process of primary aluminum includes the refining of bauxite (Bayer process) and the electrochemical reduction of alumina (Hall–Héroult process). Solid wastes are inevitably generated in modern aluminum electrolysis production [4]. Spent carbon cathode (SCC) is one of the hazardous solid wastes generated during the aluminum production process. According to statistics [5–9], primary aluminum production generates 41.59 million tons, bringing about the discharge of 1.66 million tons of SCC. Most enterprises still resort to landfill or open-air stockpiling, causing severe soil, water, and air pollution, which adversely affects the health of humans, animals, and plants [10]. Consequently, SCC has been listed in the National Catalogue of Hazardous Wastes [11]. Thus, various methods have been tried to detoxify and purify SCC, such as pyrometallurgical and hydrometallurgical methods. Hydrometallurgy can effectively achieve selective separation and recover valuable components due to their differing physical properties (solubility, density, and surface properties). Pyrometallurgy promotes the removal of harmful substances from SCC and purifies the SCC at high temperatures, thereby converting it into high-value products [12,13].

With the advancement of national sustainable development strategies, it is a critical challenge to achieve the detoxification and resource utilization of SCC for the aluminum electrolysis industry. Based on extensive literature research, this review explores the resource properties and emission patterns of SCC. Secondly, it systematically reviews the resource disposal strategies for SCC, highlighting their advantages and limitations. Finally, it analyzes the challenges and prospects of SCC disposal. This review is expected to provide new insight into the large-scale disposal of SCC.

2. Spent Carbon Cathode from Aluminum Electrolysis

2.1. Emission Properties of SCC

The aluminum electrolytic cell is used as the reaction vessel during Hall–Héroult molten salt electrolysis, as shown in Figure 1a. In this process, high-melting-point Al_2O_3 (2045 °C) is dissolved by molten Na_3AlF_6 under a direct current. Additives such as CaF_2, AlF_3, NaF, and MgF_2 are added to lower the electrolysis temperature and improve the operational efficiency. The overall reaction is shown in Equation (1). In the production process of aluminum electrolysis, the damage of the cathode lining has become a common reason for the shutdown and major overhaul of electrolysis cells [14]. The cathode linings are composed of bottom carbon blocks, side carbon blocks, cathode paste, and refractory materials. They typically form a dense structure to contain the molten aluminum and electrolytes during the electrolysis process. The bottom cathode carbon blocks play an important role in impacting the cell's energy consumption and service life [15,16]. During the electrolysis process, the lining materials of the electrolytic cell are contacted with high-temperature molten aluminum and electrolytes. This allows substances such as cryolite, sodium fluoride, and aluminum fluoride to enter the cathode carbon blocks. The electrolytic cell is damaged due to the effects of the chemical reactions, the electrochemical actions, mechanical wear, and thermal shock [7,17,18]

$$2Al_2O_3(\text{dissolved}) + 3C(s) = 4Al(l) + 3CO_2(g) \tag{1}$$

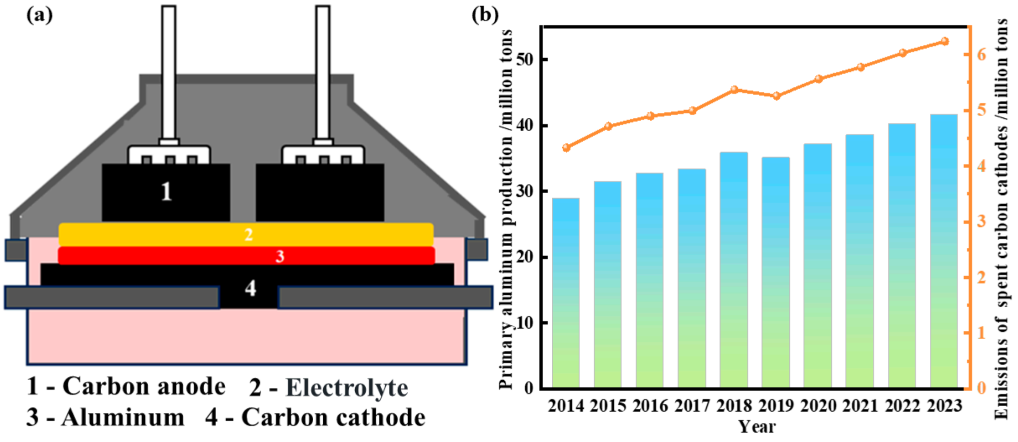

Figure 1. (**a**) Schematic diagram of an aluminum electrolysis cell [19]. (**b**) China's primary aluminum production and spent carbon cathode emissions from 2014 to 2023.

Therefore, aluminum electrolysis enterprises typically need to periodically (every 3–8 years) shut down the electrolytic cells for maintenance. This involves replacing the old cathode carbon blocks and lining materials with new ones. The removed cathode carbon blocks are referred to as spent carbon cathode [20–22]. With the development and application of new aluminum electrolysis technologies, the emission of spent cell linings per ton of aluminum has been reduced to 26 kg [23]. However, China's production capacity of aluminum electrolysis continues to increase and the quantity of spent cell linings generated continues to grow annually [24]. According to statistics, the production of 1 ton of primary aluminum generates approximately 10–15 kg of SCC [25,26]. The estimated production of primary aluminum and the emission of SCC in China from 2014 to 2023 are shown in Figure 1b (calculated based on an average discharge of 15 kg of SCC per ton of primary aluminum produced) [27]. The total production of primary aluminum and the emission of SCC in China reached 354.43 million tons and 5.32 million tons from 2014 to 2023. As a consequence, the safe disposal and resource utilization of SCC restricts the green and sustainable development of the aluminum electrolysis industry.

2.2. Resource and Environmental Properties of SCC

The cathode carbon blocks are typically made of electrically calcined anthracite, calcined petroleum coke, and modified pitch. They are prepared through processes such as mixing, forming, baking, mechanical processing, and high-temperature graphitization [28]. During the electrolysis process, the carbon blocks are continuously eroded by electrolytes, metallic sodium, and molten aluminum. The main phases and the elemental composition of the SCC are shown in Figure 2. These blocks contain a large amount of high-quality graphite carbon resources (40–70%), and a significant quantity of soluble fluorides, aluminum compounds, cyanides, and aluminosilicates [29].

Research indicates [27] that the catalytic effects of high temperature and electrolytes significantly enhance the graphitization degree of electrically calcined anthracite. The SCC has a graphitization degree as high as 80–90%, making it a highly valuable secondary resource for recycling [30]. In addition, a small portion of the fluorides in SCC can form complex phases under high-temperature and electrochemical conditions. The majority of the fluorides keep their complete crystal structure and stable phases, which can be directly returned to the electrolysis cells as raw materials for reuse. The soluble fluorides (Na_3AlF_6, NaF, and CaF_2) present in the SCC have different physical and chemical properties, meeting the requirements for detoxification disposal and graded recycling. Simultaneously, as essential raw materials for aluminum electrolysis production, the procurement prices of NaF, Na_3AlF_6, and CaF_2, are 4500–5500 RMB/ton, 5500–6500 RMB/ton, and 1500–2500 RMB/ton, respectively. Therefore, the resource recovery and recycling of SCC can alleviate the dual pressures of environmental protection and cost for the aluminum electrolysis industry.

