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Review

Summary of Research Progress on Metallurgical Utilization Technology of Red Mud

Xiao-Fei Li, Ting-An Zhang *, Guo-Zhi Lv, Kun Wang and Song Wang

Key Laboratory of Ecological Metallurgy of Multimetal Intergrown Ores of Ministry of Education, School of Metallurgy, Northeastern University, Shenyang 110819, China
* Correspondence: zta2000@163.net

Abstract: Red mud is a highly alkaline solid waste discharged in the alumina production process. Because of its large amount of discharge and high alkalinity, it is mostly stored in dams, occupying a large number of land resources and posing a great safety hazard to the ecological environment. The large-scale consumption of red mud is a global technical problem. Different alumina production processes will produce different types of red mud, mainly Bayer process red mud. In addition to its overall utilization in the field of building materials, agriculture, the environment, and the chemical industry, red mud also contains valuable metal elements, such as titanium, iron, scandium, and aluminum, and is an important secondary mineral resource. This paper focuses on the principle and characteristics of red mud metallurgical treatment for the extraction of valuable components and looks forward to the prospect of large-scale, harmless, and high-value comprehensive utilization technology for red mud in China.

Keywords: Bayer red mud; comprehensive utilization; secondary mineral resource; recovery; metallurgical

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1. Introduction

For over a century, primary aluminum production has required two distinct stages: the Bayer process produces high-grade alumina from bauxite, while the Hall process produces aluminum by the electrolytic reduction of alumina. The Bayer method was patented by Karl Josef Bayer in 1888, while the Hall–Heroult method was developed almost simultaneously and completely independently by Charles Martin Hall and Paul Heroult in 1886. Since then, both processes have undergone extensive studies, and many technical improvements have been made. However, their basic scientific principles and environmental issues remain unchanged [1]. Bayer red mud is an insoluble alkaline solid waste residue generated during the production of alumina by the Bayer process [2]. The production of alumina by the Bayer process produces 1 to 1.5 tons of red mud for every 1 ton of alumina produced [3–5]. Currently, more than 90% of the world's alumina is produced by the Bayer process, resulting in an estimated accumulation of 4.6 billion tons of red mud in the global stockpile [6]. Figure 1 shows the red mud emissions in China from 2011 to 2022 [7]. In China, red mud emissions have increased with the increase in electrolytic aluminum production, reaching 100 million tons in 2017. Emissions continued to grow in 2018, reaching 105 million tons. By 2022, the cumulative stockpile of red mud in China exceeded 1.7 billion tons, with an annual growth of more than 100 million tons. However, the comprehensive utilization rate of red mud is only 4% [3]. With over 50% of the world's alumina being produced in China, which is the world's largest producer of alumina, the problem of red mud is particularly severe in China. After more than a century of development, red mud remains an urgent problem worldwide.

With the growing awareness of environmental protection, China has introduced the objectives of "carbon neutrality" and the "carbon peak" to promote energy conservation and reduce emissions [8]. Twenty-two policies involving red mud have been issued by the Chinese government since 2015, requiring the comprehensive utilization rate of red mud to increase from 4% to 10% by 2020 and the comprehensive utilization rate of new bulk solid waste to reach 60% by 2025. The strict enforcement of pollutant emission reduction requirements is necessary, and projects that fail to meet regulations should be promptly halted. Currently, there is a paucity of reports on the industrial utilization of red mud in China. For example, in August 2021, CHALCO Shandong Enterprise (Zibo, China) and Shandong Expressway Group (Jinan, China) established a long-term partnership to comprehensively utilize red mud for highway construction [9]. In October 2021, Zhongzhou Aluminum Industry (Zhengzhou, China), Zhongzhou Aluminum Plant (Zhengzhou, China), and Jiaozuo Baiaoheng New Materials Co., Ltd., (Jiaozuo, China) signed a strategic cooperation framework agreement and park entry agreement to establish the first red-mud-based low-carbon cementitious material demonstration production line in Jiaozuo Baiaoheng. This project will directly connect with the alumina red mud discharge process and transform red mud stockpiles into new low-carbon emission products, marking a significant step in the comprehensive utilization of red mud in China. The first phase of the project has an annual capacity of 1 million tons and is expected to consume 500,000 tons of red mud per year [10].

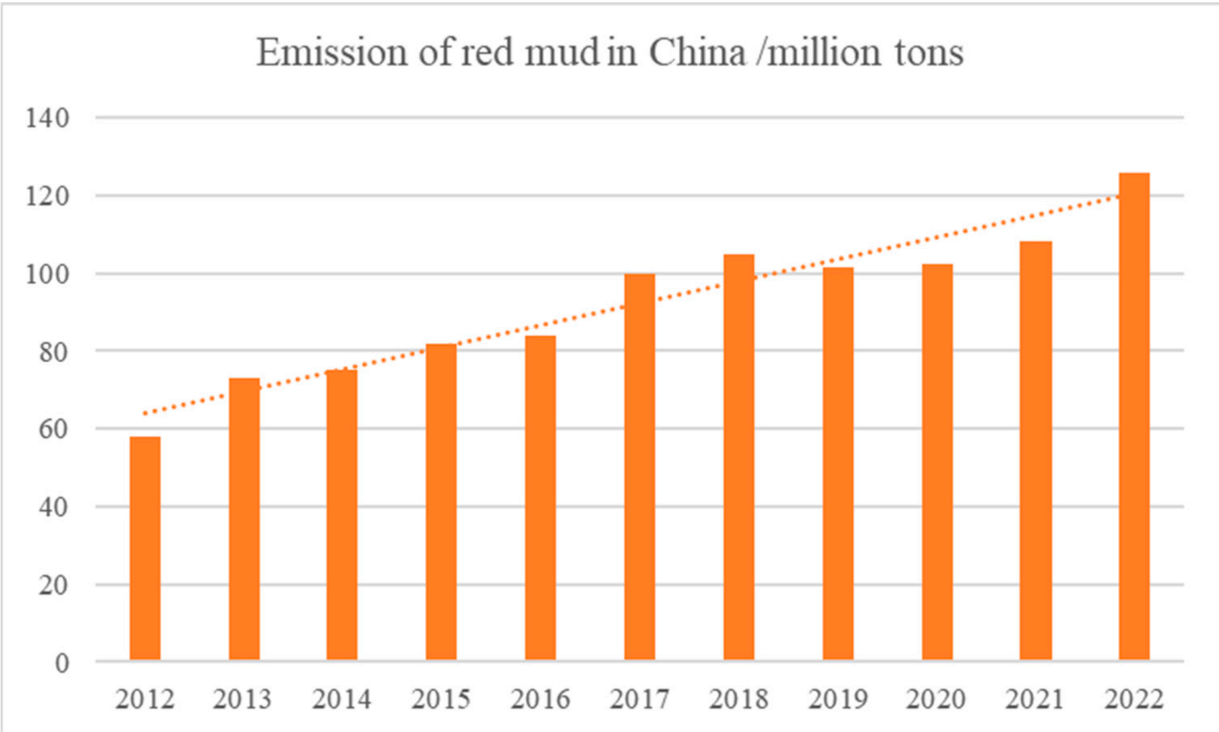

Figure 1. Emission of red mud in China from 2011 to 2022.

Primary aluminum production is one of the most energy- and CO_2-intensive industrial processes, generating 1.61 kg of CO_2 for every 1 kg of aluminum produced. At the same time, Balomenos E et al. [11] proposed in 2011 that red mud could be utilized as an industrial raw material for pig iron and mineral wool production, thereby greatly improving the total energy use efficiency of the Bayer method and contributing to energy savings and emission reduction. As one of the bulk solid wastes, the comprehensive utilization of red mud on a large scale and as a harmless resource is urgent. Over the years, researchers in various countries have conducted extensive studies on the comprehensive utilization of red mud in fields such as building materials, the chemical industry, environmental protection, and the recovery of valuable components. However, most of these studies only focus on a single field and fail to fully unlock the potential value of red mud.

This paper aims to analyze the hazards of red mud by examining its physical and chemical properties. It also provides an overview of red mud utilization in various fields, highlighting the advantages and disadvantages of different technologies. The ultimate goal is to identify the most feasible approach for the comprehensive and harmless utilization of red mud on a large scale. Based on a comparative analysis, tailored solutions need to be developed for different types of red mud. For example, high-iron red mud should be comprehensively utilized through the "calcified transformation—vortex reduction—cement preparation" method. This method involves recovering alkali by calcification, recovering iron through vortex reduction, and producing low-carbon cement from the final tailings. Calcium oxide plays a crucial role in this process and ultimately becomes a raw material for cement production, aligning with the low-carbon concept. This method holds significant potential for practical application and promotion.

2. Physical and Chemical Properties of Red Mud

Bayer method red mud contains iron oxide, and the different iron oxide contents cause red mud to usually have dark red, red, brown, and off-white colors. The higher the iron oxide content, the redder the color of the red mud [12–15]. Not only because of the grinding but also because of the leaching process itself, the red mud particle size of the Bayer method is small. For example, bauxite in Guinea is crushed to 1–2 mm, and after leaching, the particles of red mud are in a range of 5–100 μm [16,17]. The physical properties of red mud are shown in Table 1. The micromorphological results of red mud show that Bayer red mud is usually composed of small particle cohesions, agglomerates, and agglomerates, with a pore shelf-like structure and a pore ratio larger than that of soil, between 2.53 and 2.95, and the formation of cohesion voids, agglomerate voids, and agglomerate voids gives red mud a large specific surface area, which usually ranges from 64.1 to 186.9 $m^2 \cdot g^{-1}$ [18]. Red mud has a loose pore structure and therefore has a relatively low density, usually 2.7~2.9 $g \cdot cm^{-3}$, and a bulk weight of 0.8~1.0 $g \cdot cm^{-3}$ [19]. Fresh red mud has a moisture content of 82.3% to 105.9%, a saturation of 91.1% to 99.6%, and a plasticity index of 17.0 to 30.0 [18]. Due to the presence of sodium oxide, the melting point of red mud is in the range of 1200 to 1250 °C [3].

Table 1. Physical properties of red mud.

Physical Properties	Particle Size/um	Pore Ratio	Specific Surface Area/$m^2 \cdot g^{-1}$	Density/$g \cdot cm^{-3}$	Melting Point/°C
Numerical value	5~75	2.53~2.95	64.1~186.9	2.7~2.9	1200~1250

In the production of alumina by the Bayer process, the chemical composition of the bauxite ore varies, resulting in a different composition of the red mud. In addition to alumina, bauxite also contains oxides such as iron oxide, silicon dioxide, calcium oxide, titanium dioxide, and some rare earth elements. In the process of dissolving bauxite to produce alumina by the Bayer process, alumina and silicon in bauxite react with a sodium hydroxide solution, while iron oxide, calcium oxide, and titanium dioxide do not react with a sodium hydroxide solution, and finally enter red mud after solid–liquid separation. In addition, some aluminum precipitated as a desilication product (DSP) enters the Bayer process red mud due to the presence of silicon in the solution. This is the main problem of the Bayer process. The main chemical components of the Bayer method red mud shown in Table 2 are alumina, silica, iron oxide, titanium dioxide, calcium oxide, and sodium oxide [20]. Red mud also contains small amounts of rare metals and radioactive elements, such as vanadium, zirconium, chromium, scandium, germanium, gallium, niobium, rhenium, yttrium, uranium, and radium [21]. These rare earth metals are heterogeneously distributed in the red mud and exist mainly in a homogeneous form [22]. Its specific content varies depending on the origin of the raw bauxite material and the production method.

