Summary of research progress on separation and extraction of valuable metals from Bayer red mud

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Abstract
Bayer red mud is a strong alkaline solid waste discharged during alumina production. Due to large emissions and strong alkalinity, red mud is now mostly dammed or buried, which not only occupies huge land but also contaminates the surrounding ecosystem, causing the risk of collapse and landslide. In addition to its overall utilization in building materials, agriculture, the environment, and the chemical industry, red mud also contains valuable metals such as sodium, aluminum, iron, titanium, and scandium and is considered to be an important secondary resource. In this paper, the physicochemical properties and hazards of red mud are first introduced, and then, the overall utilization of red mud is summarized. Then, the latest research progress on the separation and extraction of valuable metals from red mud is reviewed in detail and a new comprehensive utilization method is recommended and evaluated. This paper also provides suggestions for the future development direction of the comprehensive utilization technology of red mud.

Keywords Bayer red mud · Overall utilization · Valuable metals · Separation and extraction · Secondary resource

Introduction

In the industrial production of alumina, there are three main production methods: the Bayer process, sintering process, and combined process (Liu et al. 2014a). The Bayer process is the most commonly used in alumina production (Liu et al. 2007), and more than 90% of alumina is produced by the Bayer process worldwide (Wang et al. 2018). Bayer red mud is an insoluble alkaline solid waste residue produced during the dissolution process of bauxite by the Bayer process (Zeng et al. 2022; Lyu et al. 2021). In the dissolution process, sodium aluminosilicate hydrate, the main phase of Bayer red mud, is generated because of the combination of sodium oxide, alumina and silicon oxide (Zhu et al. 2016b). For each ton of alumina produced by the Bayer process, about 1 to 1.5 tons of red mud will be discharged (Deng et al. 2017; Zeng et al. 2020). The applications of red mud in many fields are limited due to its strong alkalinity (the pH value of leaching solution of red mud is normally between 11 and 13) (Kinnarinen et al. 2019). At present, the vast majority of red mud can only be stored by open-air damming or discharged into landfills and sea reclamation treatments (Wang and Liu 2021; Zhang et al. 2021a). It is estimated that the global reserves of red mud have exceeded 4.0 billion tons (Carneiro et al. 2018). Figure 1 shows alumina production in the world and China. In 2021, alumina production in China exceeded 77 million tons, accounting for more than 50% of global alumina production. The alumina production and red mud emissions of Chinese provinces is shown in Fig. 2. The alumina production of Shandong, Shanxi, Guangxi, and Henan Provinces accounts for 88.7% of China’s alumina production. China has accumulated more than 1.5 billion tons of red mud, with an annual increase of 100 million tons. The comprehensive utilization of red mud in China is only 4% (Liao et al. 2019) because of its strong alkalinity. Due to its enormous emissions and strong alkalinity, the stockpiling of red mud not only occupies a large amount of land but also contaminates the surrounding soil, water and other ecosystems, resulting in soil alkalization and potential human safety risks such as collapse and landslides (Gomes et al. 2016). The red mud dam breach in Hungary...
in 2010 sounded the alarm for alumina enterprises in China and even around the world, causing alumina enterprises to attach great importance to the safety of red mud stockpiled. The treatment of red mud has become a worldwide problem. Accordingly, the development of a new comprehensive utilization technology for alkaline red mud could resolve the problem of environmental pollution and it is also an issue of the comprehensive utilization of resources, which is of great significance.

**General situation of red mud**

**Physicochemical properties of red mud**

Red mud commonly appears off-white, brown, or red due to the different contents of iron oxide (Li et al. 2020). The higher the iron oxide content in red mud, the redder the red mud is. The bauxite needs to be ground before dissolution, so the particle size of Bayer red mud is minor. The microstructure results of the red mud show that red mud is generally composed of small particle condensates and aggregates, and the specific surface area commonly ranges from 64.1 to 186.9 m²·g⁻¹ (Jing et al. 2001). The red mud has a loose pore structure with a density from 2.7 to 2.9 g·cm⁻³ and a bulk density from 0.8 to 1.0 g·cm⁻³. The water content of red mud is between 82.3 and 105.9% when it is first discharged. The saturation of red mud ranges from 91.1 to 99.6%, and its plasticity index is between 17.0 and 30.0 (Jing et al. 2001). The melting point of red mud ranges from 1200 to 1250 °C because of sodium oxide (Liao et al. 2019).

In the Bayer process, the alumina is dissolved by the alkali solution (the mother solution) from the bauxite at high temperature to form sodium aluminate solution. Nevertheless, the oxides of iron, silicon, calcium, and titanium do not participate in the reaction and ultimately enter the red mud. Some incompletely dissolved alumina from bauxite and part of the sodium oxide will also enter the red mud. Different compositions of bauxite lead to different compositions of red mud. The main chemical components of Bayer red mud in some countries are shown in Table 1 (Qi 2019; Prasad and Singh 1997; Snars and Gilkes 2009; Wehr et al. 2006; Mohapatro and Rajanikanth, 2012; Altundogan et al. 2002). Red mud also contains a small amount of vanadium, zirconium, chromium, scandium, germanium, gallium, niobium, rhenium, yttrium, uranium, radium, and other rare metals and radioactive elements. These rare earth metals are unevenly distributed in red mud and exist predominantly in the form of isomorphisms (Li et al. 2013).

**Hazard of red mud**

At present, China generates more than 77 million tons of alumina, resulting in emissions of more than 110 million tons of red mud emissions. Such a large amount of red mud not only occupies a large amount of land and farmland but also causes great harm to the surrounding environment. In addition to the free alkali, red mud likewise contains chemically bound alkali in the form of sodium aluminosilicate hydrate, which is not readily soluble in water, resulting in strong buffering capacity and extreme alkalinity (Li et al. 2018b) and causing great harm to the environment. For example, the soluble alkali contained in red mud could seep into the ground with rainwater, polluting soil, and groundwater resources. Due to the fine particle size of red mud, the surface layer of uncovered red mud will be blown into the air and spread by the wind, causing air pollution. After being breathed, the fine particles of red mud will cause damage to the respiratory systems of humans and animals. In 2010, the red mud dam in Hungary breached, releasing approximately 1 million cubic meters of red mud, flooding 40 km² of agricultural and urban land, killing 10 people, and injuring more than 150 others. When the spilled red mud flowed into nearby rivers, the pH value of the river reached 13, which ultimately led to the extinction of invertebrates and fish and then polluted the Danube River, causing panic in numerous European countries (Yang and Wu 2017). In 2014 and 2016, landslides occurred at red mud dams of alumina companies in China, burying houses, livestock, grain, and other property in a village downstream and affecting more than 300 people. How to deal with the large amount of red mud that has been accumulated and generated every year has become a bottleneck that limits the development of the alumina industry, and it is a difficult problem that must be resolved for the sustainable development of the alumina industry.