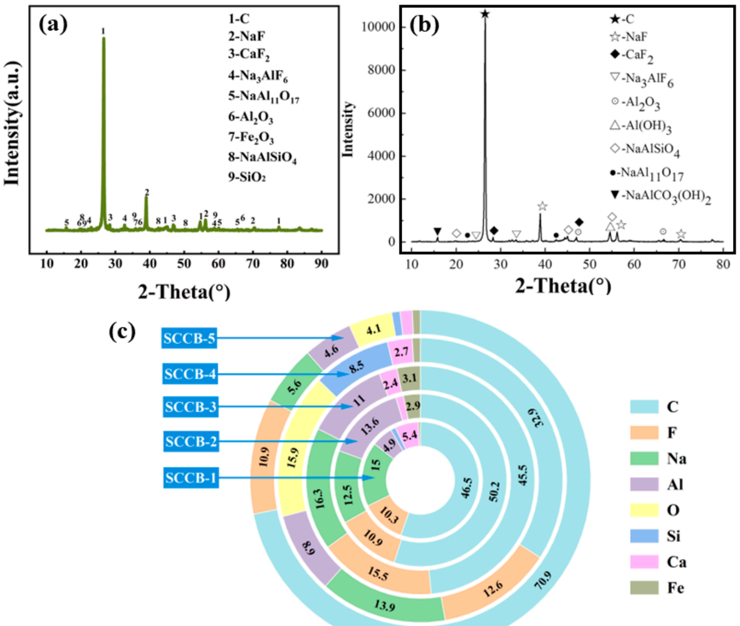

Figure 2. (**a**,**b**) Phase composition [31,32]. (**c**) Elemental composition of SCC under different environmental conditions [7,33–35].

SCC contains complex inorganic salt compositions, including fluorides (NaF, Na_3AlF_6, and CaF_2), cyanides (NaCN, $Na_3Fe(CN)_6$, and $Na_4Fe(CN)_6$), aluminum compounds (Al_2O_3, Al_4C_3, AlN, and $NaAl_{11}O_{17}$), and aluminosilicates (Al_2SiO_5, $NaAlSiO_4$, and $NaAlSi_3O_8$) [36]. As illustrated in Figure 3, the highly soluble fluorides and cyanides can be transported to nearby soil, surface water, and groundwater by rainwater. The $Na_3Fe(CN)_6$, $Na_4Fe(CN)_6$, Al_4C_3, and AlN can react with water to produce toxic gases, causing the emissions of NH_3, HCN, and CH_4. The alkali metals and their compounds react with water to form alkali solutions, which seriously harm the growth of surrounding plants and pose health risks to humans [37–40]. Research indicates [39] that the concentrations of soluble F^- and CN^- in SCC are 2000–6000 mg/L and 10–40 mg/L. These are far higher than the limits set by the national standard (GB5085.3-2007 [41]) for solid waste [11]. In view of this, the National Hazardous Waste List (2021 Edition) explicitly classifies SCC generated from aluminum electrolytic cells as a toxic hazardous waste (code: 321-023-48).

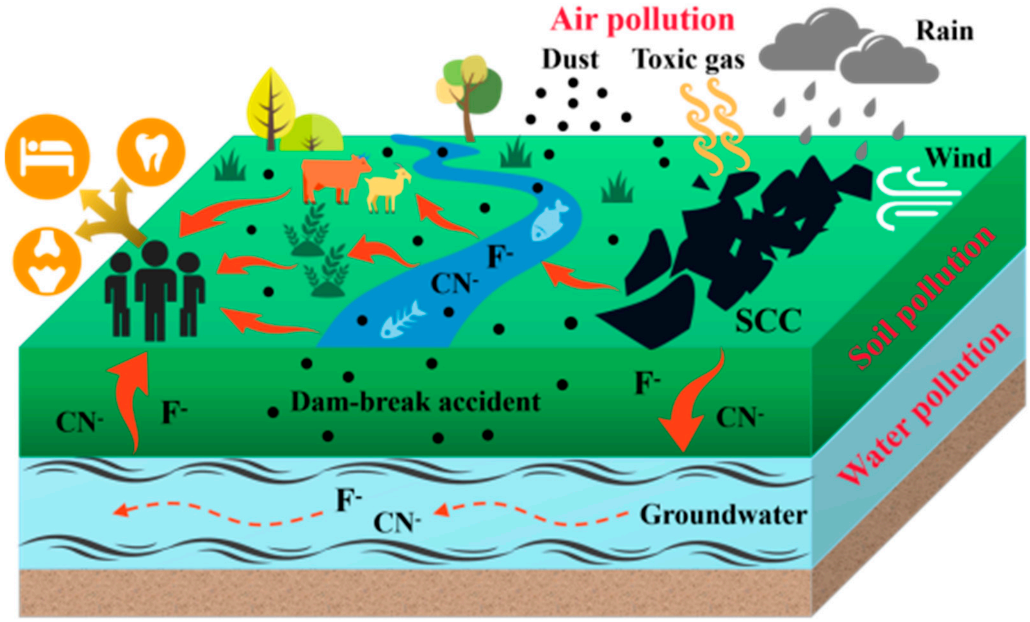

Figure 3. Environmental pollution pathways of SCC from aluminum electrolysis [42].

3. Disposal of SCC from Aluminum Electrolysis

Countries have gradually banned the landfill or open-air stockpiling disposal of SCC. Scholars and industry enterprises have conducted much related research. As shown in Figure 4, the main approaches can be categorized into hydrometallurgy, pyrometallurgy, collaborative disposal, and high-value utilization. Hydrometallurgy includes flotation, water leaching, and chemical leaching, while pyrometallurgy mainly includes vacuum distillation, molten salt roasting, and high-temperature roasting.

3.1. Hydrometallurgy

3.1.1. Flotation

The main principle of the flotation process is the hydrophobic difference between the carbon and electrolytes in the SCC. During the flotation process, carbon selectively accumulates on the solution's surface. Subsequently, bubbles are generated to separate the carbon from the electrolytes by adding additives (collectors, frothers, and inhibitors) [43–45]. The flotation process for disposing of SCC is shown in Figure 5a, mainly including crushing, screening, flotation, and filtration.

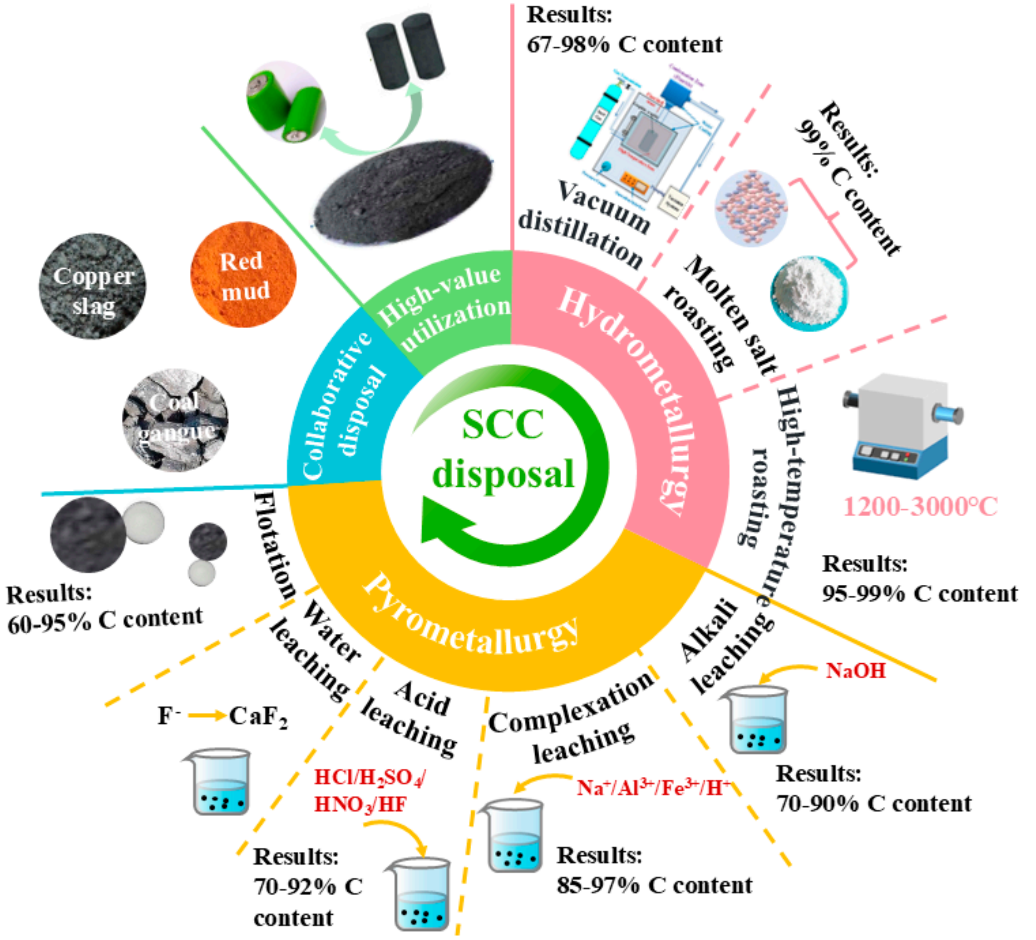

Figure 4. Disposal methods for SCC.