Table 2. Chemical composition of red mud (wt%).

Composition	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	Na_2O
Content	10%~20%	3%~20%	30%~60%	0.1%~10%	2%~8%	2%~10%

Therefore, red mud should not be seen as waste but as mineral-rich in many valuable metals. The contents and values of the main valuable elements in Chinese red mud are shown in Table 3 (in the form of pure metals or oxides) [23].

Table 3. The contents and values of the main valuable elements in per ton Chinese red mud ($).

Element	Fe	Al	Ti	Sc	V	Zr	Ca	Ce	Nb
Value	7.62	92.00	114.40	616.21	109.84	3.15	325.00	1.68	15.35

The main mineral compositions in the Chinese Bayer red mud are hematite, calcarenite, calixarene, diaspore, hydrated garnet, and illite, while the main mineral compositions in the foreign Bayer red mud method are goethite, siderite, acanthite, calcarenite, hydrated garnet, and calcite [24]. The Bayer red mud has a high alkali and iron content, which makes it difficult to be used directly for the preparation of building materials.

3. Hazards of Red Mud

With the increase in alumina demand in China, the increase in alumina production also brings the serious problem of red mud stockpiling and utilization Figure 2. In the production of alumina by the Bayer process, a sodium hydroxide solution is used to dissolve the bauxite, and thus, the resulting red mud contains a certain amount of alkali. In addition to containing free alkali, red mud contains chemically bound alkali in the form of hydrated sodium silicoaluminate and is not easily soluble in water, resulting in a strong buffering capacity and high alkalinity [25]. The pH of red mud leachate is usually between 11 and 14 [26], limiting red mud utilization in many fields. Currently, the majority of red mud can only be stockpiled and discharged into landfills for landfill disposal or reclamation by open damming [27,28]. A large amount of red mud occupies a large amount of land. Due to the high alkalinity, the stockpiling of red mud also pollutes the surrounding ecosystems, such as soil and water bodies, causing soil alkalinization and potential personal safety risks, such as collapse and landslides [29,30]. For example, soluble alkalis contained in red mud can infiltrate into the ground with rainwater and contaminate soil and groundwater resources [31]. Because of the fine grain size of red mud, the surface layer of bare piles of red mud will be blown into the air and spread with the wind, causing air pollution [32], which will cause damage to the respiratory system when breathed by people. The Hungarian red mud dam broke in 2010, resulting in the leakage of more than 1 million cubic meters of red mud, and the outflow flooded 40 km^2 of agricultural and urban land, causing 10 deaths and many injuries. The flow of red mud into nearby rivers led to a pH of 13, which eventually led to the near-extinction of invertebrates and fish [31]. This disaster has sounded an alarm to alumina enterprises in China and even around the world and has caused alumina enterprises to pay great attention to the safety of red mud stockpiling. Nevertheless, accidents still happen. Examples include the 2014 CHALCO Henan red mud pond, the 2016 Luoyang Wanji Aluminum red mud pond, and the recent dam failure at the Shanxi Dao Aluminum tailings pond in China in March 2022. Dealing with the large amount of red mud that has been stockpiled and produced every year has become a bottleneck limiting the development of the alumina industry and is a problem that must be solved for the sustainable development of the alumina industry.

Figure 2. The hazards of red mud.

4. Bayer Red Mud Comprehensive Utilization Status

At present, the comprehensive utilization of Bayer red mud is mainly divided into the following aspects. (1) Building materials include the use of red mud for the production of cement or concrete; road cornerstones or pavement materials in road construction; and geopolymers, ceramics, or composites. (2) Applications in the environmental field include the use of red mud to remove heavy metals and improve acidic soils. (3) Applications in the chemical industry include the use of red mud to produce dyes, catalysts, coagulants, or adsorbents. (4) Recovery of valuable components from red mud includes recovery of alkali and extraction of elements, such as aluminum, iron, titanium, and scandium, and important metals, such as vanadium and gallium [33–36]. Figure 3 shows the comprehensive utilization of Bayer red mud. In the following sections, we provide a detailed description of it in various fields.

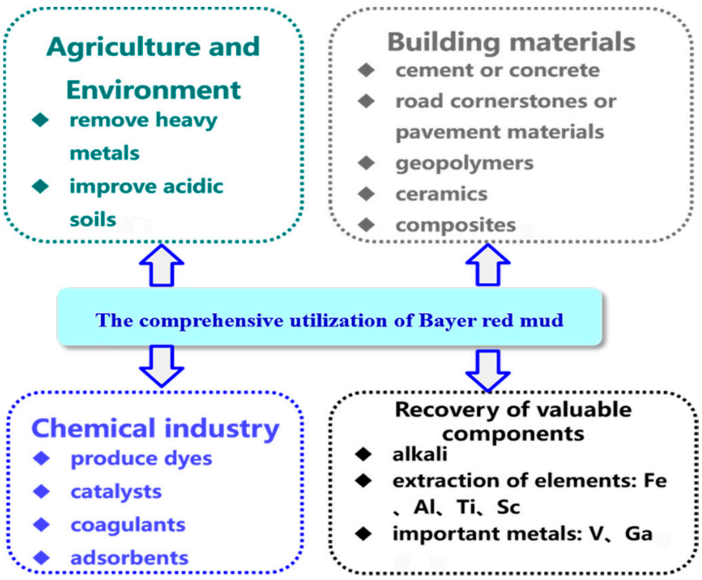

Figure 3. The comprehensive utilization of Bayer red mud.

4.1. Building Material

The main components of red mud are alumina, silicon oxide, iron oxide, titanium oxide, calcium oxide, magnesium oxide, and sodium oxide [37], which are small in volume and have some stickiness, plasticity, and formability. Silica, calcium oxide, and aluminosilicate contained in red mud have good hydraulic activity, so they can be used to prepare building materials [33,38]. At present, the main applications of red mud in the field of building materials are the preparation of bricks, cement, glass ceramics, etc. [39,40].

The specific process of using red mud to prepare bricks is to mix red mud, shale, and slag evenly in proportion; then cut into blanks; then bake through drying, preheating, and "low-temperature slow-burning" technology; and finally, heat preservation and cooling. Sintered brick products are obtained [41]. Figure 4 shows the process of applying red mud to produce sintered bricks. The bricks prepared using red mud as raw material meet the requirements of building bricks in terms of compressive strength, density, and flexural strength. The production cost is low, and a large amount of red mud can be consumed. However, due to the high alkali content of red mud, the prepared bricks are prone to "frost", which affects the strength of the bricks, thereby affecting the aesthetics and service life of the building [42]. There are also some radioactive zircon and monazite in the red mud, which can cause the bricks to exceed radiation levels and affect human health. In addition to sintered bricks, red mud can also be used to prepare permeable bricks. A company in Shandong, China, built a production line with a daily output of 3000 m^2 of permeable bricks, effectively solving the problem of leaching alkali and heavy metals from red mud. The company's products have been mass-produced, and indicators such as radioactivity and heavy metal leaching of the products meet or are better than the requirements of building materials but will be limited by the transportation radius and the scope of use.

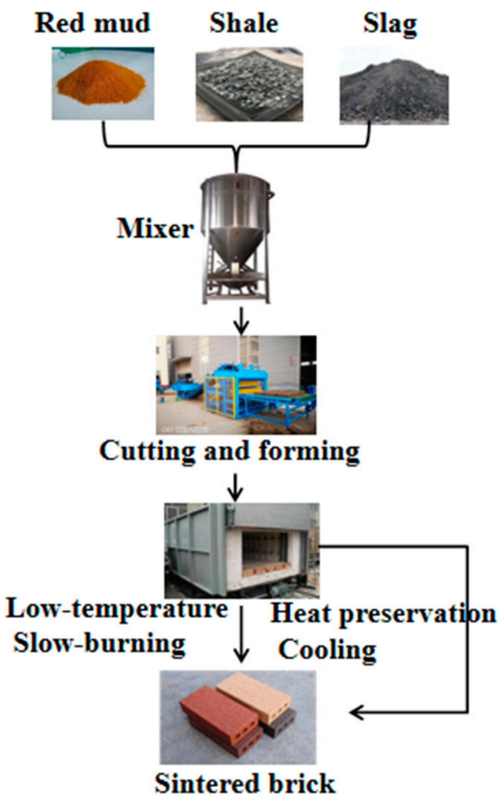

Figure 4. The process of applying red mud to produce sintered bricks.

Red mud contains a large amount of alumina, silicon oxide, and iron oxide, so it can be used to replace part of the raw material to produce silicate cement or aluminate cement clinker. Studies have shown that the iron and aluminum contained in red mud can significantly improve the setting properties and strength of cement [43]. In addition, the titanium-containing fraction contained in red mud can also be beneficial for properties such as the setting strength of cement [44]. Singh et al. [45] used gypsum and bauxite blended red mud from Indian Aluminium Company Limited to prepare a special cement clinker. The sodium alkali contained in red mud limits its admixture as a raw material for cement preparation. Tsakiridis et al. [46] and Vangelatos et al. [47] used red mud to prepare silicate cement, and the results of semi-industrial tests showed that the maximum admixture of red mud without dealkalization was only 5%, which could not fundamentally solve the current problem of a large amount of red mud generation and stockpiling.

In 2020, HINDALCO, the world's leading aluminum producer, announced that it would use red mud to produce cement clinker, with a target consumption of 2.5 million tons of red mud per year [48]. Although the compressive strength of cement prepared from red mud is better than that of ordinary cement, it is also prone to "frosting" when used in buildings because of its strong alkalinity and difficulty in removing it, reducing the service life of buildings [49–52]. Microcrystalline glass with high hardness, high bending strength, and excellent acid and alkali resistance can be prepared by using high iron red mud as raw material and mixing with quartz and talc additives, but the preparation process has high energy consumption, and the alkalinity and radioactivity in red mud can also affect the use field of microcrystalline glass [53–55]. In addition, the direct use of high-iron red mud in the field of building materials will lead to the waste of metal resources such as iron, aluminum, and titanium in red mud, and the value of utilization is greatly reduced. Therefore, before the preparation of construction materials, the high-iron red mud must be dealkalized, and then after the extraction of valuable metals such as iron and titanium from the high-iron red mud, the remaining alumina, silicon oxide, calcium oxide, and magnesium oxide enter the tailings, which can eventually be used to prepare construction materials. This process not only can eliminate the problem of "frosting" in the preparation of building materials from tailings but can also recover the valuable metals in the high-iron red mud and achieve the purpose of the large-scale, low-cost, high-value, and comprehensive utilization of high-iron red mud [56–58]. Wang et al. [59] from Northeastern University presented a new method for producing low-carbon cement using iron tailings from high iron red mud extraction. Using high iron red mud calcified dealkalized tailings as raw material, smelt reduction was used to achieve an iron recovery rate of 97.6%. Water-quenched slag was used in cement production, significantly reducing energy consumption and CO_2 emissions from the decomposition of limestone during the calcination of cement clinker. The CO_2 emissions per ton of cement clinker can be reduced by 400 kg under the condition that the water-quenched slag is mixed at 50%. The method has guiding significance for the large-scale treatment of high-iron red mud. Figure 5 shows the process of applying red mud to produce low-carbon cement.