At present, the comprehensive utilization of Bayer red mud is predominantly divided into the following aspects: (1) the overall utilization in the fields of building materials,
Fig. 2 Alumina production (a) and red mud emissions (b) of Chinese provinces in 2021 (× 104 t)
agriculture, the environment, and the chemical industry; (2) the recovery of valuable components from red mud; (3) the extraction of rare metals from red mud; and (4) the recovery of iron from red mud.

**Overall utilization status of Bayer red mud**

The main chemical components of red mud are alumina, silica, iron oxide, and sodium oxide, which have small particle sizes and a certain viscosity, plasticity and workability. Figure 3 shows the overall utilization of red mud concentrated in building materials, agriculture, environment, chemical industry, and so on (Liu et al. 2014a; Khairul et al. 2019). The silica, calcium oxide, and aluminosilicate contained in red mud have good hydration activity and can be used to prepare building materials (Wu et al. 2019). At present, red mud is predominantly used in the field of building materials in the preparation of bricks, cement, and glass ceramics. The bricks made of red mud meet the requirements of building bricks in terms of compressive strength, density and flexural strength and have the advantages of low production cost and large consumption of red mud. Nonetheless, on account of the high alkali content of red mud, the prepared bricks readily have a saltpetering phenomenon, which decreases the strength of bricks and affects the aesthetics and service life of buildings (Kong et al. 2017). Although the compressive strength of cement produced by red mud is better than that of ordinary cement, the cement is prone to saltpetering when used as building materials in construction due to its strong alkali and difficulty in removal, resulting in the loosening and shedding of wall skin and reducing the service life of buildings (Zhang et al. 2018). Glass ceramics with high hardness, high bending strength, and excellent acid and alkali resistance can be prepared by using red mud as a raw material and mixing quartz, tacle, and other additives. However, high energy consumption in the preparation process, alkalinlity, and radioactivity in red mud will also affect the application field of glass ceramics (Yang et al. 2008).

In addition to alumina, silica, and iron oxide, red mud also contains phosphorus, calcium, and magnesium, which can provide nutrients for plant growth. Consequently, red mud can be used to improve soil (Brunori et al. 2005). Due to its strong alkalinity, red mud can be used to upgrade the pH value of acidic soil (Feigl et al. 2017). Additionally, the strong adsorption performance of red mud can also be used to treat soil tainted by heavy metals and solidify heavy metals (Luo et al. 2011). Although the application of red mud to improve soil has a good effect, the application field is deeply targeted and only suitable for the improvement of acidic soil or soil tainted with heavy metals. The dosage of red mud in soil improvement is limited, which cannot achieve the purpose of large-scale treatment of red mud.

In addition to its application in agriculture, red mud can also be implemented for waste gas treatment and wastewater treatment in the environmental field (Fois et al. 2007). Alkaline red mud has superior reactivity with acid gas (Zhang et al. 2021c). Furthermore, red mud has the characteristics of small particle size, massive specific surface area, and more alkaline oxides, so it can be used for desulfurization of industrial flue gas containing H₂S, SO₂, NOₓ, and other pollutants (Li et al. 2022b). Red mud could be used as an additive to modify activated carbon to generate the dry desulfurization agent. After modification, the desulfurization rate of activated carbon with the addition of red mud was 17.9% higher than that of activated carbon alone (Niu et al. 2021). The desulfurization rate of hydrometallurgical desulfurization is superior to that of dry desulfurization. Red mud slurry was used for desulfurization in an absorption tower, and the desulfurization rate was > 95% under the optimal operating conditions (Wei 2012). Nie et al. (2019) used a red mud slurry for desulfurization. The removal rate of SO₂ reached over 98% as the pH value of the red mud slurry surpassed 7. After drying, the desulfurized red mud could be used to produce polymers with fly ash. For application in wastewater treatment, modified red mud can be used as an adsorbent to adsorb heavy metal ions in wastewater (Chen et al. 2019). Additionally, the red mud-fly ash particle electrode can be used for the degradation of atrazine in wastewater (Teng et al. 2021). Nevertheless, the application of red mud in wastewater treatment still has many problems to be resolved, and it is impractical to apply red mud in large

| Country/Region      | Alumina plant | Al₂O₃ | SiO₂ | Fe₂O₃ | Na₂O | CaO | TiO₂ |
|---------------------|---------------|-------|------|-------|------|-----|------|
| China/Guangxi       | Ping-guo      | 19.10 | 9.18 | 32.20 | 4.38 | 14.02 | 9.39 |
| Canada              | ALCAN         | 20.61 | 14.30 | 31.60 | 10.26 | 1.66 | 6.23 |
| Australia/Gove      | Rio Tinto     | 20.80 | 8.89 | 30.00 | 8.10 | 2.00 | 8.30 |
| Brazil/Balconera    | Alunorte      | 15.10 | 15.60 | 45.60 | 7.50 | 1.16 | 4.29 |
| Spain               | Alcoa         | 21.20 | 4.40 | 37.50 | 3.60 | 5.51 | 11.45 |
| United States/Arkansas | Alcoa     | 12.15 | 4.50 | 55.6  | 2~5  | —   | 4.50 |
| Hungary             | MAL           | 15.20 | 10.15 | 38.75 | 8.12 | —   | 4.60 |
| Jamaica             | ALPART        | 14.20 | 3.40 | 50.90 | 3.18 | —   | 6.87 |
| Turkey              | Seydisehir    | 20.40 | 15.74 | 36.90 | 10.10 | 2.20 | 4.90 |

Table 1 Chemical compositions of red mud in different countries (wt%)
quantities for wastewater treatment. As red mud is highly alkaline, its direct use will cause secondary pollution of water, and it can be used for wastewater treatment only after acidification and activated modification, which will increase the treatment cost and limit the application of red mud in wastewater treatment.