Li et al. [46] used the flotation process to separate the carbon from the SCC. They established a closed-circuit flotation process which achieved purities of 82.3% for the recovered carbon and 93.2% for the electrolytes. Angelopoulos et al. [47] explored froth flotation to recover valuable components from the SCC. The SCC was pre-treated with a H_2O_2 and NaOH solution to leach out the fluorides and cyanides. Besides, a methyl isobutyl carbinol (MIBC) frother and a Na_2SiO_3 solution were added during the flotation process to achieve the separation of the carbon and electrolytes. The purity of the recovered carbon was improved by 3.3% after flotation. Liu et al. [48] pretreated the SCC with a NaOH solution to remove the fluorides and ferrocyanides. The contents of the recovered carbon powder and electrolytes reached as high as 95.21 wt.% and 95 wt.%, respectively. Based on the above literature, it is obvious that the impact of the flotation reagents on the separation effect was in the order of frother < inhibitor < collector [49].

The summary of different flotation methods for treating SCC are shown in Table 1. The flotation method offers technical advantages such as a simple process, a large treatment capacity per unit time, and low processing costs. However, the purity of the recovered graphite carbon is generally low, limiting the comprehensive utilization of the recovery products. Additionally, the flotation medium produced contains various fluorides and highly toxic cyanides, posing a serious risk of secondary pollution.

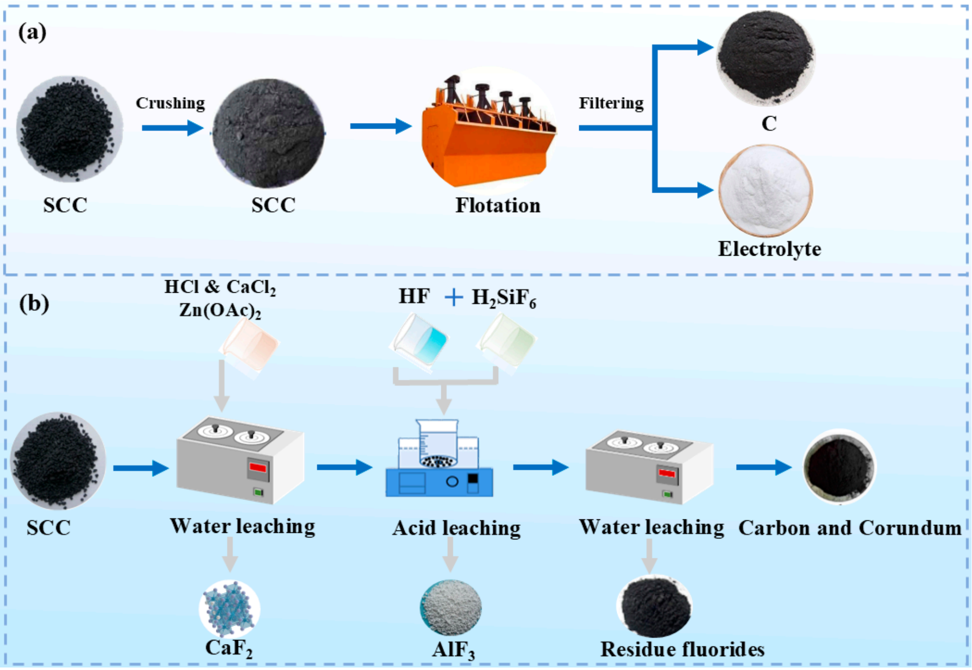

Figure 5. (**a**) Process of flotation for disposing of SCC. (**b**) Two-stage acid-leaching process.

3.1.2. Water Leaching Method

Under optimal process conditions, with a raw material particle size of 0.075 mm to 0.096 mm, a liquid-to-solid ratio of 55:1 mL/g, and a reaction temperature of 85 °C, the soluble fluoride concentration in the leachate was 45 mg/L which could be converted to CaF_2 by adding $CaCl_2$ [50]. Studies on the leaching behavior of soluble fluorides revealed that temperature controls the thermal motion of molecules. As the temperature increased, the thermal motion of molecules intensified, promoting the leaching of soluble fluorides from the SCC. The leaching process was controlled by internal diffusion (Ea = 8.79 kJ/mol) [51]. Above all, on the one hand, the water leaching method has the merits of a simple process, a low cost, and the effective fixation of fluorides. On the other hand, it wastes the graphite carbon and fluorides in the SCC, producing low resource utilization.

3.1.3. Chemical Leaching Method

Chemical leaching utilizes the appropriate chemical reagents to regulate the complex mineral phases, mainly consisting of alkali leaching, acid leaching, and combined alkali–acid leaching.

The acid-leaching method is effective for recovering valuable components from SCC. The main reactions occurring are as follows:

$$NaAl_{11}O_{17} + 34HCl = NaCl + 11AlCl_3 + 17H_2O \tag{2}$$

$$CaF_2 + 2HCl = CaCl_2 + 2HF\uparrow \tag{3}$$

Under the optimal conditions of a liquid–solid ratio of 25 mL/g, temperature of 140 °C, leaching time of 270 min, and hydrochloric acid concentration of 4 mol/L, the purity of the recovered carbon material was 97.3%. By adjusting the pH of the filtrate and evaporation crystallization, calcium fluoride, cryolite, and sodium chloride products were obtained [52,53]. Figure 6a–h show the comparison of the SCC before and after acid leaching treatment. After acid leaching, the carbon content significantly increased and the content of electrolyte components significantly decreased. The microstructure tended to become smoother. However, the recovered carbon powder contained small amounts of corrosive fluorine and aluminum. Figure 6i–k illustrate the obtained calcium fluoride, cryolite, and sodium chloride products. The XRD patterns indicated that the synthesized calcium fluoride, cryolite, and sodium chloride exhibited a high degree of crystallization and were suitable for direct application.