4.2. Agriculture and Environment

In addition to alumina, silicon oxide, and iron oxide, red mud contains elements such as phosphorus, calcium, and magnesium that provide nutrients for crop growth and can be used to improve soil or produce fertilizers [60–63]. Red mud is strongly alkaline and therefore can be used to adjust the pH of acidic soils [64,65]. The iron and aluminum mineral fractions contained in red mud are beneficial for enhancing the phosphorus fixation effect of the soil and contribute to the growth of microorganisms and plants in the soil. In addition, the strong adsorption properties of red mud can be used to treat soil contaminated with heavy metals and serve as a solidification of heavy metals. Summers et al. [66] used red mud for the improvement of acidic soils and showed that the addition of red mud effectively neutralized the acidity of the soil and effectively inhibited the loss of phosphorus, thus promoting the growth of forage grasses. Snars et al. [67] and Menzies et al. [68] studied the use of red mud, gypsum, sludge, and sewage to remediate contaminated sandy soils, and the results showed that after remediation, the levels of exchangeable sodium and aluminum in the soil could be effectively reduced and that the remediated sandy soil was suitable for vegetation growth. Although the use of red mud to improve soil has good results, it is only applicable to acidic or heavy-metal-contaminated soil. This method uses a small amount of red mud and has strong pertinence, which cannot achieve the purpose of the large-scale treatment of red mud.

Figure 5. The process of applying red mud to produce low-carbon cement.

Bayer red mud is the solid waste of the alumina industry; if it is used in the environmental field, it not only can achieve the purpose of environmental treatment but can also realize the green and sustainable development of treating waste with waste. The main applications of red mud in the environmental field are exhaust gas treatment and wastewater treatment [35,69,70]. Red mud is characterized by a small particle size, large specific surface area, and high content of effective sulfur fixation components such as alumina, iron oxide, calcium oxide, magnesium oxide, and sodium oxide, so it can be used to treat waste gases containing pollutants such as H_2S, SO_2, and NO_x [18]. Exhaust gas treatment is mainly divided into dry and wet treatments [30,49]. The dry treatment uses the characteristics of red mud, such as a large void size and high surface mineral activity, to directly adsorb waste gases. Wet treatment involves the passage of sulfur-containing waste gas into a red mud slurry, using the alkaline substances contained in the red mud to react directly with the acidic gas in the waste gas to absorb the sulfur-containing waste gas and achieve desulfurization. The reaction with acidic sulfur-containing waste gas can remove the alkalinity in red mud and at the same time realize the sustainable development of waste management [71,72].

Research shows that with dry desulfurization, 1 kg of red mud can adsorb 11.3 g SO_2, and the desulfurization rate is approximately 50%, while wet desulfurization is better than the dry method, and its desulfurization rate is as high as 90%. Red mud has a high water content at the time of discharge, and dry desulfurization requires drying the red mud and grinding it into fine particles, which increases the cost of waste gas treatment [29]. Moreover, small particles of red mud are prone to agglomeration, which is likely to cause clogging of the pipeline and limit the application of red mud in the dry process of waste gas treatment. Since the red mud is discharged with a large amount of water, it facilitates the realization of wet desulfurization. Using wet red mud as raw material, Chen et al. [73] investigated the process of absorbing industrial SO_2 exhaust gas using a packed absorption tower. The process is simple to operate and has an obvious desulfurization effect, which can reduce SO_2 exhaust gas with concentrations over 400 mg·m^{-3} to 150 mg·m^{-3} and can reach a maximum of 1 kg of red mud absorbing 28 g of SO_2, with an absorption efficiency above 95%. The main role in the absorption process is played by the neutralization reaction, while a part of the physical absorption also occurs. The red mud slurry that absorbs SO_2 can be used to prepare geopolymers. Nie et al. [74] mixed desulfurized red mud with a type of fly ash in a ratio of 1:1 for 10 min and then added different concentrations of alkaline reagents with a liquid-to-solid ratio of 0.5. Finally, it was cured and molded in a plastic mold. Figure 6 shows the process of applying red mud after desulfurization to the preparation of geopolymers.

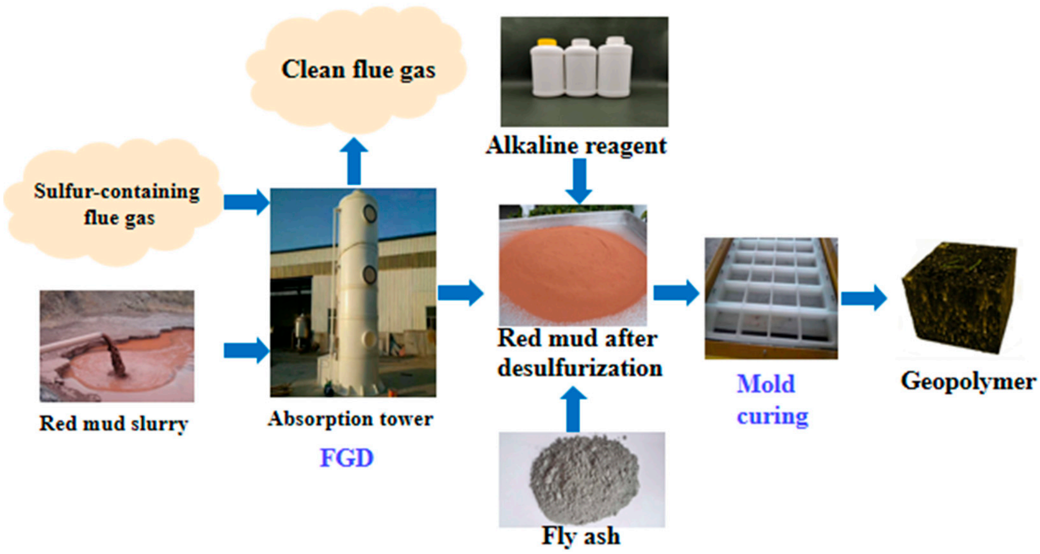

Figure 6. The process of applying red mud after desulfurization to the preparation of geopolymers.

In addition to being used for waste gas treatment, red mud can also be applied for wastewater treatment. Red mud has a high porosity, a large specific surface area, and a pore-like structure, which allows it to adsorb some heavy metal ions or other substances. Additionally, it can play an active role in ion exchange and increased chemical activity. For example, red mud was prepared as a wastewater treatment agent after modified treatment for the adsorption of heavy metal ions (Cd^{2+}, Ni^{2+}, Pb^{2+}, Cu^{2+}, Cr^{6+}, etc.), nonmetal ions (F^-, $PO_4{}^{3}$-, As^{3+}, As^{5+}, etc.), and radioactive elements (U, Sr, Th, Cs, etc.) contained in wastewater [75]. Han et al. [76] used modified red mud as an adsorbent to adsorb Cr^{6+} in wastewater, and the results showed that adsorption equilibrium could be reached by using a 10 g·L^{-1} red mud addition at 20 °C for 2 h at pH = 2. The removal rate of Cr^{6+} from wastewater exceeded 96%, which achieved a high removal and purification effect. However, there are still many problems to be solved in the use of red mud for wastewater treatment. Red mud is strongly alkaline, and its direct application will cause the secondary pollution of water bodies, so it needs to be modified by acidification and activation before it can be used for wastewater treatment. This would increase the cost of treatment and limit the application of red mud for wastewater treatment [77].

4.3. Chemical Industry

The main applications of red mud in the chemical industry are the preparation of catalysts, ceramics, and filler materials [78–80]. Red mud has a fine particle size, a porous internal structure, and a large specific surface area, so it can be modified to prepare industrial catalysts. Sushil et al. [81] reported the study of red mud modified as a catalyst to be used for catalytic hydrogenation, methane degradation, and hydrochlorination with some results. Porous ceramic materials prepared from red mud can be used in water treatment processes [82]. Xu et al. [83] prepared ceramic filter media with red mud as the main raw material, which can replace quartz sand filter media for the water treatment industry. The experimental results showed that the ceramic filter media prepared with red mud can adjust the particle size and specific gravity, the decontamination efficiency is much greater than that of quartz sand, and the performance indexes are up to or better than the national standard, which has good application prospects. Although the economic value of red mud for the preparation of catalysts or ceramics is high, the amount of red mud applied in this field is relatively small. Compared to Chinese annual red mud production of more than 100 million tons, applications in the chemical industry can only utilize a very small portion of the red mud and cannot fundamentally solve the problem of red mud discharge and stockpiling.

4.4. Extraction of Valuable Components

Significant metallic values with appreciable concentrations make red mud a potential polymetallic source [84]. The following sections present a critical overview of the laboratory, pilot, and commercial processes employed to recover iron, aluminum, sodium, titanium, scandium, and REEs from various red muds.

4.4.1. Recovery of Sodium and Aluminum

In the production of alumina by the Bayer process, a sodium hydroxide solution is required for the dissolution of bauxite. Sodium-alkali losses account for approximately 20% of the direct alumina production costs [85]. The high sodium-alkali content of red mud limits its application in many fields. During the dissolution of bauxite by the Bayer process, part of the aluminum is lost in the red mud by reacting with silicon oxide and sodium oxide to form hydrated sodium silicoaluminate. As the bauxite grade decreases, more aluminum is lost. Sodium and aluminum in the red mud produced by the Bayer process are mainly present in the hydrated sodium silicate aluminate phase, and if they can be recovered simultaneously, the economic efficiency of alumina production can be greatly improved [86–89]. The commonly used methods for the dealkalization of red mud include water washing, acid leaching, lime dealkalization, and acid gas neutralization [90–92]. The main methods for the recovery of alumina from red mud are acid leaching, alkaline leaching, and calcification–carbonation [93–96].

The water washing method is the simplest method to remove the soluble alkali from the red mud by soaking the red mud for a long time and washing it several times. Zhu et al. [97] conducted a water leaching dealkalization experiment using Bayer red mud with 5.72% sodium oxide content as the raw material. The results showed that the alkali removal rate from red mud could reach 71% when the ratio of the liquid–solid product was 9 $mL \cdot g^{-1}$, washed four times with water, and leached at a temperature of 90 °C for 60 min. The water leaching dealkalization process of red mud was controlled by a diffusion step with an apparent activation energy of 11.72 $kJ \cdot mol^{-1}$. Although the water washing method is simple, it can only remove the soluble alkali from the red mud, and the alkali removal rate is limited. The water washing method will consume a large amount of water, and the water immersion time is also longer, while the large amount of dilute lye produced cannot be effectively treated, which limits the application of the water washing method. Therefore, this method is usually used in combination with other dealkalization methods.