The main application of red mud in the chemical industry is the preparation of catalysts, ceramics and filler materials (Sutar et al. 2014). Commercial catalysts prepared by modified red mud can be used for catalytic hydrogenation, methane degradation, dehydrochlorination, etc. (Sushil and Batra 2008). Starch and manganese dioxide can also be used as foaming agents to prepare red mud-and fly ash-based foam ceramics (Hou et al. 2017). Shao et al. (2021) researched the preparation of the layered ferroelectric perovskite $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ from red mud by a molten-salt growth method. As a result, the photocatalytic activity of red mud-doped samples was enhanced. Porous ceramic materials prepared by red mud can be used in the water treatment process (Li 2008). Although the preparation of catalysts or ceramics by red mud is of significant economic value, the amount of red mud used in this field is comparatively limited. Compared with the yearly emissions of more than 100 million tons of red mud, the chemical industry can only utilize a very small part of the red mud and is unable to fundamentally resolve the problem of red mud emissions and stockpiling.

**Recovery of valuable components from Bayer red mud**

**Dealkalization of red mud**

In the Bayer process, alkali consumption accounts for approximately 20% of the direct production cost of aluminum hydroxide. The high content of sodium alkali in red mud limits its application in many fields. Therefore, it is necessary to deal with the red mud. The commonly used methods of red mud dealkalization include water washing, acid leaching, lime dealkalization, and acid gas neutralization (Li et al. 2017b; Sanchez-Segado et al. 2015; Zhang and Mo 2019). The water washing method utilizes the solubility of alkaline substances contained in red mud in water to soak red mud for a long time and wash it many times to remove soluble alkali in red mud to achieve the purpose of dealkalization of red mud. It is the simplest method for red mud dealkalization at present. Zhu et al. (2016a) used Bayer red mud with a sodium oxide content of 5.72% as a raw material for water leaching dealkalization experiments, and the results showed that the process of water leaching dealkalization of red mud was controlled by diffusion steps, and the removal rate of alkali was 71%.

For the acid leaching method, inorganic acids or organic acids are used to react with alkaline substances in red mud to achieve the dealkalization of red mud.
Commonly used inorganic acids are hydrochloric acid, sulfuric acid, and nitric acid. Liang et al. (2014) used hydrochloric acid, nitric acid, and sulfuric acid to acidify the Bayer red mud for dealkalization. The results demonstrated that in the acid leaching process, the acid can not only remove the free alkali in red mud but also react with part of the bound alkali to achieve depth control of the red mud alkalinity.

In the lime dealkalization process, $\text{Ca}^{2+}$ with a stronger ion exchange capacity in lime is used to replace $\text{Na}^+$ in sodium aluminosilicate hydrate. Then, $\text{Na}^+$ forms soluble sodium hydroxide, which is dissolved in the liquid phase. On the other hand, $\text{Ca}^{2+}$ can combine with free basic anions in the red mud slurry to generate insoluble calcium salts and stable chemically bound bases so that the alkalinity of red mud is controlled (Liu et al. 2017; Xu et al. 2010). Zhu et al. (2018) researched the selective leaching of sodium oxide from red mud with CaO by the pressure leaching method, and the process steps are shown in Fig. 4. Under the optimum technological conditions, the dissolution rate of sodium oxide exceeded 85%, and the content of sodium oxide in the final tailings was less than 1%. Zhong et al. (2009) extracted $\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}$ from red mud utilizing a hydrothermal method. After a two-step hydrothermal reaction, the recoveries of alumina and sodium oxide were 87.8% and 96.4%, respectively. The content of $\text{Na}_2\text{O}$ in the final residues was less than 1%, which could be used for the production of construction materials.

![Diagram of lime dealkalization process](image)

The acidic gas neutralization method utilizes acid gases $\text{CO}_2$ or $\text{SO}_2$ to neutralize alkaline substances in red mud based on the acid–base neutralization reaction and ultimately achieves the dealkalization of red mud. There are two main acid gas neutralization methods: $\text{CO}_2$ carbonization and $\text{SO}_2$ neutralization. Each ton of red mud can absorb roughly 53 kg of $\text{CO}_2$ (Yadav et al. 2010). Han et al. (2017) investigated the carbon mineralization of red mud by ambient $\text{CO}_2$. The results indicated that ambient $\text{CO}_2$ favored the neutralization of pore water alkalinity without the addition of an extra Ca source. However, the addition of Ca induced further neutralization to form $\text{CaCO}_3$. Wang et al. (2015) adopted $\text{SO}_2$ and $\text{SO}_2$-based dealkalization agents ($\text{SO}_2 + \text{N}_2$ and $\text{SO}_2 + \text{CO}_2 + \text{N}_2$) to simulate flue gas for the dealkalization treatment of red mud. The results demonstrated that under the optimum conditions, no matter what type of simulated flue gas was utilized, the residual $\text{Na}_2\text{O}$ in red mud after dealkalization could be reduced to less than 1%. When $\text{SO}_2 + \text{CO}_2 + \text{N}_2$ was used to remove $\text{Na}_2\text{O}$ from red mud, it would take a long time because of the decrease in $\text{SO}_2$ concentration in the simulated flue gas.

Although the process of dealkalization by water washing is simple, it can only remove soluble alkali from red mud, and the removal rate of alkali is limited. At the same time, the water washing method will consume a large amount of water, the immersion time is likewise long, and a large amount of dilute alkaline liquor generated at the same time cannot be effectively treated, which limits the application of the water washing method. For the acid leaching method, not only will a large amount of waste acid be generated in the process of dealkalization but also a large amount of iron oxide and other alkaline substances in red mud will consume a large amount of acid, which will lead to an increase in the cost of dealkalization. The acidic gas neutralization method has good results for alkali removal, but its industrial application is restricted due to the gas concentration, equipment, and transport of red mud. The alkalinity of red mud can be regulated by the lime desalination method, during which $\text{Ca}^{2+}$ is used to replace $\text{Na}^+$ in sodium aluminosilicate hydrate. If this method is only used to eliminate alkali from red mud, the economic benefit is poor, so it is generally used in combination with the alumina extraction method.