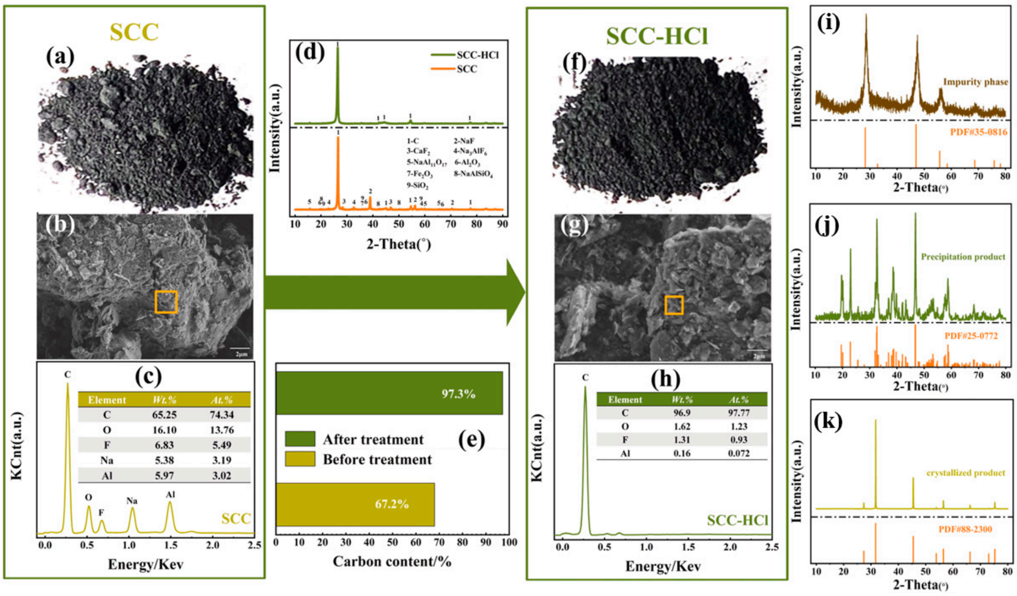

Figure 6. (**a**–**h**) Comparison of SCC before and after acid-leaching treatment; (**i**) calcium fluoride; (**j**) cryolite; and (**k**) sodium chloride [52].

Figure 5b shows the two-stage acid-leaching process. Firstly, it removed the soluble fluorides by way of water leaching and obtained CaF_2 through adding $CaCl_2$ to the leachate solution. Then, the two acid-leaching stages were designed to solubilize Al species. Hydrofluoric acid (HF) can react with hydroxides, aluminum oxides, and silicates, converting them into a solution. Subsequently, adding silicate removed cryolite and allowed for the recovery of AlF_3 products. Finally, the carbon and residue fluorides were separated after water leaching and filtration [54]. Introducing Al^{3+} during the acid-leaching process can promote the dissolution of fluorides [55–57]. Lisbona et al. [57] used an aqueous $HNO_3/Al(NO_3)_3 \cdot 9H_2O$ solution to treat SCC. Through simulation calculations and experimental verification, they found that the leaching rate of fluorine reached as high as 96.3%. What is more, the fluorine mainly existed in the forms of AlF^{2+} and $AlF_2^{\ +}$ in the leaching solution. These were the key ions controlling the dissolution of calcium fluoride and cryolite.

Acid leaching can effectively dissolve the insoluble components and obtain high-purity graphite carbon. However, the leaching process carries risks such as the release of harmful gases (HF and HCN), high impurity content in the leachate, and the secondary treatment of waste acid. Multistage acid leaching improves the leaching rate and increases the complexity of the process and the large amounts of acid waste liquid. In light of the preceding analysis, acid-leaching disposal strategies for SCC should focus on the treatment of acid waste liquid, the simplification of the process, and the management of harmful gases in the future.

Alkali solutions can convert insoluble compounds in SCC into soluble substances. The reactions occurring are as follows [57–59]:

$$Al_2O_3 + 2NaOH + 3H_2O = 2NaAl(OH)_4 \tag{4}$$

$$Na_3AlF_6 + 4NaOH = NaAl(OH)_4 + 6NaF \tag{5}$$

$$AlF_3 + 4NaOH = 3NaF + NaAlO_2 + H_2O \tag{6}$$

$$CaF_2 + 2NaOH = 2NaF + Ca(OH)_2 \tag{7}$$

$$Al(OH)_3 + NaOH = NaAl(OH)_4 \tag{8}$$

Under high-pressure alkali-leaching conditions, the leaching concentration of F^- decreased to 22.19 mg/L, and the recovered carbon content increased from 60.02% to 88.63% [60]. Ultrasonic-assisted leaching has a strong penetrating ability. It can efficiently promote the separation of non-carbon impurities from the carbon matrix and shorten reaction time [61,62]. Figure 7a shows a schematic diagram of ultrasonic cavitation bubbles acting on carbon materials. Under the influence of ultrasound, the liquid–solid interface undergoes impact, stripping, and erosion, which is difficult to achieve by mechanical stirring. This allows for a more thorough and rapid separation of inorganic salt impurities from the SCC.

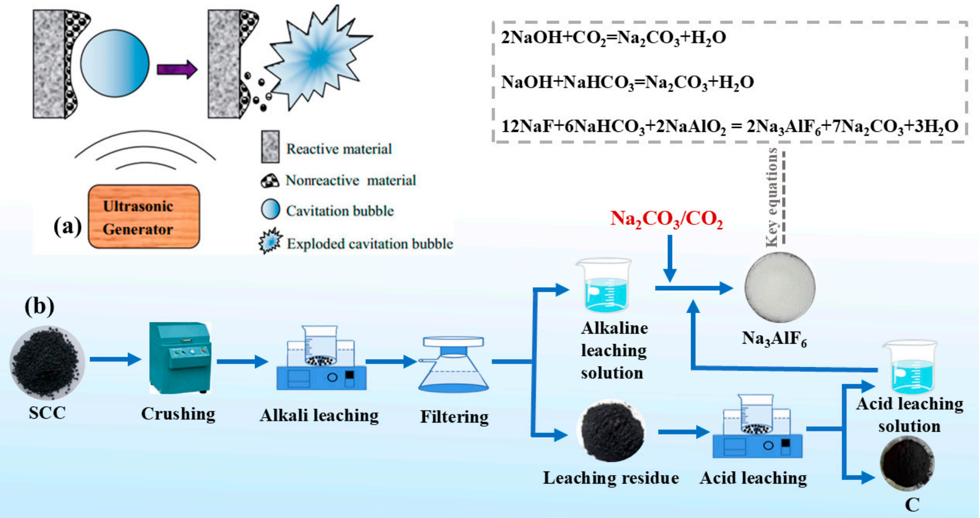

Figure 7. (**a**) Schematic diagram of ultrasonic cavitation bubbles acting on carbon materials [32]. (**b**) Process of the combined alkali–acid leaching method.

Table 1. Different flotations for SCC disposal.

Methods	Reagents	Recovered Products/%	Merits	Defects	References
Flotation	Kerosene gasoline; cetylpyridinium bromide; kerosene.	Carbon content: 82.3, electrolyte purity: 93.2; Carbon content: 90, electrolyte purity: 95; Carbon content: 80.67.	Simple process, low cost, high efficiency, achieves preliminary recovery of graphite carbon and electrolytes.	Low content of recovered carbon, produces waste water and harmful gas.	[46] [63] [49]
Alkali flotation	Kerosene Diesel	Carbon content: 85.6, electrolyte purity: 85.1. Carbon content: 95.21, electrolyte purity: 95 CaF_2: 94.96.	High efficiency, recycling of flotation waste water, achieves separation of aluminosilicates and safe disposal of toxic substances.	Complex process, low purity of recovered carbon, secondary pollution risk exists.	[47] [48]

The alkali leaching method can dissolve insoluble fluorides and prevent the volatilization and release of cyanides, yet the recovery grade is low. Ultrasonic-assisted alkali leaching can effectively shorten the leaching time but increases energy consumption.

Combined leaching has been widely applied in hydrometallurgy. The process of the combined alkali–acid leaching method for treating SCC is depicted in Figure 7b. The process can synthesize Na_3AlF_6 by adding Na_2CO_3/CO_2 to the acid–alkali leaching solution; the key equations can be seen in Figure 7b. Shi et al. [64] achieved a graphite carbon recovery purity of 96.4% through NaOH-HCl leaching. Additionally, they recovered 95.6% of the Na_3AlF_6 products by controlling the precipitation conditions (pH = 9, 70 °C, 2 h).

The combined alkali–acid leaching method combines the merits of single acid–alkali solutions, which can effectively recover valuable components from the SCC and significantly reduce leaching toxicity [65]. However, the complex process, the low safety of reagents, toxic gases, and the strong alkali–acid environments limit its application.