The acid leaching method uses inorganic or organic acids to react with the alkaline substances in the red mud, thus achieving dealkalization. Commonly used inorganic acids include hydrochloric acid, sulfuric acid, and nitric acid [98]. Liang et al. [99] used hydrochloric acid, nitric acid, and sulfuric acid to acidify the Bayer method red mud to release sodium and aluminum into the solution. The disappearance of diffraction peaks of sodium squared and calcium chalcocite in the XRD of the acid leach residue proves that the acid leaching process of red mud not only removes the free alkali from the red mud but also reacts with some of the bound alkalies, thus achieving a deep regulation of the red mud alkalinity.

Lime dealkalization is a method that uses Ca^{2+}, which has a stronger ion exchange capacity, to replace Na+ in hydrated sodium aluminosilicate in red mud to produce soluble sodium hydroxide for the purpose of dealkalization. On the other hand, Ca^{2+} can combine with the free alkaline anions in the red mud slurry to produce insoluble calcium salts and stable chemically bound bases, allowing the alkalinity of the red mud to be controlled [100,101]. The generated $Ca(OH)_2$ has low solubility under normal conditions, so a large amount of lime needs to be added to ensure the removal rate of the sodium base. Zhu et al. [102] investigated the selective leaching of Na from red mud by CaO using the pressure leaching method. The results showed that the dissolution of sodium could reach more than 85% under optimal conditions. The order of influence of the factors on the sodium leaching efficiency was CaO dosage > liquid-to-solid ratio > leaching time > leaching temperature > leaching pressure. During the selective leaching process, the calcium chalcocite in the red mud is decomposed. The decomposition products silica oxide and aluminum oxide react with calcium oxide, and the final calcium silicate and calcium aluminate produced are retained in the leaching slag. The other decomposition product is sodium oxide dissolved in the leaching solution. The other components of the red mud remain almost unchanged during the leaching process. Wang et al. [103] used the calcium oxide hydrothermal method to dealkalize red mud. The results showed that the addition of calcium oxide could effectively remove sodium oxide from the red mud, and the alkali concentration in the filtrate of the red mud after dealkalization gradually increased with increasing the calcium oxide addition. When calcium oxide is added at 5% and washed three times, the alkali recovery in red mud is 75%, and the recovery is mainly related to the number of washes. Reactions (1)–(5) are the main reactions of lime dealkalization.

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{1}$$

$$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O + Ca(OH)_2 \rightarrow CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O + 2NaOH \tag{2}$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH \tag{3}$$

$$Na_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH \tag{4}$$

$$Na_2SiO_3 + Ca(OH)_2 + H_2O \rightarrow CaO \cdot SiO_2 \cdot H_2O + 2NaOH \tag{5}$$

The acid gas neutralization method uses an acid–base neutralization reaction using acid gas CO_2 or SO_2 to neutralize the alkaline material in red mud, and there are two main methods of CO_2 carbonation and SO_2 neutralization [90]. Wang et al. [56] studied the wet carbonization and dealkalization of Bayer red mud using CO_2 gas and explored the effects of experimental conditions, such as reaction temperature, liquid–solid ratio, reaction time, and CO_2 pressure, on the carbonization and dealkalization effect of Bayer red mud. Under the conditions of a CO_2 pressure of 4 MPa, a liquid–solid ratio of 7:1, a reaction temperature of 50 °C, and a carbonation time of 2 h, the alkali removal rate from red mud reached more than 50%. Reactions (6)–(9) are the main reactions of the carbonation method.

$$NaAlO_2 + CO_2 + H_2O \rightarrow Al_2O_3 + NaHCO_3 \tag{6}$$

$$NaOH + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2O \tag{7}$$

$$Na_2SiO_3 + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2O + SiO_2 \tag{8}$$

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3 \tag{9}$$

Wang et al. [72] used SO_2 and SO_2-based dealkalizers ($SO_2 + N_2$ and $SO_2 + CO_2 + N_2$) to simulate flue gas for the dealkalization of red mud. The effects of factors such as reaction time, reaction temperature, solid–liquid ratio, and SO_2 concentration on red mud dealkalization were investigated. Under optimal conditions, the residual Na_2O in the red mud after dealkalization can be reduced to less than 1% regardless of the simulated flue gas used. During the reaction, the structure of hydroxy sodalite ($Na_8Al_6Si_6O_{24}(OH)_2$) was destroyed, and the soluble sodium salt formed in the suspension was easily neutralized by the acidic gas, leading to a decrease in Na_2O.

The Institute of Special Metallurgy and Process Engineering, Northeastern University, proposed the calcification–carbonation method to recover alumina from low-grade bauxite, and then alkali-free red mud was constructed [104–106]. This method is also applicable to the treatment of Bayer red mud. Figure 7 shows the process and principle of the calcification–carbonation method.

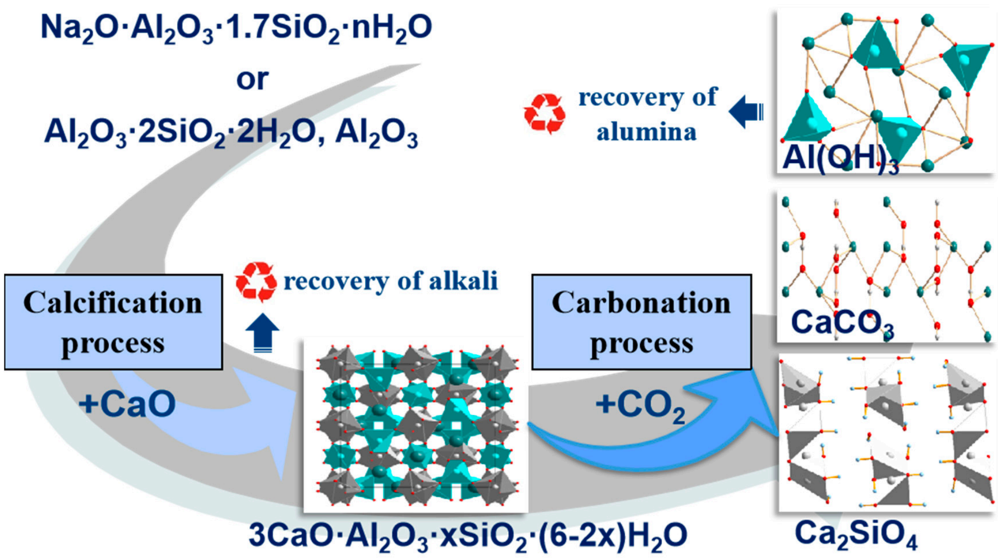

Figure 7. The process and principle of the calcification–carbonation method.

The calcification process of red mud or low-grade bauxite (Reactions (10) and (11)) is as follows:

$$Na_2O{\cdot}Al_2O_3{\cdot}1.7SiO_2{\cdot}nH_2O + CaO + H_2O \rightarrow CaO{\cdot}Al_2O_3{\cdot}1.7SiO_2{\cdot}nH_2O + 2NaOH \quad (10)$$

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O + Al_2O_3{\cdot}3H_2O + 3CaO + H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}(6-2x)H_2O \quad (11)$$

The carbonation process (Reaction (12)) is as follows:

$$3CaO{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}(6-2x)H_2O + (3-2x)CO_2 \rightarrow xCa_2SiO_4 + (3-x)CaCO_3 + 2Al(OH)_3 + (3-2x)H_2O \quad (12)$$

Most of the sodium oxide and alumina in the red mud can be recovered after the calcification–carbonation treatment. The final tailings are theoretically alkali-free and aluminum-free new structured red mud, which can be used for both cement clinker preparation and soil preparation after tempering, realizing the large-scale, low-cost, and slagless comprehensive utilization of red mud. Zhu et al. [107] examined the effect of important parameters, such as temperature, CaO addition, and CO_2 partial pressure, on the recovery of alkali and alumina from red mud. The results showed that 95.2% of alkali and 75.0% of alumina could be recovered from the red mud using the calcification–carbonation method. The Na_2O content in the red mud treated by the calcification–carbonation method is less than 0.5%, which can be used as construction material. Wang et al. [108] analysed the feasibility of using calcified–carbonated tailings for cement production and soil preparation. The results show that the chemical composition of calcified–carbonated tailings is very close to that of silicate cement clinker and can increase the amount of red mud in cement production. The comparison between calcified–carbonated tailings and ordinary soil shows that calcified–carbonated tailings perform well in terms of soil parameters such as alkalinity and salinity and have great potential for soil preparation. Therefore, the calcification–carbonation method combined with cement production or soil preparation is a sustainable process to achieve full resource utilization of Bayer red mud and finally solve the problem of red mud stockpiling Table 4.

Table 4. Evaluation of different red mud dealkalization processes.

Form of Alkali Presence	Dealkalization Methods	Process Evaluation
Free alkali	Water washing method	The process is the simplest, with low dealkalization efficiency, high water consumption, and large amounts of dilute lye produced.
Combined alkali	Acid neutralization method	It can effectively remove alkali, but the acid consumption is too high due to the iron and aluminum oxides in the red mud
	Acid gas neutralization method	Using acid gas CO_2 or SO_2 to neutralize the alkaline material in red mud. High equipment requirements and insignificant dealkalization effect.
	Lime dealkalization method	Good dealkalization under high pressure but high cost. High lime consumption and high requirements for pressurized equipment.
	Salts dealkalization method [109]	General dealkalization efficiency; the introduction of Cl^- to the equipment corrosion is large.
	Bacterial dealkalization method [110,111]	Significant effect of dealkalization, bacteria require high culture environment, difficult to realize industrialization.
	Calcification–carbonation method	Good dealkalization effect while recovering aluminum, simple process equipment, easy to realize industrialization.

4.4.2. Recovery of Titanium

Red mud is rich in titanium dioxide, which is generally in the range of 4% to 12% and has a great recovery value [112]. During the production of alumina by the Bayer process, more than 95% of the titanium dioxide contained in bauxite goes into the red mud [113], offering the possibility of titanium dioxide recovery.

At present, there are three main methods to recover titanium dioxide from red mud: the pyro–hydrometallurgy combined method; the hydrometallurgy method; and the mineral processing–metallurgical combined method. The principle of the combined pyro–hydrometallurgy method is to remove the iron, aluminum, and silicon from the red mud by high-temperature roasting or smelt reduction so that the titanium dioxide is enriched in the slag, and then the titanium dioxide in the slag is leached out using sulfuric acid. The main process of the hydrometallurgy method to recover titanium is to first use dilute hydrochloric acid to leach alumina, iron oxide, and other substances in the red mud. Then, sulfuric acid is used for secondary leaching, and after extraction and reverse extraction, titanium dioxide is extracted from the red mud. The most suitable acid for the extraction of titanium dioxide from red mud is sulfuric acid because titanium dioxide can react with sulfuric acid to form soluble $TiOSO_4$ [16,114]. However, to enrich titanium dioxide, the other elements in the red mud are generally leached out with hydrochloric acid first. Reactions (13)–(16) are the main reactions of hydrochloric acid leaching.