**Recovery of alumina**

The content of alumina in Bayer red mud is approximately 20%, which has great value for extraction and recovery. At present, the main recovery methods of alumina from red mud are the acid method and alkali method. The acid method is predominantly based on the reaction of organic and inorganic acids (hydrochloric acid, sulfuric acid, phosphoric acid, oxalic acid and citric acid, etc.) with the alumina in red mud to generate aluminum hydrate ions.
Pepper et al. (2016) explored the effects of four acids (nitric acid, hydrochloric acid, sulfuric acid, and phosphoric acid) on the leaching behaviors of iron, titanium, aluminum, and silicon in red mud and found that phosphoric acid and hydrochloric acid were beneficial to the leaching of iron and titanium, while phosphoric acid was favorable to the leaching of silicon and aluminum, and the leaching rate of alumina was up to 50%. Although the acid method has the characteristics of a simple process, simple operation, and low energy consumption, the large amount of alkaline substances contained in the red mud will lead to excessive acid consumption and produce a large amount of waste liquid, which readily causes secondary pollution.

The alkali method principally includes the alkali dissolving method, sintering method, and sodium (Wang et al. 2019b). Sun et al. (2008) treated Bayer red mud by the NaOH sub-molten salt method and investigated the effects of temperature, alkali/mud ratio, calcium oxide addition amount, and other conditions on the composition and phase of red mud. The results demonstrated that increasing the temperature and alkali/mud ratio was profitable for recovering alumina. Under the optimal conditions, the alumina recovery reached 79.22%, and the Al/Si ratio in the tailings was reduced to 0.39. Li et al. (2009a) surveyed the influence of the calcium ratio, alkali ratio, sintering temperature, and time on the dissolution rate of alumina in red mud by the sintering method after mixing lime, soda ash, and Bayer red mud. Under the optimum sintering conditions (calcium ratio of 2.4, alkali ratio of 1.8, sintering at 1030 °C for 40 min), the recovery of alumina attained 83.12% after the sintering clinker dissolved in dilute alkali solution at 85 °C for 25 min. The final alumina content in tailings was 4.72%, and the alumina/silica ratio was decreased from 1.33 in red mud to 0.19 in tailings. Li et al. (2009b) recovered alumina and ferric oxide from high-iron red mud with the process of solid reduction sintering and leaching followed by magnetic separation. The results demonstrated that the reduction temperature and carbon addition were the primary factors affecting the alumina recovery. With the optimal reduction sintering parameters, alumina recovery reached 89.71%. Li et al. (2014b) verified the feasibility of extracting Fe, Al, and Si from red mud by the processes of roasting reduction and magnetic separation followed by sulfuric acid leaching. The results indicated that sodium salts were appropriate for the reduction of iron oxides and facilitating the growth of reduced metals. Furthermore, the activation of Al and Si components was reinforced by sodium salts during the roasting reduction process. A total of 95.0% of iron was recovered in the form of magnetic concentrate after magnetic separation. Then, 94.7% Fe, 98.6% Al, and 95.9% Si were extracted from the nonmagnetic material by a sulfuric acid leaching process. TiO2 was refined in the final leaching tailings with a content of 37.8%, which could be used for the extraction of TiO2.

To extract alumina from hydrated garnet, Liu et al. (1999) studied the effects of temperature, time, liquid–solid ratio, type of mother liquor, and saturation coefficient on the extraction rate of alumina in the decomposition process of hydrated garnet by sodium carbonate solution. The results implied that increasing the temperature was beneficial to the decomposition of hydrated garnet, while the increase in the silicon saturation coefficient led to a more stable structure of hydrated garnet, which was not conducive to the decomposition process. To extract alumina from high-sulfur bauxite, high-sulfur bauxite and Bayer red mud were used as raw materials to recover alumina by synergistic alkaline roasting (Fig. 5) (Xiong et al. 2021). The effects of roasting temperature, dissolution temperature, dissolution time, liquid–solid ratio, sodium hydroxide concentration, and sodium carbonate solution concentration on alumina dissolution were researched in detail. The results indicated that the increase in temperature was beneficial to the formation of sodium aluminate. Fe2O3 in red mud preferentially reacted with FeS2 in high-sulfur bauxite to generate Fe3O4. The alumina dissolution rate reached 92.16% under the optimal roasting and dissolution conditions.

![Fig. 5 Recovery of alumina from red mud and high-sulfur bauxite by synergistic roasting](image-url)
Extraction of rare metals from Bayer red mud

In the Bayer process of alumina production, the rare metals contained in bauxite are ultimately enriched in red mud. After enrichment, the content of rare metals in red mud is approximately twice that in bauxite (Ochsenkühn-Petropulu et al. 1994). The main rare metals in red mud are titanium, followed by scandium, vanadium, yttrium, and lanthanide rare earth (Khairul et al. 2019).

Extraction of titanium

Red mud is rich in titanium dioxide, whose content is normally 4~12%, which has great recycling value (Li et al. 2016). In the process of alumina production by the Bayer process, more than 95% of titanium dioxide contained in bauxite will be enriched in red mud (Li et al. 2014a). At present, there are two main methods of extracting titanium dioxide from red mud: the pyrometallurgical method and the hydrometallurgical method.

For the pyrometallurgical process, iron, aluminum, silicon, and other elements in red mud are removed through high-temperature roasting or smelting reduction so that titanium dioxide is enriched in the slag. Then, sulfuric acid is used to leach titanium dioxide from the slag. For the hydrometallurgical extraction process, the dilute hydrochloric acid is used to leach alumina, ferric oxide and other substances in red mud, and then the leaching residue is leached by sulfuric acid to extract titanium dioxide. After solvent extraction and reverse extraction, the titanium was eventually extracted (Sayan and Bayramoglu 2004). Sulfuric acid is the most applicable acid for hydrometallurgical extraction of titanium dioxide from red mud because titanium dioxide can react with sulfuric acid to produce soluble TiOSO₄ (Zou et al. 2021). Nonetheless, to improve the purity of titanium dioxide, other elements in the red mud are generally leached with hydrochloric acid first so that the titanium dioxide can be enriched in the leaching residue, which is convenient for further recovery. Kasliwal and Sai (1999) first extracted calcium, iron, and sodium from red mud with hydrochloric acid. Then, alumina and silica were converted into water-soluble sodium aluminate and sodium silicate by sodium carbonate roasting. The main component of the final leaching residue was titanium dioxide. The titanium dioxide recovery was 36% by hydrochloric acid leaching, and the recovery of titanium dioxide could be increased to 76% after roasting sodium carbonate. Zhu et al. (2021) prepared titanic-rich material from red mud by an activated roasting-combined leaching method, as shown in Fig. 6. The influence of acid leaching, roasting, and water leaching conditions on the leaching process of valuable elements in red mud was investigated. The results indicated that the leaching rates of aluminum, iron, and sodium were 81.2%, 76.3%, and 99.2%, respectively. In addition, the leaching rates of vanadium, scandium, and yttrium all surpassed 95% in the acid leaching process. After roasting and water leaching, the leaching rate of silicon was 85.7%, and the grade of TiO₂ in the titanium-rich material was 71.8%. Zhu et al. (2015) proposed using citric acid in sulfuric acid to recover titanium from red mud to enhance the acid leaching efficiency of red mud. The effects of the amount of citric acid, concentration of sulfuric acid, leaching temperature, leaching time, and liquid-solid ratio on titanium recovery were carried out, and the kinetics of titanium leaching from red mud were studied in detail. The results demonstrated that citric acid enhanced the recovery rate of titanium and reduced the dosage of sulfuric acid, and the recovery rate of titanium was up to 82%. Citric acid could readily dissolve the perovskite, plate titanium, and hematite in red mud, and the acid leaching process was controlled by diffusion in the shrinkage core model.