Table 2 analyzes and summarizes the merits and defects of the chemical leaching methods for treating SCC. In summary, hydrometallurgy can effectively recover valuable components such as carbon, fluorine, and aluminum from the SCC. Moreover, the recovered carbon powder can be used as fuel and the electrolytes can produce cryolite and aluminum fluoride. In other words, the hydrometallurgy can effectively address the environmental hazards and resource recovery issues of SCC. In contrast, it not only produces a great number of complex acid and alkali waste liquids but also releases noxious gases during the operation.

Table 2. Chemical methods of SCC disposal.

Methods	Conditions	Recovered Product/%	Merits	Defects	References
Acid leaching	Liquid–solid ratio 25 mL/g, temperature 140 °C, time 270 min, and acid concentration 4 mol/L; Liquid–solid ratio 15 mL/g, temperature 60°C, time 120 min, and acid concentration 4 mol/L.	Carbon content: 97.3 CaF_2, NaCl Na_3AlF_6; Carbon content–ash content < 1%.	Simple operation; large processing capacity; mild processing conditions; high grade; high recovery rate; achieves recovery of graphite carbon and fluoride salts.	Releases toxic and harmful gases; prone to secondary pollution from slag; generates acid wastewater.	[52] [66]
Alkali leaching	Liquid–solid ratio 5.5 mL/g, temperature 100 °C, time 3 h; Alkali concentration 1.5mol/L, temperature 200 °C, liquid–solid ratio 20 mL/g, time 8 h; Temperature 60 °C, time 60 min, liquid–solid ratio 5mL/g, ultrasonic power 300 W.	Carbon content: 84%; Carbon content: 88.63 Na_3AlF_6; Carbon content: 97.53 SiC; Carbon content: 80.	High processing capacity; no harmful gases; low cost; capable of directly producing high-value products (Na_3AlF_6).	Low recovery rate; produces secondary pollution residue; high energy consumption (ultrasonic-assisted alkali leaching).	[55] [60] [67] [68]
Combined leaching	NaOH 1.5 mol/L, $HClO_4$ 2.5 mol/L, liquid–solid ratio 2.5 mL/g, temperature 50 °C; Particle size 0.15 mm, temperature 80–85 °C, time 3 h, liquid–solid ratio 4:1, stirring rate 600 rpm, 500 g sodium hydroxide and 1000 mL concentrated hydrochloric acid; Acid leaching: leaching temperature 60 °C, liquid–solid ratio 5:1, initial acid concentration 3 mol/L, ultrasonic power 300 W, time 60 min; Temperature 60 °C, time 50 min, liquid–solid ratio 10 mL/g, alkali concentration 1 mol/L, particle size < 0.15 mm.	Carbon content: 96.4 NaF, CaF_2, NaCl, Na_3AlF_6; Carbon content: 94.39.	Simple operation; high resource-utilization efficiency; low energy consumption; minimal pollution; mature process.	Lengthy process; high cost; difficult treatment of generated acid and alkali waste liquids.	[69] [31]

3.2. Pyrometallurgy

Pyrometallurgy utilizes different saturated vapor pressure or boiling points of the complex inorganic salt systems within the SCC, promoting the desorption of fluorides and cyanides under high-temperature conditions.

3.2.1. Vacuum Distillation Method

In recent years, vacuum distillation technology has been widely used in solid waste treatment and metal smelting [70]. The principle of the vacuum distillation method is the volatility difference. The greater the volatility difference, the better the separation effect [65,71].

The temperature, time, and pressure were 1700 °C, 120 min, and 3000 Pa; the purity of the recovered graphite carbon reached 97.89%. The leaching concentrations of the soluble fluorides and cyanides reached 3.5 mg/L and $\leq$0.025 mg/L, respectively [72]. As displayed in Figure 8, the electrolytes formed white particles that adhered to the surface of the carbon blocks. It can volatilize in a gaseous form under suitable temperature and vacuum pressure, yet the thermodynamic analysis revealed that the volatilization temperature of CaF_2 was much higher than that of NaF, AlF_3, Na_3AlF_6, and KF. Under low-pressure and high-temperature vacuum conditions, the fluorides generally transitioned directly from solid to gas. The Na_3AlF_6 decomposed into NaF and AlF_3. They subsequently transformed back into solid Na_3AlF_6 through condensation [72]. In a word, the temperature and vacuum pressure were key factors affecting the separation efficiency of the carbon and electrolytes.

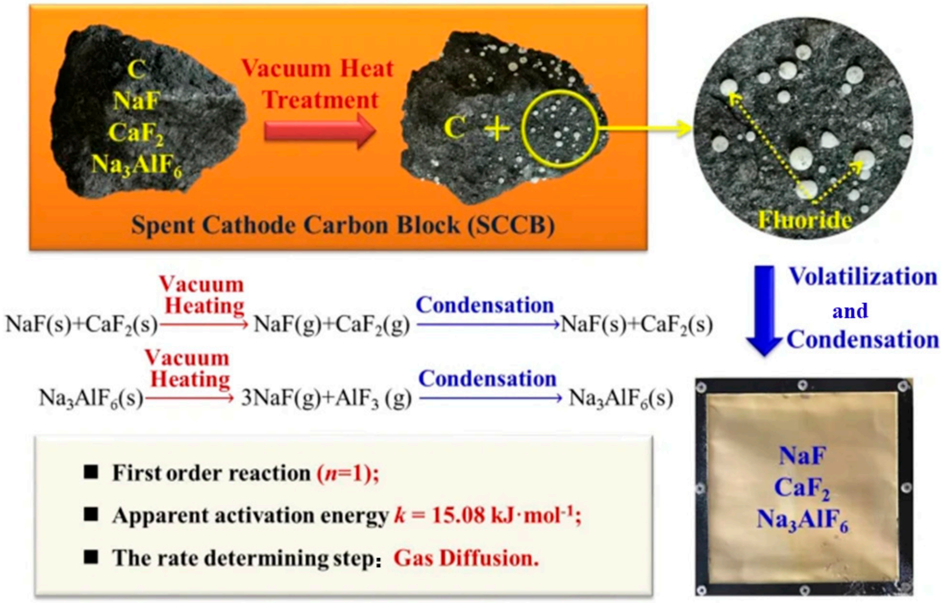

Figure 8. Separation process of carbon and electrolytes [72].

3.2.2. Molten Salt Roasting Method

Molten salt roasting technology matches the characteristics of various inorganic salts. This technology has been widely applied to difficult-to-treat minerals and solid waste [73,74]. Figure 9a shows the process of the molten salt roasting method for treating SCC. It utilizes the high reactivity, decomposition characteristics, and mild corrosiveness of Na_2CO_3. Firstly, the SCC, NaOH, and Na_2CO_3 were activated and mixed with the mechanical activation conditions of a rotating speed of 250 rpm, a ball-to-material mass ratio of 6:1, and an activation time of 4 h. Then the mixture was roasted at 900 °C. Finally, based on the solution equilibrium calculations and the principle of carbonation decomposition, high-concentration CO_2/CO roasting flue gas was used to prepare Na_3AlF_6 from the leachate. It simultaneously achieved the dissociation of toxic substances, recovery of valuable components, harmless utilization of flue gas, and recycling of reaction reagents [75].