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O \quad (13)$$

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2 \quad (14)$$

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O \quad (15)$$

$$Na_2O + 2HCl = 2NaCl + H_2O \quad (16)$$

The reaction of sulfuric acid leaching is as follows (Reaction (17)):

$$TiO_2 + 2H_2SO_4 = Ti(SO_4)_2 + 2H_2O \quad (17)$$

The high-temperature hydrolysis reaction is as follows (Reactions (18) and (19)):

$$Ti(SO_4)_2 + H_2O = TiOSO_4 + H_2SO_4 \quad (18)$$

$$TiOSO_4 + 2H_2O = H_2TiO_3 + H_2SO_4 \quad (19)$$

The calcination reaction (Reaction (20)) is as follows:

$$H_2TiO_3 = TiO_2 + H_2O \quad (20)$$

Kasliwal et al. [115] used hydrochloric acid to extract calcium, iron, and sodium from red mud. Then, sodium carbonate roasting was performed to convert alumina and silica in the red mud to water-soluble sodium aluminate and sodium silicate, with titanium dioxide as the main component of the final leach residue. After hydrochloric acid leaching, the recovery of titanium dioxide is 36%, and then after roasting with sodium carbonate, the recovery of titanium dioxide can be increased to 76%.

The mineral processing–metallurgical combined method is a process that combines traditional beneficiation processes, such as re-election, magnetic separation, and flotation, with the acid leaching process and roasting process. The beneficiation process can enrich the titanium element and improve the efficiency of subsequent acid leaching. Gao et al. [116] conducted an experimental study on the extraction of TiO_2 from high-iron red mud. The iron concentrate was obtained by reducing magnetic separation, and the silica slag was removed by gravity separation so that the mass fraction of TiO_2 was enriched to more than 20%. Then, the titanium slag was selectively leached with sulfuric acid, and the leaching solution was decomposed, dried, and calcined to obtain pigment-grade titanium dioxide. Titanium in red mud is mainly recovered by leaching using the acid leaching method, which is easy to operate and can be multimetal leaching, but it also leads to the dissolution of a variety of minerals in red mud, resulting in higher acid consumption and higher costs. Long et al. [117] examined the effects of magnetic field strength, sulfuric acid concentration, liquid-solid ratio, temperature, and leaching time on titanium recovery by single-factor experiments. The experimental results showed that the leaching rate of titanium was 85.15% when red mud was leached with 5 mol/L sulfuric acid at 90 °C for 2 h under a magnetic field strength of 0.41 T and a liquid-to-solid ratio of 3:1. The recovery was improved compared to the condition without a magnetic field. The U.S. Bureau of Mines [118] developed a combined reduction roasting–magnetic separation–acid leaching process to recover titanium from red mud. Figure 8 shows the process of recovery of titanium from red mud.

Because the high content of iron oxide and alumina in high-iron red mud leads to higher acid consumption and higher cost for titanium dioxide recovery from high-iron red mud, industrial applications are limited. At the same time, because of the high alkalinity of the red mud, additional acid is consumed during the acid leaching process. The hydrometallurgy method for titanium extraction is simple and has low energy consumption. The main acid leaching media are sulfuric acid, hydrochloric acid, nitric acid, citric acid, etc. Titanium can be effectively extracted and recovered from red mud using either a single sulfuric acid or multiple acids. However, the acid leaching conditions are harsh and require high acid corrosion resistance of the equipment, and acid leaching cannot selectively extract titanium. In addition, certain metallic elements may dissolve in the acid and prove challenging to separate, leading to a loss of resources. Furthermore, a significant amount of waste acid will be generated. The pyro–hydrometallurgy combined method roasts the red mud at high temperatures to change the mineral structure and improve the selectivity of leaching, thus achieving the enrichment of titanium. At the same time, other valuable metal elements are also enriched, but this process is more complex and energy-intensive. The combined mineral processing–metallurgical method is an optimization improvement on the basis of the combined pyro–hydrometallurgy method and hydrometallurgy method. Through the multistage process, different valuable metal elements in red mud can be recovered step by step, which improves the overall separation efficiency and can create greater economic benefits, but there are also problems such as complex process flow and high energy consumption. At present, there is a lack of common and key technologies with significant driving effects, the existing methods have low technical content, and most domestic research is still confined to the laboratory.

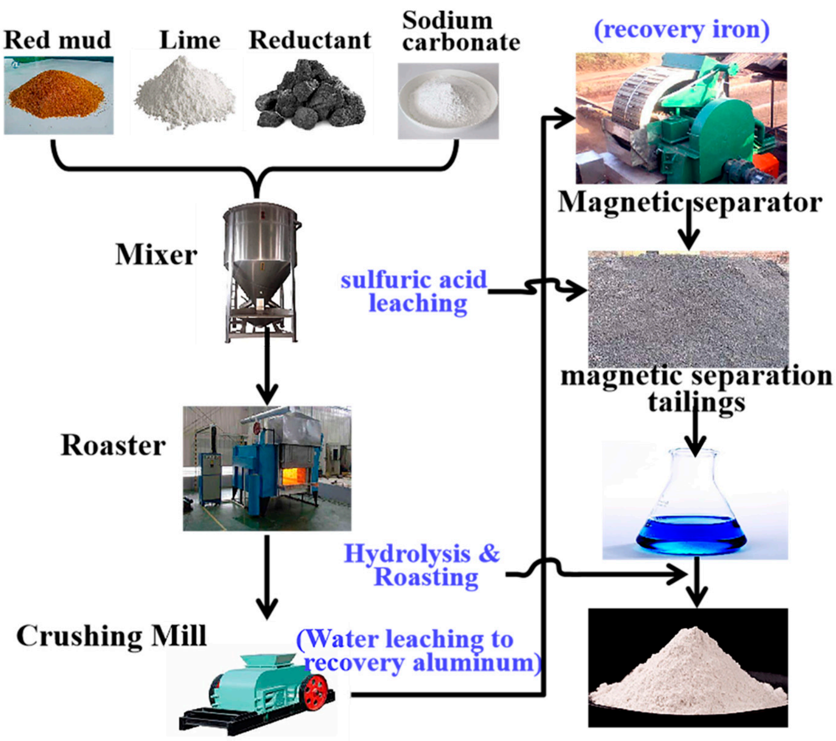

Figure 8. The process of recovery of titanium from red mud.

4.4.3. Recovery of REEs (Rare Earth Elements)

During the production of alumina by the Bayer process, the REEs contained in the bauxite ore will be enriched in red mud. After enrichment, the content of REEs in red mud is approximately twice as high as that in bauxite [119]. The main rare metal contained in red mud is scandium, followed by yttrium, and lanthanide rare earth elements [35]. Scandium is a rare earth element that is rarely found in the Earth's crust and rarely has independent deposits, mostly associated with bauxite, ilmenite, rare earth ores, phosphorite, and zirconite in a homogeneous form [16]. Approximately 80% of naturally occurring scandium is found in bauxite ores [68]. During the production of alumina, more than 98% of the scandium oxide in bauxite goes into the red mud to achieve enrichment, with some red mud containing up to 0.02% scandium oxide [120,121]. The current methods of red mud extraction include pyrometallurgy (smelting reduction) and hydrometallurgy (acid leaching extraction). The former is based on the principle that scandium is further enriched by roasting the red mud to remove iron [122], extracting alumina from the slag, and recovering scandium by acid leaching extraction or ion exchange. The latter is a direct acid leaching treatment of red mud to recover scandium by acid leaching and extraction. The extraction of scandium is usually performed by a combination of liquid–liquid extraction and chemical precipitation. The main commonly used extractants are P204, P507, and TBP [121]. The leaching extraction reactions are as follows (Reactions (21)–(25)).

Acid leaching reaction:

$$Sc_2O_3 + 6HCl = 2ScCl_3 + 3H_2O \tag{21}$$

$$Sc_2O_3 + 3H_2SO_4 = Sc_2(SO_4)_3 + 3H_2O \tag{22}$$

Precipitation reaction:

$$ScCl_3 + 3NaOH = Sc(OH)_3\downarrow + 3NaCl \tag{23}$$

$$Sc_2(SO_4)_3 + 6NaOH = 2Sc(OH)_3\downarrow + 3Na_2SO_4 \tag{24}$$

Calcination reaction:

$$2Sc(OH)3 = Sc2O3 + 3H2O \tag{25}$$

SHINDE et al. [123] used red mud, coke powder, and limestone as raw materials for the smelting reduction in an electric arc furnace, and the product of the melting was pig iron and slag containing aluminum, silicon, and scandium. After the recovery of alumina from the slag, the final slag contained 2.65 times more scandium than the red mud. Chi et al. [124] explored the extraction of scandium from red mud. First, the iron in the red mud is recovered by molten reduction, while aluminum–calcium slag is obtained. Then, the aluminum–calcium slag is dissolved using a sodium carbonate solution. Finally, scandium was leached using hydrochloric acid, and the purity of the scandium obtained was >99.7% with a recovery of 60%–80%.

For low-iron red mud, the hydrometallurgy method of acid leaching extraction can be used to recover scandium. It can also be recovered by sulfation roasting followed by leaching and extraction. Figure 9 shows the process of recovery of scandium from red mud.

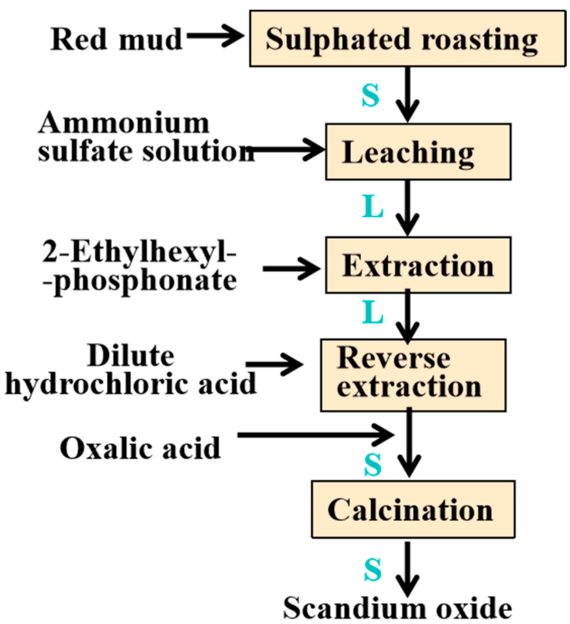

Figure 9. The process of recovery of scandium from red mud [125].

As shown in Figure 10, Rychkov et al. [126] proposed a carbonate leaching method for the recovery of scandium from red mud. The contributions of increasing CO_2 pressure, mechanical activation, and sonication to the degree of scandium leaching were investigated during the leaching process. Mechanical activation increased the degree of scandium leaching from 22.9% to 30.9% at a CO_2 pressure of 6 bar, while further sonication increased it by 39.3%. The recovery of scandium from red mud using mechanical activation and ultrasonic treatment is economically justified.