Due to the massive content of iron oxide and alumina in red mud, the recovery of titanium dioxide will result in high acid consumption and high cost, which limits its commercial application.

Extraction of scandium

Scandium is a rare metal with minimal content in the Earth’s crust and few independent ore deposits (Liu et al. 2022). It
normally coexists with bauxite, ilmenite, and rare earth ores (Hu et al. 2020). Approximately 80% of scandium in nature occurs in bauxite (Yan et al. 2020). In the process of alumina production, more than 98% of scandium oxide in bauxite will enter the red mud, and the content of scandium oxide in some red mud can reach up to 0.02% (Wang et al. 2010). There are two main methods to extract scandium from red mud: pyrometallurgical extraction and hydrometallurgical extraction. The hydrometallurgical extraction method of acid leaching and extraction can be used for extracting scandium from low-iron red mud. In acidic media, red mud is first treated with acid leaching, during which scandium reacts with bisulfate ions to form a complex $\text{HSc(SO}_4\text{)}_2$, as shown in Eq. (1), then the $\text{HSc(SO}_4\text{)}_2$ reacts with the organic extractant Cyanex 923 and can be extracted from the acid leaching solution (Eq. (2)) (Junior et al. 2021).

$$\text{Sc}^{3+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq}) + \text{HSO}_4^-(\text{aq}) \rightarrow \text{HSc(SO}_4\text{)}_2(\text{aq}) \quad (1)$$

$$\text{HSc(SO}_4\text{)}_2(\text{aq}) + (\text{HX})_2(\text{org}) \rightarrow \text{HSc(SO}_4\text{)}_2(\text{HX})_2(\text{org}) \quad (2)$$

In the solvent extraction process of scandium, acidic organophosphorus extraction agents (P204, P507, Cyanex272, etc.) are commonly used to extract scandium (Zhang et al. 2021b). It can also separate and recover scandium by extraction of leaching solution after sulfatizing roasting followed by leaching process. Borra et al. (2017) recovered alumina from red mud by an alkali roasting process. Metallic iron was retrieved from the roasting residue by the smelting method. Then, the rare-earth elements were extracted from reduced slag by acid leaching. The results showed that, except for scandium, the recovery of rare-earth elements was drastically diminished due to the generation of perovskite. The formation of $\text{CaTiO}_3$ was suppressed by water quenching, enhancing the dissolution of the rare-earth elements and titanium in acidic solutions at 25 °C.

For high-iron red mud containing scandium, a more reasonable treatment method is to extract iron first from the high-iron red mud by roasting reduction or smelting reduction. In the reduction process, scandium oxide does not participate in the reaction and eventually enters the reduction slag. After extracting alumina from the reduction slag, scandium can be extracted from the tailings by acid leaching and extraction methods.

### Recovery iron from Bayer red mud

The main form of iron in red mud is hematite ($\text{Fe}_2\text{O}_3$), and a small amount of iron is in the form of goethite ($\text{FeOOH}$) (Klauber et al. 2011). Depending on the source of the raw materials, the $\text{Fe}_2\text{O}_3$ content in red mud ranges from 6.8 to 71.9%. Generally, red mud with more than 30% $\text{Fe}_2\text{O}_3$ content is considered high-iron red mud (Gu et al. 2018), which is considered a potential iron resource. Red mud with $\text{Fe}_2\text{O}_3$ contents below 30% is called low-iron red mud. Due to the low iron content, the economic value of iron extraction is low. Hence, low-iron red mud is rarely utilized as a raw material for iron extraction.

The external bauxite has a high iron content, and the red mud produced is predominantly high-iron bauxite red mud. For example, the content of $\text{Fe}_2\text{O}_3$ in high-iron red mud in Australia is as high as 60%. Most of the bauxite in China is monohydrate bauxite, among which the bauxite contained in Guangxi Pingguo area is high-iron monohydrate bauxite. Consequently, the red mud produced after the production of alumina from this bauxite is called high-iron monohydrate bauxite red mud.

Due to the geographical advantage of the ocean, most alumina enterprises in Shandong utilize imported foreign bauxite as a raw material to produce alumina. The red mud produced from this bauxite is high-iron red mud. The other domestic alumina enterprises utilize low-iron monohydrate bauxite, so the red mud essentially belongs to low-iron monohydrate bauxite red mud. There is a small amount of low-iron sintering red mud.

At present, numerous investigations have been carried out on the recovery of iron from high-iron red mud, including physical magnetic separation, hydrometallurgical recovery method, solid phase reduction-magnetic separation, and smelting reduction.

### Physical magnetic separation method

Hematite contained in high-iron red mud has a weak magnetism. The recovery of iron by the physical magnetic separation method takes advantage of the weak magnetism of hematite in the high-iron red mud and uses magnetic separation equipment with high magnetic field intensity to carry out the magnetic separation experiments to achieve the separation of hematite and aluminum-silicon impurities in the high-iron red mud. After magnetic separation, an iron-rich concentrate is obtained.

Guan (2000) used Bayer high-iron red mud as a raw material to recover iron concentrate with an SLon-type vertical ring pulsating high gradient magnetic separator. The recovery of iron in high-iron red mud was 35.36%, and the TFe content in the obtained iron concentrate was 54.7%. Nonetheless, the yield of iron concentrate obtained by this process was only 12.28%, and the remaining non-magnetic tailings were not treated, which could not fundamentally resolve the problem of red mud stockpiling.