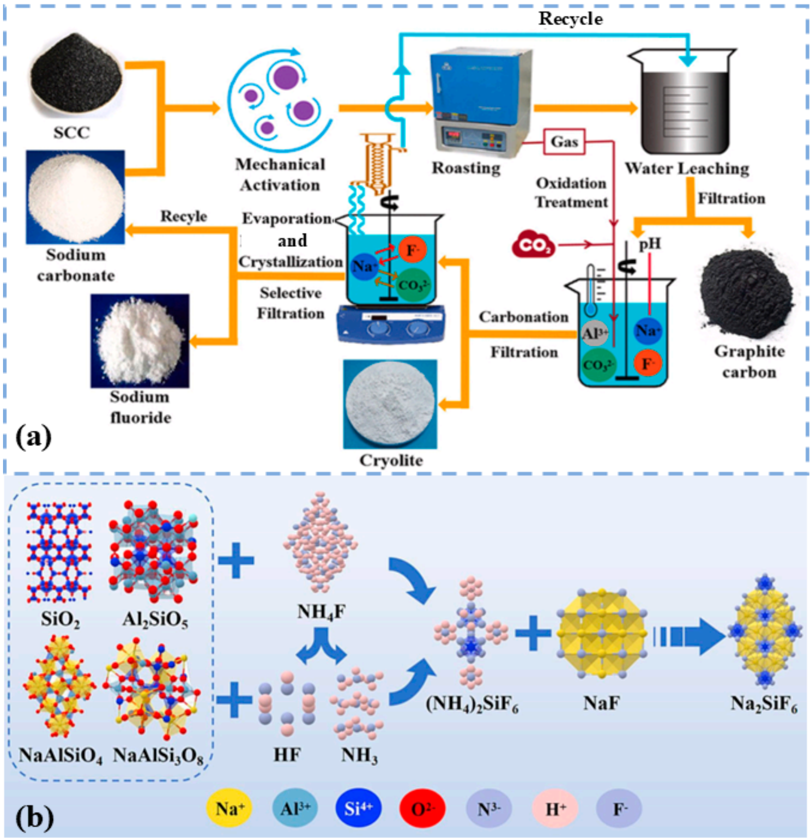

Figure 9. (**a**) Molten salt roasting method for separating toxic substances and recovering valuable components from SCC [75]. (**b**) Deep separation mechanism of insoluble aluminosilicates during low-temperature roasting [76].

Although the abovementioned method effectively dissociated insoluble aluminosilicates, the Na_2CO_3 (851 °C) necessitates heating the process to 900–950 °C. Therefore, Yao et al. [76] further developed a low-melting-point molten salt system (NH_4F). Combined with a leaching process, this method achieved a high carbon content (99.52%) and low fluoride-ion leaching concentration (7.6 mg/L). The recovered carbon can partially replace calcined petroleum coke for the production of carbon anodes in aluminum electrolysis. Figure 9b illustrates the deep separation mechanism of insoluble aluminosilicates. Studies have shown that the separation mechanism can be divided into two types. The first type involved the direct solid–solid or solid–liquid reaction of insoluble aluminosilicates in the SCC with NH_4F. The second type involved the preferential decomposition of NH_4F at 250 °C into HF and NH_3. This changed the reaction pathway of insoluble aluminosilicates from the liquid–solid reaction to the gas–solid reaction, ultimately converting them into soluble Na_2SiF_6 at 250 °C.

3.2.3. High-Temperature Roasting Method

Fluorides and cyanides can decompose at high temperatures. In an inert atmosphere, carbon will not combust [77]. Under optimal conditions with a particle size of 10 mm, temperature of 1499 °C, and holding time of 3.33 h, the fluorine removal rate was 88%.

The defluorination rate can be significantly improved by increasing the roasting temperature and extending the roasting duration. The recovered carbon material attained 100% purity and exhibited a high degree of graphitization, smaller interlayer spacing, and a small amount of graphene structure with the temperature of 2600 °C [78,79]. During microwave-assisted heating, the thermal stress generated by the difference in microwave absorption between the graphite carbon and fluorides broke the carbon block and enhanced the melting and removal of fluorides, increasing the degree of fragmentation and interlayer spacing of the SCC matrix [80].

Table 3 shows the summary of pyrometallurgical disposal methods for SCC. Pyrometallurgical methods offer technical advantages such as a simple process, high processing efficiency, and large treatment capacity per unit time. Unfortunately, they cause significant energy consumption and considerable carbon emissions due to the high temperature. Moreover, the equipment involving vacuum and microwave functions is expensive. Additionally, the fluorine-containing flue gases generated are highly corrosive to the high-temperature equipment.

Table 3. Summary of analysis of pyrometallurgy for SCC.

Methods	Conditions	Recovered Product/%	Merits	Defects	References
Vacuum distillation	Particle size, 3–5 mm, temperature 1700 °C, time 2 h, pressure 3000 pa;	Carbon content: 97.89;	Recovery and utilization of graphite carbon, efficient separation of electrolyte components.	Low purity, high energy consumption, high equipment investment costs, generates highly corrosive fluorine-containing exhaust gases.	[72]
	Particle size < 2 cm, temperature 1200 °C, air pressure <10 pa, time 1.5 h;	Carbon content: 91.2;			[81]
	Temperature 700 °C, time 90 min, pressure 60 pa;	Carbon content: 67.08;			[65]
	Particle size 1–3 mm, temperature 1000 °C, time 2 h, pressure 10 pa.	Carbon content: 89.89.			[82]
Molten salt roasting	Milling speed 250 rpm, ball-to-material mass ratio 6:1, milling time:4 h, NaOH-to-Na_2CO_3 ratio: 1:4;	Carbon content: 96.98 Na_3AlF_6, NaF;	Selects valuable materials for separation, low energy consumption, low calcination temperatures.	Produces waste liquid, causes equipment corrosion.	[75]
	Mixed alkali to SPL ratio: 1:1, temperature 900 °C, time 3 h, particle size < 0.15 mm, NH_4F-to SCC mass ratio 2:1, roasting temperature 250 °C, time 1 h, heating time 50 min, leaching temperature of 60 °C, leaching time 60 min, liquid–solid ratio 28:1, stirring rate 1200 rpm.	Carbon content: 99.52.			[76]
High-temperature roasting	Temperature 2600 °C, time 0.5 h; Temperature 1400 °C, time 2 h;	Carbon content: 100; Carbon content: 93.7;	Simple process, achieves the recovery and high-value utilization of graphite carbon, efficient separation of non-carbon impurities.	High energy consumption, high equipment investment costs, generates highly corrosive fluorine-containing flue gas, does not recover electrolyte components.	[78,79]
	Temperature 1600 °C, time 1 h, particle size < 0.074 mm.	Carbon content: 97.22.			[35]

3.3. Collaborative Disposal

In recent years, many researchers have focused on exploring the resource-interaction properties of SCC with other industrial solid wastes. Collaborative disposal integrates the characteristics of two or more types of waste to achieve detoxification and resource recovery.

3.3.1. Red Mud

Red mud is a large-scale solid waste discharged from the alumina industry. Its main components are alumina, silica, iron oxide, sodium oxide, calcium oxide, and titanium oxide [83–85]. The carbon in SCC can convert weakly-magnetic iron-based particles into magnetite or metallic iron [86]. Lu et al. [87] used a reduction roasting–magnetic separation method to co-treat SCC and red mud. The recovery rates reached 83.12% for the Na_2O, 91.80% for the Al_2O_3, and 65.30% for the metallic Fe in red mud. The fluorides in the SCC entered the residue.

Xie et al. [88] pretreated red mud using an alkali fusion–water leaching process for the synthesis of 4A zeolite. As a result, the temperature, time, and SCC addition were 900 °C, 4 h, and 7%, and the Fe recovery efficiency from red mud reached 88.84%. Furthermore, the fluorides in the SCC were converted into $CaF_2/Ca_4Si_2F_2O_7$. The Ca, SiO_2, and Al_2O_3 compounds in the red mud significantly enhanced the conversion efficiency of the NaF/Na_3AlF_6 to CaF_2 [89].

3.3.2. Copper Slag

Copper slag is a type of non-ferrous metallurgical slag generated during the copper smelting process, containing valuable components such as Cu (0.5–5%) and Fe (40%). Approximately 2–3 tons of copper slag are produced for every ton of copper [90,91]. Using the SCC as a reducing agent, the recovery rate of the copper reached 98.24% and the soluble fluoride concentration was only 4.32 mg/L. Additionally, the fluorine-containing components (CaF_2 and NaF) in the SCC can reduce slag viscosity and promote the enrichment and settling of matte–copper [92].