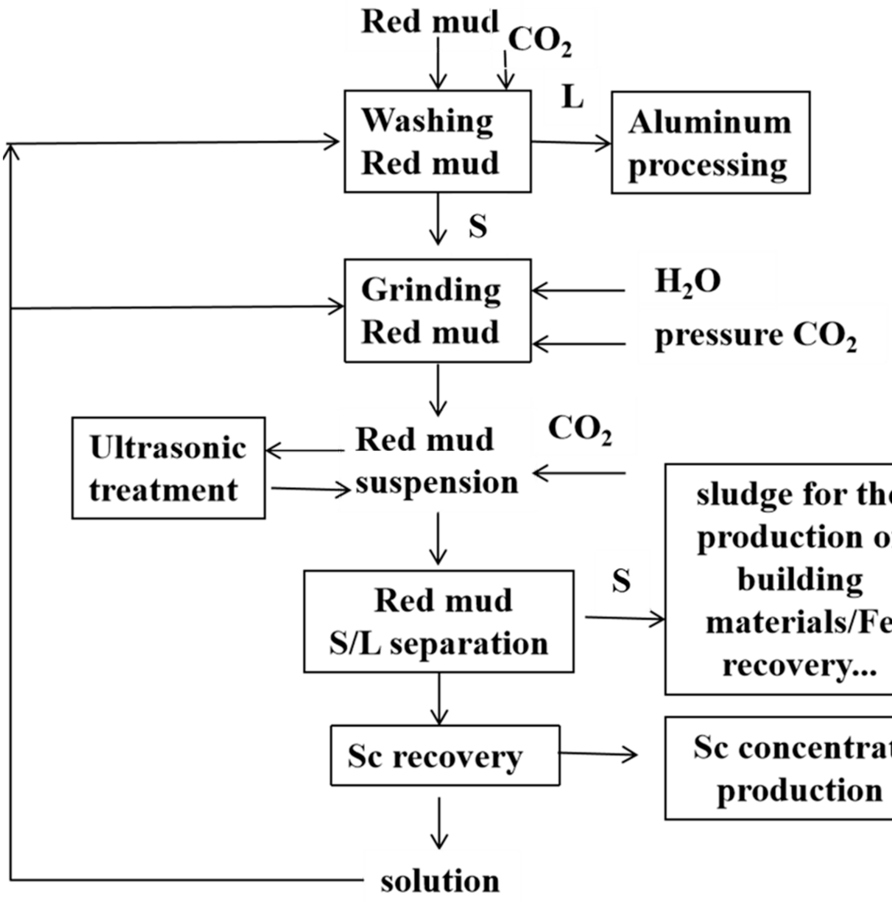

Figure 10. The process of the carbonate leaching method for the recovery of scandium from red mud.

Borra et al. [127] studied leaching experiments on Greek red mud with different acids at different concentrations, liquid-to-solid ratios, leaching times, and temperatures. The extraction of REEs leached in HCl solution was the highest compared to other acids, with a maximum extraction of approximately 80%. However, the solubility of Fe was also high (60%). This posed difficulties for subsequent separation and purification. In connection with the dissolution of iron, numerous studies have recently been conducted on the selective extraction of REEs from red mud. Iron was successfully separated from Greek bauxite residue by using different mixtures of coke, CaO, and SiO_2 at a temperature of 1500 °C in the study of Rivera et al. [128]. Then, slags were treated by high-pressure acid leaching (HPAL) with HCl and H_2SO_4 to selectively extract REEs. In the study of Zhou et al. [129], EDTA was chosen as the chelating agent to re-distribute the species of Sc and Fe ions in the leaching process, which greatly enhanced the selectivity of Sc over Fe.

Although the value of REEs in red mud is significant, their content is small, and a large amount of tailings still exists after extraction, which cannot realize the large-scale consumption of red mud. The recovery of REEs such as scandium from red mud is of great significance to improve the economic efficiency of the comprehensive utilization of red mud and still needs to be studied in depth. At the same time, the synergistic recovery of other valuable components and the full utilization of tailings should also be considered.

4.4.4. Recovery of Iron

The main form of iron present in red mud is hematite (Fe_2O_3) or goethite (FeOOH) [130]. The Fe_2O_3 content in red mud ranges from 6.8% to 71.9% due to different sources of raw materials [131]. Usually, red mud with a Fe_2O_3 content of over 30% is considered a high-iron red mud [22] and is considered a potential iron-containing resource that can be used as a raw material for iron extraction. Red mud with a Fe_2O_3 content below 30% is called low-iron red mud, which is rarely used as raw material for iron extraction alone because of its low iron content and low economic value for iron extraction. The iron content of foreign bauxite ores is very high, so the red mud produced is mostly high-iron red mud. For example, the content of Fe_2O_3 in Australian high-iron red mud is as high as 60%. Most of the Chinese bauxite is diaspore bauxite, among which the bauxite in the Pingguo area of Guangxi is diaspore high-iron bauxite, and the produced red mud is high-iron red mud. Most alumina refineries in Shandong have the geographical advantage of being by the sea, so they mostly use imported gibbsite bauxite, and the red mud produced is high-iron red mud.

At present, researchers in various countries have conducted much research on the recovery of iron from high-iron red mud, mainly by the physical sorting method, hydrometallurgical recovery, and pyrometallurgical recovery. The following is a detailed description of the different methods of recovering iron.

(1) Physical sorting method to recover iron

The physical sorting method to recover iron from high-iron red mud mainly consists of two methods: magnetic separation and re-election [2]. This type of sorting method does not involve chemical reactions during the sorting of high-iron red mud and does not involve physical phase changes.

The hematite contained in the high-iron red mud is weakly magnetic. The magnetic separation method uses the weak magnetism of hematite present in high-iron red mud. High-strength magnetic separation equipment is employed to separate the hematite from the aluminum and silicon impurities, resulting in the separation of high-iron red mud raw materials. This process yields iron-rich magnetic separation concentrate and tailings. Guan et al. [132] used high-iron red mud produced by Pingguo Aluminum Company as raw material and conducted magnetic separation experiments on it using a SLon-type vertical ring pulsating high-gradient magnetic separator for iron extraction. After a semi-industrial test with continuous operation for 72 h, a better index of the investigation was obtained. After the magnetic separation of high-iron red mud with a TFe of 19%, the recovery of Fe in high-iron red mud was 35.36%, the Fe content in the obtained iron concentrate was 54.7%, and the iron concentrate could be used as a raw material for blast furnace ironmaking. However, the yield of iron ore concentrate obtained by this process is only 12.28%, and the remaining 87.72% of magnetic separation tailings are not further treated, which cannot fundamentally solve the problem of red mud stockpiling. In addition, the amount of water used in the magnetic separation process is large. The large amount of alkaline wastewater produced after magnetic separation also causes some pollution to the environment. Xu et al. [133] used a selective hydrophobic flocculation-magnetic separation method to test the recovery of microfine-grained iron ore from the Bayer high-iron red mud produced by Wenshan Aluminum. After the flocculation treatment of red mud with a TFe content of 21.39% by this method, the recovery of Fe in red mud was 50.93% at a magnetic field strength of 0.85 T, and the content of Tfe in the obtained concentrate was 40.65%.

The size of red mud Is small and distributed in agglomerates, and there is a wrapping phenomenon between the particles, so the re-election of high-iron red mud needs to be reclassified. In response to the problem of the difficult sorting of iron-containing materials in red mud due to the high content of microfine particles in high-iron red mud, Liu et al. [134] used a full re-election scheme combining a two-stage cyclone and suspended vibration cone concentrator to conduct experimental research on the re-election of iron-containing materials in high-iron red mud. The results showed that after the two-stage cyclone was used for the particle size classification of red mud with a TFe content of 26.75% and then sorted by a suspended vibration cone concentrator, the obtained iron concentrate had a TFe mass fraction of 48.83%, the yield of iron concentrate was 15.96%, and the recovery of iron from red mud was 19.84%. This process also generates a large amount of alkali-containing wastewater that cannot be treated during the sorting process.

Although the direct physical magnetic separation method and re-election method are simple and easy to operate, the iron recovery rate of the two sorting methods does not exceed 55%. The iron ore concentrate obtained by the direct magnetic separation method contains a certain amount of sodium oxide, which will corrode the blast furnace lining, so the iron ore concentrate obtained by magnetic separation cannot be used directly as raw material for blast furnace ironmaking. The re-election method requires the preparation of red mud with water into a slurry, and the free alkali in the red mud will be dissolved into the water, which will produce a large amount of alkali-containing wastewater in the re-election process that cannot be treated, and if discharged directly, it will cause environmental pollution. Whether by direct magnetic separation or re-election, the yield of the resulting concentrate is less than 20%, and the remaining 80% of the red mud remains untreated, without actually solving the problem of stockpiling high-iron red mud.

(2) Hydrometallurgical recovery of iron

Hydrometallurgy for iron recovery is a process that uses acid to react with iron oxide in high-iron red mud and then separates and recovers iron ions from the leachate. Currently, the main acids used are hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, and oxalic acid.

Since hematite is insoluble in inorganic acids such as hydrochloric acid at room temperature, the leaching process requires the use of concentrated acid solutions and heating conditions to achieve the leaching and extraction of iron. Xie et al. [135] studied the leaching of red mud using the hydrochloric acid solution and investigated the effects of different red mud particle sizes, acid leaching temperatures, leaching time, liquid–solid ratios, and mass concentrations of hydrochloric acid on the leaching effect. The results showed that the main factors affecting leaching were the acid leaching temperature and hydrochloric acid mass concentration. When red mud with a particle size of 150 μm was leached using 10 $mol \cdot L^{-1}$ hydrochloric acid, both aluminum and iron could be leached into the solution, and the leaching rates of aluminum and iron were 96.7% and 95.1%, respectively. During the leaching process, both iron and aluminum enter the solution, which is more difficult to achieve for recovering iron from the leachate alone, so the iron and aluminum leachate can be used as raw materials to prepare flocculants for the water treatment industry.

Pepper et al. [136] studied the leaching efficiency of four inorganic acids (nitric acid, hydrochloric acid, sulfuric acid, and phosphoric acid) on four elements (Fe, Ti, Al, and Si) in red mud. The effects of acid type, acid mass concentration, and experimental conditions on the leaching process were investigated. The results showed that the highest recoveries of Fe and Ti were obtained with phosphoric acid and hydrochloric acid leaching, and the highest recoveries of Si and Al were obtained with phosphoric acid leaching. When using nitric acid to extract aluminum and silicon, the iron and titanium do not react with the nitric acid and are retained in the leaching tailings.

Hydrometallurgy for iron recovery is simple, with low energy consumption and a high iron leaching rate, but during the leaching process, some other oxides in the red mud (alumina, silicon oxide, and titanium dioxide) also react with the acid, resulting in a high content of impurities in the leachate, making it difficult for the subsequent separation and removal of impurities. In addition, due to the strong alkalinity of high iron red mud, it contains a certain amount of sodium oxide that can also react with acid, which will increase acid consumption and increase the cost of recovery. It also generates a large amount of waste acid that cannot be disposed of and causes secondary pollution to the environment.