The recovery of iron by the physical magnetic separation method is simple and easy to operate; however, the recovery
of iron by this method is less than 50%. The iron concentrate obtained by magnetic separation still contains a certain amount of sodium oxide, which will corrode the lining of the blast furnace. Therefore, the iron concentrate cannot be used directly as a raw material for blast furnace ironmaking. Generally, the yield of iron concentrate is less than 20%, and the remaining red mud over 80% cannot be treated, which has not actually solved the problem of high-iron red mud stockpiling.

For the physical magnetic separation method, the process is simple and easy to operate. Nonetheless, due to the fine grain size of red mud, both the recovery of iron and the efficiency of the conventional physical magnetic separation method are low. The weak magnetic fine hematite particles are inclined to enter into the tailings on account of the weak magnetic force. Consequently, the recovery rate of iron concentrate in the magnetic separation process is low, generally less than 20% and the remaining 80% of alkaline nonmagnetic tailings are not further utilized, which cannot fundamentally resolve the problem of red mud stockpiling.

Hydrometallurgical recovery method

For the hydrometallurgical recovery method, the high-iron red mud is leached by acid solution, and then, the iron ions are recovered from the leach solution. Hydrochloric acid, sulfuric acid, phosphoric acid, nitric acid, and oxalic acid are the primary acids used in the hydrometallurgical recovery method.

Xie et al. (2017) carried out acid leaching experiments of high-iron red mud with hydrochloric acid solution. The influence of different red mud particle sizes, leaching temperatures, leaching times, liquid–solid ratios, and mass concentrations of hydrochloric acid on the leaching results was investigated in detail. The results proved that the leaching temperature and mass concentration of hydrochloric acid were the main factors affecting leaching. When 10 mol·L⁻¹ hydrochloric acid was used to leach red mud with a particle size of 150 μm, the leaching rates of aluminum and iron were 96.7% and 95.1%, respectively. In the leaching process, both iron and aluminum entered into the solution, and it was difficult to recover iron separately from the leaching solution. Therefore, iron and aluminum leaching solutions could be used as raw materials to prepare flocculants applied in the water treatment industry.

The hydrometallurgical recovery method has the advantages of a simple process, low energy consumption, and high leaching rate. Nevertheless, in the leaching process, the alkaline oxide in red mud will also react with acid, resulting in an increase in acid consumption and recovery cost. At the same time, a large amount of waste acid cannot be treated, causing secondary pollution to the environment. The content of impurities in the leaching solution is high, which makes subsequent separation and impurity removal problematic.

In addition to the hydrometallurgical acid leaching method, Wang et al. (2019a) recovered iron and aluminum from red mud by the rice stalk hydrothermal method. In this method, hematite in red mud was reduced to magnetite in an alkaline system using waste rice stalks as a reducing agent. Alumina was extracted during the dissolution process, and high purity magnetite could be obtained from tailings by magnetic separation. The results indicated that when the mass ratio of rice stalk to red mud was 20%, the reaction temperature was 300 °C, the mass concentration of caustic soda was 220 g·L⁻¹, the ratio of liquid to solid was 5:1, the stirring speed was 600 r·min⁻¹, the dissolution rate of alumina was 91.2%, and the reduction rate of iron oxide was 98.1%. This method can not only dissolve alumina by the hydrothermal method but also reduce hematite in red mud under the action of a reducing agent and eventually recover alumina and iron in red mud. Moreover, the reaction temperature is lower, and the magnetite concentrate obtained by magnetic separation has a high grade, which can be used as a raw material for ironmaking.

At present, there are relatively few reports on the hydrometallurgical extraction of iron from red mud. For the hydrometallurgical recovery method, in addition to the acid consumption of hematite, a large amount of acid should be consumed to neutralize red mud during acid extraction due to the high alkalinity of red mud. This would result in an increase in iron extraction costs and a large amount of waste liquid, causing secondary pollution. The hydrometallurgical recovery method has mild reaction and high extraction rate of iron, but the subsequent separation of iron from other metals will increase the cost.

Solid phase reduction-magnetic separation method

For the solid phase reduction-magnetic separation method, high-iron red mud, reducing agent, and additives are mixed and roasted at high temperature. Hematite (Fe₂O₃) in high-iron red mud is reduced to magnetite (Fe₃O₄) or metallic iron (granular iron) at high temperature (Liu et al. 2021; Xiao et al. 2022a, b). After grinding the reduction sample, magnetite or metal iron powder (sponge iron) products can be obtained through physical magnetic separation. Nonmagnetic tailings can be used as raw materials to prepare building materials or to further extract alumina. The reducing agents commonly used in the solid phase reduction process predominantly include coal-based reducing agents (coke, coking coal, bituminous coal, anthracite, graphite powder, activated carbon, carbon powder, waste cathode carbon block, etc.), gas reducing agents (carbon monoxide, natural gas, hydrogen, etc.), biomass reducing agents (charcoal, sawdust, bagasse, etc.), and pyrite reducing agents.
Liu et al. (2008) used Bayer high-iron red mud as a raw material, activated carbon as a reducing agent, and calcium carbonate and magnesium carbonate as additives and recovered sponge iron products after solid phase reduction and magnetic separation (Fig. 7). The iron content in the magnetic concentrate was 89.05%, the iron recovery was 81.40%, and the metallization rate of iron in the concentrate was 96.98%. Nonmagnetic tailings were used to produce steam curing brick products by adding slaked lime and through the process of extrusion forming and steam curing. The compressive strength of the steam curing brick was 24.10 MPa, and the strength of the products satisfied the requirements of steam curing bricks. Bayer red mud with 19.6% iron content was blended with 50% carbon powder and 4% additive and then roasted at 700 °C for 20 min. The roasted products were ground and magnetically separated to obtain a magnetite concentrate with 60% total iron and an iron recovery of 91% (Liu et al. 2016). In the study of Lu, the waste cathode carbon block was used as the reducing agent to reduce the high-iron red mud to obtain the iron concentrate powder by magnetic separation. After roasting at 1050 °C for 100 min, iron concentrate with an iron grade of 43.71% was obtained by magnetic separation when the cathode carbon powder content was 15%. Nevertheless, the yield of iron concentrate was only 44.31% (Lu 2015).