Electroplating sludge is mainly composed of metal hydroxides and contains metals such as Cr, Ni, Cu, Zn, Fe, and Ca [93]. Yu et al. [92] conducted a collaborative disposal of electroplating sludge, SCC, and copper slag. Figure 10 illustrates the migration and transformation pathways of valuable metals during the collaborative disposal process. The presence of Fe in the copper slag and F in the SCC collectively enhanced the recovery of Cr. With optimal process parameters, the recovery rates for the Cr, Ni, and Cu reached 75.56%, 98.41%, and 99.25%, respectively.

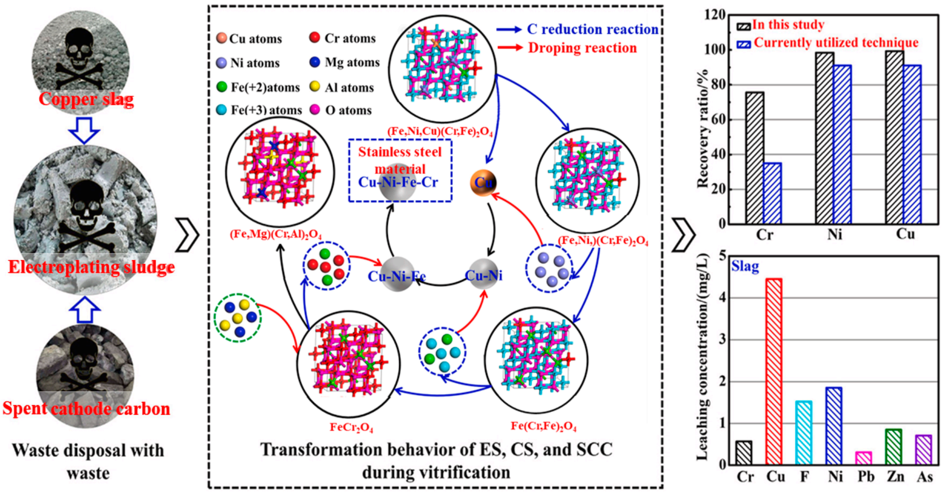

Figure 10. Migration and transformation pathways of valuable metals during the collaborative disposal of electroplating sludge, SCC, and copper slag [92].

3.3.3. Coal Gangue

Coal gangue is a complex industrial solid waste discharged during the mining and washing of coal [94,95]. It consists of kaolinite, SiO_2, Al_2O_3, and small amounts of alkali metal oxides [96,97]. Silicon carbide is known for its high thermal conductivity, high wear resistance, and high chemical stability. It is typically produced using the carbothermal reduction method [98]. Xiao et al. [99] used a hydrothermal acid-leaching method to achieve the separation of different components in SCC. The impurity elements such as Al, F, and Fe entered the solution, while carbon and silicon were retained in the filter residue. In addition, they synthesized silicon carbide products with a median particle size of 18.15 μm through the carbothermal reduction method (1600 °C, 5 h). Fibrous silicon carbide can be obtained under the conditions of 1550 °C, a C/Si ratio of 3:1, and a time of 3 h [100]. Although it is feasible to use carbon-rich solid waste and coal gangue to prepare SiC, the high processing temperature and low economic benefits are significant drawbacks.

Table 4 presents a summary of the collaborative disposal methods for SCC. Based on the strong reducing properties/high energy density of graphite carbon, this approach can achieve the comprehensive recovery of some valuable components and the safe disposal of toxic substances simultaneously. Nevertheless, this method fails to fully exploit the economic utilization value of SCC due to the low-value use of graphite carbon as fuel or a reducing agent. Moreover, the cross-regional transportation of hazardous waste causes secondary pollution risks.

Table 4. Summary of analysis of the collaborative disposal methods for SCC.

Solid Waste	Principles	Merits	Defects	References
Red mud	$C + Fe_2O_3 \rightarrow Fe$; $F^- + CaO/SiO_2 \rightarrow CaF_2/Ca_4Si_2F_2O_7$; $F + CaO/SiO_2 \rightarrow CaF_2/Ca_4Si_2F_2O_7$ $CN^- + O_2 \rightarrow N_2 + CO_2$.	Simple process, comprehensive utilization of graphite carbon, stable solidification of fluorides, safe disposal of certain toxic substances.	Low fluoride fixation rate, release of HF/CO_2 gas, low utilization value of residues.	[87] [88] [89]
Copper slag	$C + (Cu,Fe,Ni)(Fe,Cr)_2O_4 \rightarrow Cu\text{-}Ni\text{-}Fe\text{-}Cr$ $F^- + CaO \rightarrow CaF_2$; $C + Cu_2O/CoO/Fe_3O_4 \rightarrow Cu/Co\text{-}Fe$ $F^- + CaO \rightarrow CaF_2$ $CN^- \rightarrow N_2 + CO_2$.	Simple process, recovery of Cu/Ni/Fe/Cr/Co, achieves safe disposal of toxic substances and comprehensive utilization of graphite carbon.	Emission of HF gas, wastage of fluoride salt resources, low residual utilization value.	[101] [102]
Coal gangue	$F^- + H^+ \rightarrow HF$ $HF + Al_2Si_2O_5(OH)_4 \rightarrow AlF_3 + 2H_2SiF_6$ $C + SiO_2 \rightarrow SiC$.	Simple process, achieves resourceful utilization of graphite carbon, fluoride salts, and aluminum–silicon components.	Produces HCN gas, acid leaching wastewater, secondary pollution exists.	[99]
Textile dyeing sludge	$C + O_2 \rightarrow CO_2$ $F^- + CaO \rightarrow CaF_2$ $CN^- + O_2 \rightarrow N_2 + CO_2$.	Simple process, achieves comprehensive utilization of graphite carbon and safe disposal of some toxic substances.	Emission of $HCN/NH_3/HF/CO_2$ gases, waste of fluoride salt resources, low residue utilization value.	[6]

3.4. High-Value Utilization

Graphite is used in battery materials due to its high conductivity and low potential [79,103–106]. The recovered carbon materials from the SCC with high graphitization become a potential anode material. High temperatures further increased the amount of graphene and significantly enhanced the degree of graphitization of the SCC. After water leaching and ultra-high-temperature treatment (2600 °C), the carbon content of the SCC reached 100%, which had unique structural characteristics such as small defect structures, slight expansion structures, and a small amount of graphene structure. It meant that it could be used as graphite material in batteries for providing more active sites for the migration of Li^+. Electrochemical tests showed that the reversible capacity was 460.1 mAh/g after 50 cycles at 0.1 C [78,79]. Zhou et al. [107] used the recovered carbon material with a purity of 94.63% to prepare anode materials for lithium-ion batteries. The initial charge capacities were 195.4 and 490.0 mAh/g, with coulombic efficiencies of 78.9% and 67.8%, respectively. It offered alternative materials resembling graphite, which would decrease the reliance on artificial graphite and lower costs, while also demonstrating significant economic value.

Yao et al. [75] used the recovered carbon material obtained from molten salt roasting to prepare carbon anodes for aluminum electrolysis. The performance of the blended carbon anodes is shown in Figure 11. As exhibited in Figure 11, when the graphite carbon material blending ratio was 2 wt.%, the ash content, bulk density, resistivity, compressive strength, CO_2 and air loss rates of blended carbon anodes were 0.64 wt.%, 1.56 g·cm^{-3}, 76.78 μΩ·m, 27.34 MPa, 10.05 wt.%, and 30.46 wt.%, respectively. It performed better than the carbon anodes made entirely from petroleum coke. This indicated that SCC had the potential to be used as raw materials for the production of aluminum electrolysis carbon anodes.