In addition to acid leaching, Wang et al. [137] used the straw hydrothermal method to reduce the treatment of high-iron red mud to recover iron and aluminum from red mud. The process of the straw hydrothermal method is shown in Figure 11. The method uses waste rice stalks as a reducing agent to reduce hematite in red mud to magnetite in an alkaline system while extracting alumina during the dissolution process, and the tailings can be magnetically sorted to obtain high-purity magnetite. It was shown that when the mass ratio of rice straw to red mud was 20%, the reaction temperature was 300 °C, the mass concentration of caustic soda was 220 g·L^{-1}, the liquid–solid ratio was 5:1, the stirring speed was 600 r·min^{-1}, the dissolution rate of alumina reached 91.2%, and the reduction rate of iron reached 98.1%. This method dissolves alumina by the hydrothermal method while reducing hematite in red mud under the action of the reducing agent and finally recovers alumina and iron in red mud. The reaction temperature is low, and the magnetic separation to a high grade of magnetite concentrate can be used as a raw material for iron making, which has good application prospects.

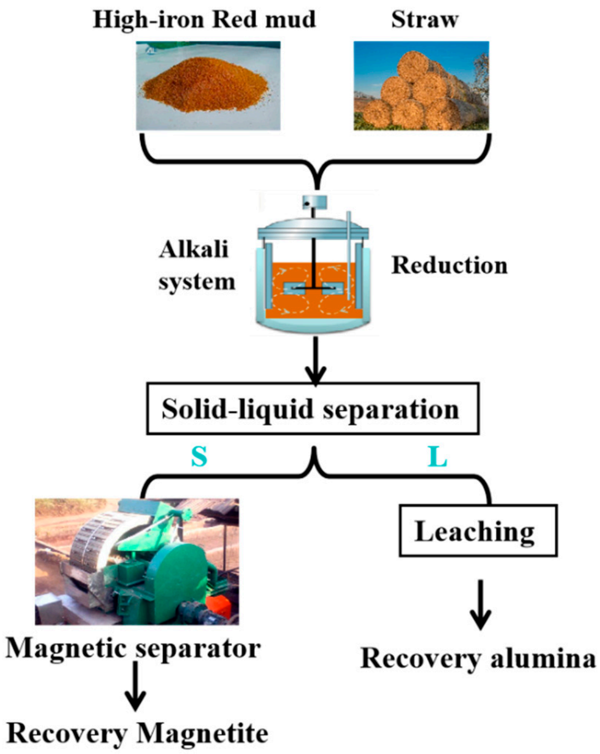

Figure 11. The process of the straw hydrothermal method to recover iron and aluminum.

The latest work on reductive Bayer is conducive to improving the Bayer process, aiming to achieve the cleaner production of commercial alumina. This is a purely alkaline method but with the transfer of iron to a commercial product with simultaneous dealkalization. Wang et al. [138] proposed a novel design incorporating both reductive Bayer digestion and iron recovery into diasporic bauxite processing to remarkably reduce red mud discharge. During the test, relative alumina recovery of 98% and a reduction of 10.9% in the amount of red mud generated were achieved by substituting 2 wt.% iron powder for 10 wt.% lime of bauxite in the high-temperature digestion. Meanwhile, 60% of the iron minerals were converted to magnetite by iron powder, meaning that processing the resulting red mud by magnetic separation could obtain an iron concentrate with a total iron concentration of 55.2% and iron recovery of 60.1%.

(3) Pyrometallurgical recovery of iron

Pyrometallurgical recovery of iron mainly includes two methods: solid-phase reduction magnetic separation and molten reduction.

The solid-phase reduction magnetic separation method to recover iron involves mixing high-iron red mud, reducing agents, and additives and then carrying out reduction roasting under high-temperature conditions to reduce the hematite in high-iron red mud to magnetite or metallic iron with strong magnetic properties [139]. The samples are then ground and magnetically sorted to obtain magnetite or metallic iron powder products (sponge iron) [16]. Magnetic separation tailings can be used as raw materials to prepare building material products or to further extract alumina and sodium oxide [140]. The common reducing agents used in the solid-phase reduction process are mainly coal-based reducing agents, such as coke, coking coal, bituminous coal, anthracite, graphite powder, activated carbon, toner, and cathode carbon briquettes; gaseous reducing agents, such as carbon monoxide, natural gas, and hydrogen; biomass reducing agents, such as charcoal, sawdust, and bagasse; and pyrite reducing agents.

Liu et al. [26] used Bayer high-iron red mud as raw material, activated carbon as a reducing agent, and calcium carbonate and magnesium carbonate as additives and recovered the sponge iron product after solid-phase reduction magnetic separation treatment. The iron content in the magnetic separation concentrate was 89.05%, the iron recovery was 81.40%, and the iron metallization in the concentrate was 96.98%. The magnetic separation tailings were mixed with nitrate ash, and after the extrusion molding and steam maintenance process, the compressive strength of the product reached 24.10 MPa, and the strength of the product meets the requirements of building materials, such as steam-formed bricks. After mixing the magnetic separation tailings with nitrate lime, the compressive strength of the obtained samples reached 24.10 MPa after the extrusion molding and steam curing process, and its strength meets the requirements of building materials, such as steam-formed bricks. Li et al. [93] used Bayer high-iron red mud as raw material, soda powder and lime as additives, and carbon powder as a reducing agent, and the materials were mixed and preheated in a muffle furnace at 800 °C for 20 min to obtain sintered ore. Then, the sintered ore was roasted in a muffle furnace at 600 °C for 20 min, and the roasted product was ground and leached to recover alumina. The leached slag was magnetically sorted to obtain magnetite products. The results showed that under the optimal sintering conditions, the recovery of alumina from Bayer red mud reached 89.71%, the iron recovery was 60.67%, and the iron grade in the recovered magnetite concentrate was 61.78%. Liu et al. [141] used Bayer red mud with an iron content of 19.6%, mixed it with 50% toner and 4% additives, and roasted it at 700 °C for 20 min. The roasted product was milled and magnetically sorted to obtain a magnetite concentrate with a total iron grade of 60% and an iron recovery of 91%. Lu et al. [142] used spent cathode carbon blocks as a reducing agent to reduce high-iron red mud, which was roasted and reduced after mixing and pelletizing, and finally, the iron concentrate was obtained by magnetic separation. The results showed that an iron concentrate with an iron grade of 43.71% could be obtained after magnetic separation with roasting at 1050 °C for 100 min with 15% cathode toner addition, but the output of the iron concentrate was only 44.31%. In the investigation of Sadangi et al. [143], the iron values were successfully recovered by reduction roasting followed by magnetic separation. During the process, the hematitic and goethiteitic iron-phase minerals present in the red mud sample are converted into magnetite and metallic iron, which are subsequently recovered using a low-intensity magnetic separator. The results showed that an iron recovery of 61.85% with an iron content of 65.93% could be obtained at a roasting temperature of 1150 °C, a roasting time of 60 min, and magnetic field intensity of 0.18 Tesla.

There are also many studies around the world using gas reducers to reduce high-iron red mud. The iron in Bayer high-iron red mud exists mainly in the form of hematite, and pure reducing gases, such as H_2 or CO, can reduce hematite to metallic iron. After the high-iron red mud was dealkalized by CO_2 and reduced under a H_2 atmosphere at 1000 °C for 4 h, the reduction of hematite reached 99.5%, and almost all the iron in the reduction product was in the form of metallic iron. The main factor affecting the reduction effect is the reduction temperature. The absence of agglomerates in the reduction product facilitates direct physical magnetic separation to separate metallic iron from the tailings [144].

Biomass is mainly composed of lignin, cellulose, and hemicellulose and contains elements such as C, H, O, N, and S and a small amount of ash, which is suitable for use as a reducing agent to reduce high-iron red mud. Experiments using pine sawdust and bituminous coal as reducing agents to reduce roasted high-iron red mud separately showed that pine sawdust was more susceptible to pyrolysis reactions than bituminous coal. The reduction temperature of pine sawdust is approximately 200 °C lower than that of bituminous coal, and the reduction time is shorter than that of bituminous coal, which has great advantages [145].

Pyrite is widely available and inexpensive. It is often used as a reducing agent due to the negative 1 valence of sulfur it contains. Liu et al. [146] used anaerobic roasting experiments of high-iron red mud using pyrite to convert hematite to magnetite in red mud and then recovered the iron from the red mud by magnetic separation. The results showed that pyrite can be decomposed into ferrous sulfide, magnetic pyrite, and elemental sulfur after heating, and these substances can reduce hematite to magnetite, and the iron in hematite can be reduced from 9.24% to 0.61% in the magnetic separation tailings after roasting at 600 °C for 30 min in a N_2 atmosphere for magnetic separation. The results showed that pyrite can be decomposed into ferrous sulfide, magnetic pyrite, and elemental sulfur after heating, and these substances can reduce hematite to magnetite. The iron content in the red mud was 9.24%, while the iron content in the magnetic separation tailings was 0.61% after roasting for 30 min at 600 °C in a N_2 atmosphere for magnetic separation.

During the solid-phase reduction of high-iron red mud, the intermediate product FeO produced by the reduction easily reacts with impurities Al_2O_3 and SiO_2 in the red mud to form hard-to-reduce iron olivine (Fe_2SiO_4) and iron spinel ($FeAl_2O_4$) [147], which will reduce the reduction effect and recovery of Fe. Therefore, it is necessary to add a certain amount of additives to the red mud to destabilize the structure of Fe_2SiO_4 and $FeAl_2O_4$ to replace FeO and thus improve the reactivity of FeO [148]. Commonly used additives include oxides of calcium, magnesium, and sodium or the corresponding carbonates and sulfates. They not only act as fluxes but also improve the efficiency of coal-based direct reduction of high-iron red mud [149]. Jia et al. [150] conducted a deep reduction–magnetic separation iron extraction experiment on high-iron red mud using coke as a reducing agent and found that increasing the amount of reducing agent, increasing the reduction temperature, and extending the reduction time appropriately were beneficial to the deep reduction process of red mud. A certain range of increasing additive dosage is also beneficial to improving iron recovery. The recovery of the iron concentrate with a 5% additive increased from 91.86% to 93.13%, and the grade of iron in the iron concentrate increased from 85.66% to 91.23%. Proper sodium carbonate can improve the reduction of iron oxide and facilitate the conversion of alumina to soluble sodium aluminate during the reduction process, which facilitates the recovery of alumina and iron oxide from red mud [151].

In addition to the electric heating method, the solid phase reduction process is also studied by microwave heating, plasma heating, and other heating methods. Samouhos et al. [152] developed a process using the selective microwave reduction of high-iron red mud from lignite followed by wet magnetic separation to produce a feedstock suitable for sponge iron or cast iron production. It was found that the reduction sequence of hematite followed the sequence of $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$, and due to the low reduction temperature, hematite was mostly reduced to magnetite, and a magnetized concentrate with a total iron mass fraction of 35.15% and a metallization rate of 69.3% was obtained under optimal process conditions. The comparison of conventional roasting and microwave reduction roasting processes shows that microwave reduction roasting shortens the roasting time by approximately 40%.