Iron in Bayer high-iron red mud predominantly exists in the form of hematite, which can be reduced to metal iron by pure H₂ or CO reduction gases. During the reduction of high-iron red mud dealkalized by CO₂, the reduction degree of hematite reached 99.5% in a H₂ atmosphere reduced at 1000 °C for 4 h (Hao et al. 2015). Almost all the iron in the reduction products existed in the form of metallic iron. The main factor affecting the reduction result was the reduction temperature, and there was no sintering phenomenon in the reduction products, which was conducive to separating metal iron and slag by direct physical magnetic separation.

Biomass is primarily composed of lignin, cellulose, and hemicellulose, mainly containing C, H, O, N, S, and a small amount of ash, which is suitable for reducing high-iron red mud. The experimental results of reducing high-iron red mud with pine sawdust and bituminous coal as reductants indicated that pine sawdust more readily underwent pyrolysis reactions than bituminous coal (Li et al. 2017a). The reduction temperature of pine sawdust was approximately 200 °C lower than that of bituminous coal, and the reduction time was shorter than that of bituminous coal.

Pyrite is widely available and inexpensive and is often used as a reducing agent because of the negative 1 value of sulfur it contains. Liu et al. (2014b) carried out anaerobic co-roasting experiments on high-iron red mud with pyrite. The hematite in high-iron red mud was converted to magnetite, and then, the reduced magnetite was recovered by a magnetic separation process. The results revealed that pyrite could be decomposed into ferrous sulfide, pyrrhotite, and elemental sulfur after heating, which could reduce hematite to magnetite. After roasting at 600 °C for 30 min in a N₂ atmosphere, the iron content could be reduced from 9.24% in red mud to 0.61% in magnetically separated tailings. Approximately 4.5 g magnetic
iron concentrate with a total iron content of 36.9% could be obtained by magnetic separation from 30 g red mud.

Solid phase reduction-magnetic separation technology is mainly composed of low-temperature reduction roasting-magnetic separation (usually lower than 1200 °C) and high-temperature reduction roasting-magnetic separation (usually higher than 1200 °C). For the former method, the energy consumption and cost are low; however, the total grade of iron concentrate is relatively low. Also, it has a poor iron recovery rate, and the index of iron concentrate does not meet the requirements of iron making. For the high-temperature reduction roasting method, although high-quality iron concentrate could be obtained, it consumes high energy and the reduction process is costly.

The most important thing is, after magnetic separation, the remaining tailings still contain alkali, which does not solve the problem that the red mud containing alkali cannot be used on a large scale. This solid phase reduction-magnetic separation method will have a potential application prospect for the dealkalized red mud if recovery of iron could be improved and the amount of reducing agent could be reduced.

**Smelting reduction method**

For the smelting reduction method, high-iron red mud, reducing agent, and additives are mixed and melted at high temperature. Due to the high reduction temperature, molten iron containing carbon and molten slag is obtained. Molten iron-containing carbon can be directly used as a raw material for steelmaking, and reduction slag can be further used to extract alumina and rare metals or directly used to prepare building materials. The iron in high-iron red mud can be recovered effectively by the smelting reduction method. The high temperature of smelting reduction provides good conditions for the settlement separation of slag and molten iron. In the smelting reduction process, a coal-based reducing agent is used to reduce hematite in high-iron red mud, and the combustion of CO generated in reduction will also provide heat for the system.

Liu et al. (2020b) prepared anti-wear and low-alloy white cast iron from Bayer red mud. Bayer red mud and coke were mixed and pelletized by a disk pelletizer and dried in an oven. The dried pellets were then melted in an intermediate frequency induction furnace and reduced. The results indicated that the smelting reduction of hematite in high-iron red mud was carried out to generate CO. High hardness and hypoeutectic white cast iron were obtained after reduction at 1600 °C for 20 min. After testing, the wear property of metal iron was excellent. Li et al. (2018a) adopted the method of “direct reduction in rotary hearth furnace and melting in gas furnace” to reduce the Bayer red mud. After reduction and melting, the iron content in the molten iron was 93%, and the molten iron and slag were completely separated. Wang et al. (2012) prepared iron beads from carbon-containing pellets consisting of high-iron red mud and coal powder by direct reduction and melting at high temperature. Temperature and the amount of calcium fluoride were the key factors affecting the reduction and melting of pellets. Under optimal conditions, the slag and iron could be separated after reduction. The contents of carbon and sulfur in the obtained iron beads were 2.72% and 0.48%, respectively, which could be directly used directly as raw materials for steelmaking. After reduction, the content of scandium oxide in slag was 0.0184%, which could be used as a high-quality raw material for scandium extraction. Guo et al. (2013) carried out reduction experiments on red mud by the orthogonal test method, and iron nuggets were obtained by the smelting reduction of carbon-containing pellets with high-iron red mud and coal. Temperature was the most important factor affecting the separation of molten iron and slag. At 1400 °C and a C/O molar ratio of 1.6:1, iron nuggets were obtained when pellets with a basicity of 1.0 were reduced for 30 min. The separation of molten iron and slag was comparatively thorough. The total iron content in the obtained iron nuggets was higher than that of the molten iron from the blast furnace. The contents of Si and Mn in the iron nuggets were low, while S and P were high.

The smelting reduction method is a promising method to recovery iron from red mud. The reduction efficiency of the smelting reduction method is higher than that of the solid phase reduction-magnetic separation method, and the iron grade of the final metal product is higher. The quality of molten iron-containing carbon gained by smelting reduction is comparable to that of blast furnace pig iron. Therefore, the reduced pig iron can be directly used as a raw material for steelmaking. However, the sodium-bearing alkali slag seriously corrodes the refractory lining in the reduction process, and the alkali content of the reduced slag is still very high, which prevents the reduced slag from being used as a cement cinder.

**Large-scale consumption of Bayer red mud: novel technology based on the “calcification-carbonization” method**

In the dissolution process of bauxite by the Bayer process, part of alumina and sodium oxide combine with silica to form sodium aluminosilicate hydrate (Na2O·Al2O3·1.7SiO2·nH2O) and are lost in red mud. In sodium aluminosilicate hydrate, the ratio of alumina to silica (A/S, mass ratio of alumina to silica) is 1:1, and the ratio of sodium oxide to silica (N/S, mass ratio of sodium oxide to silica) is 0.608:1. In other
words, 1 kg of silica in bauxite will remove 1 kg of alumina and 0.608 kg of sodium oxide in the resulting red mud. As the alumina grade of bauxite decreases, more alumina and sodium oxide are lost in red mud. It is this solid phase of sodium aluminosilicate hydrate that leads to the high alkali content of red mud, which makes it difficult to utilize red mud economically and on a large scale. The large-scale utilization of red mud has become a global problem. Evidently, the problem of red mud can be fundamentally solved only by breaking the existing equilibrium solid phase and restructuring the structure of red mud.