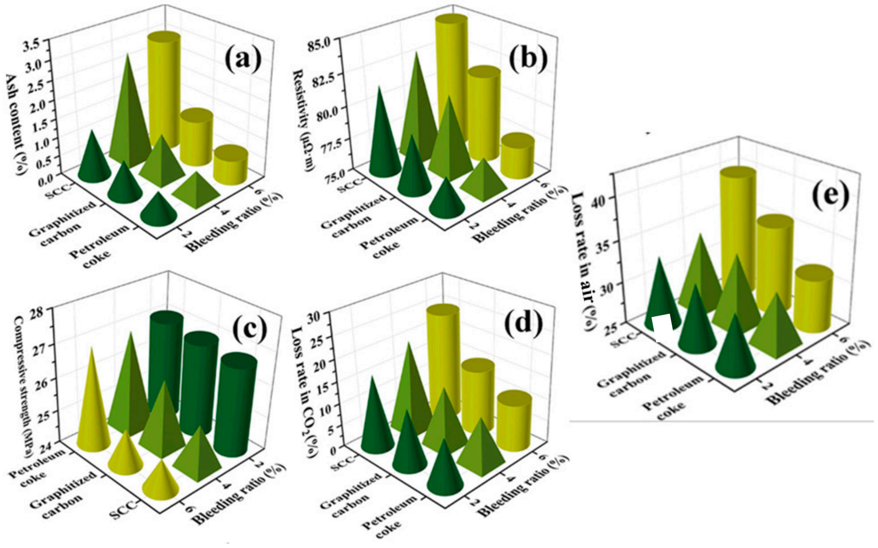

Figure 11. The performance of the blended carbon anodes. (**a**) ash content, (**b**) resistivity, (**c**) compression strength, (**d**) loss rate in CO_2, and (**e**) loss rate in air. [75].

Table 5 shows the summary of the technical characteristics of the high-value utilization of SCC. Currently, the high-value utilization of recovered carbon materials focuses on the preparation of battery materials and carbon anodes for aluminum electrolysis. This approach achieves the detoxification and resource recovery of SCC, and significantly reduces the consumption of raw materials (petroleum coke and artificial graphite), offering an innovative method for achieving the sustainable recycling of hazardous-waste containing carbon in the aluminum electrolysis industry.

Table 5. Summary of analysis of high-value utilization methods for SCC.

Application Areas	Resource Properties	Merits	Defects	References
Lithium-ion Batteries	Rich graphite carbon structure.	High economic value, excellent product performance.	Complex process, high cost.	[78,79]
Carbon anode	Low electrical resistance, high density, and high strength of graphite carbon.	Simple process, easy operation, saves processing costs, achieves recycling of graphite carbon and fluoride salt.	Lacks theoretical guidance for blending, no consideration of fluoride precipitation during prebaked anode baking, corrosion on equipment.	[75]

3.5. Comparison of Different Disposal Methods

The hydrometallurgical process for treating SCC can be divided into the physical and chemical leaching methods. Flotation is a mature process that does not use acid–base reagents and has been successfully applied to the industrial disposal of SCC. While ultrasonic-assisted chemical leaching can enhance the leaching rate, it is costly and has limited scalability for large-scale industrial applications. The alkali–acid combined leaching method is suitable for small- to medium-sized raw materials with complex compositions, efficiently recovering valuable components from the SCC. However, this method generates substantial amounts of complex acid and alkali wastewater, with the potential release of harmful gases (HF, HCN, and NH_3) during the leaching process. In summary, although hydrometallurgy has the advantage of low energy consumption, it produces significant wastewater due to the use of chemical reagents. The treatment cost is closely related to the treatment of chemical reagents and waste liquid, limiting its large-scale application due to secondary pollution and secondary wastewater. Currently, the secondary wastewater was treated by adding reagents such as $CaCl_2$, Na_2CO_3, and CO_2, which can recover F and Al from the wastewater and achieve harmlessness.

The pyrometallurgical process is well-suited for raw materials with large particle sizes and high carbon content. However, it incurs high energy consumption, high investment cost for equipment with high-temperature and vacuum conditions, and low processing capacity. Moreover, the high-temperature process generates harmful flue gases, leading to secondary pollution and necessitating a flue-gas purification system. The molten salt roasting method breaks the limitations of traditional pyrometallurgy, and the low-temperature molten salt system significantly reduces energy consumption and pollution risks, offering a new direction for the recycling of SCC. The industrialization of pyrometallurgy is still under exploration.

Collaborative disposal maximizes the resource potential of SCC and other waste materials, effectively mitigating resource wastage. At the same time, it lowers the disposal costs of hazardous waste, eliminates environmental risks, and enables the recovery of valuable components, thus providing both environmental and economic advantages. Nevertheless, the proportion of the SCC used in collaborative disposal is currently limited to 4%–15%, resulting in a low utilization rate and remaining at the experimental stage. Therefore, a process for large-capacity collaborative disposal of SCC with other wastes should be explored.

The aim of high-value utilization is to employ the carbon materials with high carbon content and high graphitization degree obtained after SCC purification to produce high-value products, which can enhance economic benefits. The recovered carbon materials have been utilized in the preparation of batteries and carbon anodes for aluminum electrolysis, demonstrating satisfactory performance. However, industrialization has not yet been achieved due to the technical challenges and significant investment required by this technology. Therefore, it is essential to continuously explore efficient conversion processes in order to facilitate the realization of high-value utilization of SCC.

4. Conclusions and Perspectives

SCC is one of the primary solid wastes discharged during the major overhaul of aluminum electrolysis cells. SCC contains significant resource properties and leaching toxicity. Landfill or open-air stockpiling result in substantial resource waste and severe environmental pollution. If the valuable components within SCC can be effectively utilized, it will become a fortune. This paper presents the resource and environmental properties, emission patterns, and disposal strategies for SCC. Additionally, it provides an in-depth introduction to the principles and research progress, as well as the advantages and disadvantages of various treatment methods. The main conclusions of this review are listed as follows:

Hydrometallurgy exploits the differences in the physical and chemical properties of the various components in SCC, thereby achieving the separation and purification of carbon and electrolytes from SCC by using water or chemical reagent leaching processes. It not only not only yields high-carbon-content materials but also produces Na_3AlF_6, CaF_2, and AlF_3 from the SCC. However, the leaching process generates complex acid and alkali waste liquids and harmful gases such as HF and HCN, leading to secondary pollution. The recovered products do not meet commercial-grade standards, and further feasibility studies are necessary to assess and optimize the process for industrialization.

Pyrometallurgy can decompose fluoride and cyanide because of the volatility difference in different components. It is currently the most effective method for the separation and purification of SCC. Although they yield high-purity recovery products with significant application value, the equipment required for high-temperature and vacuum operations leads to high costs. This process generates flue gases, limiting its application.

Collaborative disposal combines the properties of different solid wastes to realize detoxification and resource recycling. It has the potential to realize the large-scale disposal of hazardous waste containing carbon in aluminum electrolysis. High-value utilization significantly reduces the consumption of raw materials and performs high economic value in terms of recovered carbon. In contrast, mature processing technologies have not yet been developed, and further in-depth research is needed.

The disposal of hazardous carbon-containing waste in the aluminum electrolysis industry continues to face numerous challenges. Future research should focus on the following aspects: first, developing more efficient and low-cost recovery technologies, particularly in reducing energy consumption and minimizing secondary pollution; second, exploring new high-value utilization pathways for SCC, such as the development of high-performance composite materials; third, the establishment of a comprehensive life-cycle assessment system that considers economic, environmental, and social benefits; fourth, machine learning and molecular dynamics algorithms that can be used to explore the reaction mechanisms of SCC, enhancing the efficiency and accuracy of the research. In summary, new methods for the safe disposal of toxic substances and the recovery of valuable resources from SCC in aluminum electrolysis should be explored from the perspectives of clean production and circular economy.

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