The smelting reduction method to recover iron involves mixing high-iron red mud, a reducing agent, and additives and then melting it under high-temperature conditions. The iron oxide in the red mud is reduced to singlet iron; eventually, iron water and molten slag are obtained. Wang et al. [153] similarly confirmed that the reduction sequence of iron oxide in red mud is $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$. The reducing agent used can be carbon or a carbon-based reducing agent [154]. The molten reduction product is carbonaceous iron, which can be directly used as raw material for steel making, and the reduction slag can be further used to extract alumina and rare metals or directly used to prepare building materials such as low-carbon cement [59,155]. This is in line with the Chinese "double carbon" environmental protection policy. The iron in the high-iron red mud can be effectively recovered using smelting reduction. Its high-temperature conditions provide good conditions for the settling and separation of slag and iron [156]. The reduction process uses a coal-based reductant to reduce the hematite in the high iron red mud, and the resulting CO combustion will also provide heat to the system.

Liu et al. [157] prepared anti-wear low-alloy white cast iron from red mud by the Bayer method, with the process of mixing red mud with coke, followed by granulation in a disc granulator, drying, and then melting and reducing in an intermediate frequency induction furnace. The results showed that the smelting reduction of iron in red mud proceeds according to the reaction of CO generation, and after a 20 min reduction at 1600 °C, high hardness sub-eutectic white cast iron can be obtained. After testing, the wear performance of the metallic iron pieces is excellent. Li et al. [158] used the method of "rotary bottom furnace direct reduction—gas furnace fusion" to reduce Bayer red mud, and the results showed that after the red mud pellets were reduced by a rotary bottom furnace and melted by a gas furnace, the iron content in the iron water obtained was 93%, and the slag–gold separation effect was good. Wang et al. [159] made carbonaceous pellets by mixing high-iron red mud and pulverized coal and prepared iron beads by direct reduction under high-temperature conditions. The results showed that the temperature and calcium fluoride addition were the key factors affecting the reduction of pellets. The effective separation of reduced slag iron was achieved at 1400 °C, a carbon to oxygen molar ratio of 1.2:1, a calcium fluoride addition of 2%, and 14 min of reduction. The carbon and sulfur contents of the obtained iron beads were 2.72% and 0.48%, respectively, which can be directly used as raw materials for steel making. The content of scandium oxide in the reduction slag was 0.0184%, which can be used as a high-quality raw material for scandium extraction. Guo et al. [160] conducted a red mud reduction experiment using the orthogonal test method, and iron lumps could be obtained by melting and reducing a mixture of red mud and coal pellets. The results showed that the temperature was the most important factor affecting the separation of iron and slag, and the separation of iron and slag was more complete. The iron lump was obtained by pellet reduction for 30 min at a temperature of 1400 °C, a carbon to oxygen molar ratio of 1.6:1, and an alkalinity of 1.0. The resulting iron lump has a higher TFe content, which is higher than that of the blast furnace iron. The Si and Mn contents of the slag were lower, and the S and P contents were higher. The main phases in the reduced slag were SiO_2, the unreduced Fe_2SiO_4 amorphous phase, and a small amount of reduced metallic iron.

Based on the original research about the calcification–carbonation of red mud, the Institute of Special Metallurgy and Process Engineering, Northeastern University, has proposed a new process of the iron extraction and tailings cementation by different vortex smelting reductions for different types of high-iron red mud. In detail, the "direct vortex smelting reduction—tailing cementation" process for low-alkali high-iron red mud, "calcification—vortex smelting reduction—tailing cementation" process for high-alkali high-iron red mud, and "calcification—carbonation—vortex smelting reduction—tailing cementation" process for high-alkali high-alumina high-iron red mud. The team applied for a related series of patents [161–165], and the flow chart of the direct vortex reduction of high-iron red mud is shown in Figure 12.

The process of recovering iron by direct physical sorting is simple and easy to operate, but the recovery rate of iron is very low, and the grade of the iron concentrate obtained after sorting is low.

In addition, the yield of iron concentrate in the sorting process is also very low, usually less than 20%, and the remaining 80% of the magnetic separation tailings are not further utilized, which cannot fundamentally solve the problem of red mud stockpiling. In addition to the acid consumed by the hematite ore in the hydrometallurgy for iron recovery, the large amount of impurities contained in the red mud also consumes additional acid, resulting in increased costs for iron extraction and secondary pollution due to the large amount of waste liquid generated. The pyrometallurgical recovery of iron uses a reducing agent to directly reduce hematite and eventually obtain metallic iron, which has great application prospects. Melt reduction technology is more efficient than solid-phase reduction magnetic separation to recover iron, and the final iron metal product has a higher iron grade. The carbonaceous iron from reduction can be directly used as raw material for steel making, and the reduction slag can be further used to extract aluminum and scandium or directly prepare building materials. It is a promising recovery method for high-iron red mud. The evaluation of different processes for iron recovery from red mud is shown in Table 5.

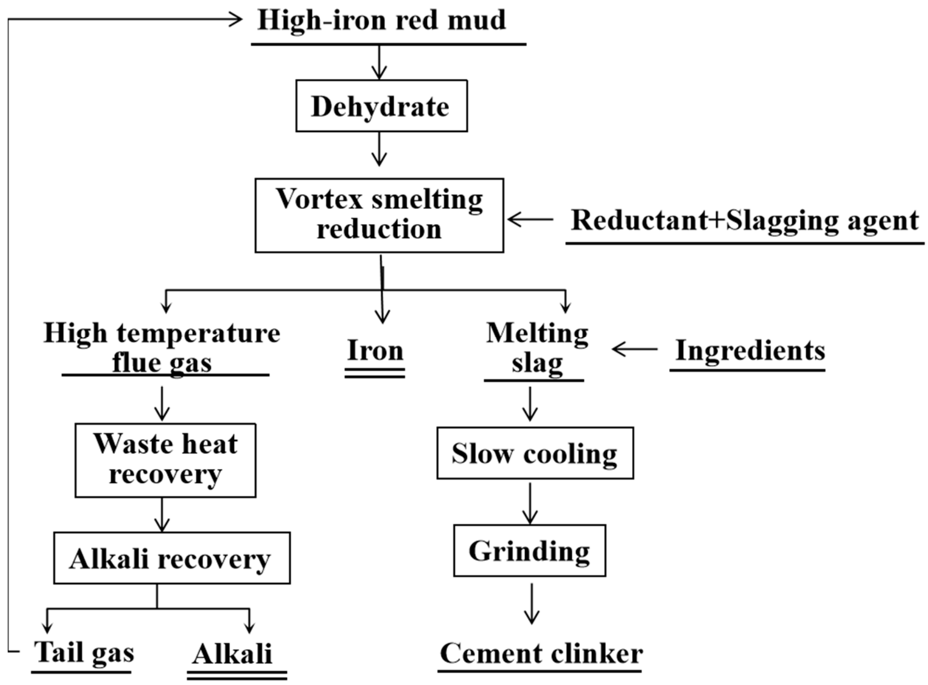

Figure 12. Flow chart of direct vortex reduction of high-iron red mud and production of cement clinker with reduced slag.

Table 5. Evaluation of different processes for iron recovery from red mud.

Process Classification	Process Name		Process Evaluation
Direct physical sorting	Magnetic separation		Simple process, low energy consumption, iron recovery under magnetic field conditions, low iron recovery rate, untreated tailings, and a large amount of wastewater generated.
	Re-election		Simple process, low energy consumption, iron recovery under gravity field conditions, low iron recovery rate, untreated tailings, and a large amount of wastewater generated.
Hydrometallurgy	Acid leaching	Hydrochloric acid	Simple process, low energy consumption, high iron recovery rate; many impurities in leachate, difficult to separate and purify; high acid consumption, generating a large amount of waste acid and increasing costs.
		Sulfuric acid	
		Phosphoric acid	
		Nitric acid	
		Oxalic acid	

Table 5. *Cont.*

Process Classification	Process Name		Process Evaluation
Pyrometallurgy	Solid-phase reduction magnetic separation	Coal-based reducing agents	The process is relatively complex, the overall energy consumption is relatively high, and the product is magnetite with an iron recovery rate of 60%–90%.
		Gaseous reducing agents	High equipment requirements, good iron reduction in red mud, H_2 reduction is low carbon, and environmental protection.
		Biomass reducing agents	Biomass reduction is clean and environmentally friendly.
		Pyrite reducing agents	Produces SO_2 exhaust gas, easily causing air pollution.
	Molten reduction	Molten melt state reduction separation technology	High-quality pig iron can be obtained, high energy consumption, and tailings can be reused.

In recent years, the Chinese red mud iron extraction project has encountered difficulties due to the decline in the import of high iron bauxite and the iron content in bauxite, the rising market demand for high-grade iron ore, the squeeze of imported iron ore on the Chinese market space, and the strict national control of iron production capacity.

5. Conclusions

This paper shows more interesting data on Chinese state programs to minimize the harmful effects of red mud. This includes Chinese policy on how to deal with bulk solid waste such as red mud and the red-mud-related projects that are already underway, demonstrating China's efforts towards global environmental protection and the sustainable development of the global alumina industry.

The use of red mud as construction material has the advantages of a large amount of usage, low cost of raw materials, and a large amount of product market. However, the problem of "frosting" building materials made of red mud seriously affects the applications of building materials. The limitation of transportation distance of products and raw materials will also increase the cost of red mud in building material applications. In addition, the direct use of high-iron red mud in the field of building materials will lead to the waste of metal resources such as iron, aluminum, and titanium in red mud, and the value of the utilization is greatly reduced. Therefore, before the preparation of building materials, the red mud needs to be dealkalized, valuable metals such as iron and titanium in the high-iron red mud are extracted, and the remaining alumina, silicon oxide, calcium oxide, and magnesium oxide enter the tailings, which can eventually be used to prepare building materials.

This process not only can eliminate the problem of "frost" in the preparation of building materials but can also recover the valuable metals in red mud to achieve the purpose of the large-scale, low-cost, high-value, comprehensive utilization of high-iron red mud. In addition, The composition of valuable components in red mud is complex, and the content varies. Red mud, such as low-alkali high-iron red mud, high-alkali high-iron red mud, and high-alkali high-iron high-aluminum red mud, should be classified. Corresponding methods of recovering valuable components should be developed to achieve comprehensive recovery with low energy consumption. It is also necessary to consider the harmless treatment of the tailings to avoid causing secondary tailings and secondary pollution. In conclusion, the comprehensive utilization of red mud will be the next profit growth point of the alumina industry. The "calcified transformation—vortex reduction—cement preparation" method may be the most reasonable method for the comprehensive utilization of red mud to realize the comprehensive utilization of red mud in a harmless, large-scale, and resourceful way.

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