Based on this, from the perspective of the reconstruction of the balanced solid phase structure in the dissolution process of alumina, the special metallurgical innovation team of Northeastern University proposed the “calcification-carbonization” method (CCM) to treat Bayer red mud after more than 20 years of effort (Zhang et al. 2011, 2014, 2019). In the first step, calcium oxide is added in the dissolution process to form a new equilibrium solid phase hydrogarnet, known as the calcification process. In the second step, carbon dioxide is used for carbonization treatment of calcified slag, making it decompose into calcium silicate, calcium carbonate, aluminum hydroxide, and iron oxide, called the carbonization process. In the third step, the alumina is dissolved with sodium hydroxide solution, and the tailings theoretically contain no alkali and no alumina called calcified-carbonized slag. If the iron content in the calcified-carbonized slag is high, the iron can be recovered further. This calcification-carbonization method successfully reconstructs the equilibrium solid phase in the dissolution process of bauxite, and a new red mud structure with no alkali and no aluminum in theory is attained through two core steps of calcification and carbonization. The CCM essentially solves the problem that red mud cannot be used on a large scale due to the alkali content.

The equations for the calcification-carbonization method reaction are shown as follows:

**Calcification reaction process:**

\[
Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot (6 - 2x)H_2O + 3[3CaO + H_2O \rightarrow 3CaO Al_2O_3 \cdot xSiO_2 \cdot (6 - 2x)H_2O] + 2NaOH \tag{3}
\]

**Carbonization reaction process:**

\[
3CaOAl_2O_3 \cdot xSiO_2 \cdot (6 - 2x)H_2O + (3 - 2x)CO_2 \rightarrow xCa_2SiO_4 + (3 - 2x)CaCO_3 + 2Al(OH)_3 + (3 - 2x)H_2O \tag{4}
\]

**Alumina leaching reaction process:**

\[
Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4 \tag{5}
\]
Low-iron red mud: large-scale absorption technology of “calcification-carbonization” method

For low-iron red mud, a novel low-cost and large-scale absorption technology of the “calcification-carbonization” method is proposed, as shown in Fig. 8. Using this technology to treat low-iron red mud, sodium alkali and part of alumina in red mud can be recovered, and the content of sodium oxide in the final tailings is less than 1%, which can be directly used to prepare cement or soil.

Wang et al. (2018) researched the recovery of alkali and alumina from Bayer red mud by a calcification-carbonization process. After calcification and carbonization treatment, the extraction rate of alumina was 46.5%, and the Na_2O content in CCM slag was reduced to less than 0.3%. The resulting CCM slag, which was harmless and virtually neutral, could be used not only for cement clinker production but also for soil preparation. The results demonstrated that the chemical composition of CCM slag was very close to that of Portland cement clinker, which could improve the doping amount of red mud in cement production. Compared with ordinary soil, CCM slag has good properties for many soil parameters such as alkalinity and salinity and has great application potential in soil preparation. Liu et al. (2019) proposed a new approach to enhance the alumina extraction rate by dry mechanical activation utilizing a planetary ball mill. It was proven that the alkali recovery was more than 93%. Mechanical activation destroyed the compact structure of hydrogarnet and improved its carbonization decomposition rate. The alumina leaching rate increased from 32.9 to 43.1%. Due to the mechanical activation of calcified slag, only a few carbonization cycles could reach the leaching limit. In terms of improving alumina recovery, in addition to dry mechanical activation, wet grinding could also be used to improve the extraction rate of alumina from red mud (Liu et al. 2020a). Wet grinding could destroy the compact structure of spherical hydrogarnet, thus enhancing the carbonization efficiency and alumina extraction. After wet grinding, the alumina extraction rate achieved 44.1%. Wang et al. (2019d) prepared cement clinker from CCM slag by a sintering method. After sintering, the CCM slag was converted into the active components of the cement clinker. The chemical compositions of clinker, f-CaO content and cement strength were in accordance with the national standards of China. By CCM, more than 80% of alkali and 40% of alumina could be recovered, and the salinity and alkalinity of the red mud could also be considerably reduced (Wang et al. 2019c). After treatment by CCM, the content of Na in the percolate diminished significantly from 1340 mg·L⁻¹ in red mud to 0.26 mg·L⁻¹ in CCM slag. The saltiness of CCM slag was very close to that of natural soil, and its bulk density, porosity, water retention capacity, and nutrient retention capacity all met the requirements of agricultural soil.

In industrial applications, an industrial calcification-carbonization experiment of 120,000 t/year has been completed, and good results have been achieved in sodium alkali recovery and aluminum extraction.

High-iron red mud: comprehensive utilization by the “calcified transformation - vortex reduction - cement preparation” method

The iron content of high-iron red mud is commonly more than 30%, which is considered a potential iron resource. It is estimated that approximately 15 million tons of iron, with an economic value of approximately 70 billion yuan, are lost each year due to the discharge of high-iron red mud. In view of the fact that high-iron red mud cannot be utilized on a large scale due to its alkali content and the fundamental problem of red mud has not been solved due to the low iron recovery rate and alkali content in the tail slag of existing technologies, the special metallurgical innovation team of Northeastern University proposed a novel comprehensive utilization of high-iron red mud by the “calcified transformation-vortex reduction-cement preparation” method (as shown in Fig. 9). During this method, the sodium alkali in the high-iron red mud is first extracted through the calcified transformation process, and the calcified slag is then reduced by vortex smelting reduction to obtain the pig iron for steelmaking. The molten reduction slag with low alkali is directly modulated directly at high temperature and then quenched with water to prepare a low-carbon cement clinker. The equations for the vortex reduction reaction are shown as follows:

\[3Fe_2O_3 + C = 2Fe_3O_4 + CO\] (6)

\[Fe_3O_4 + C = 3FeO + CO\] (7)

\[FeO + C = Fe + CO\] (8)

\[3Fe - C = Fe_3C\] (9)

The advantages of the novel method are as follows: (1) sodium alkali in high-iron red mud can be extracted through calcified transformation to solve the problem of alkaline high-iron red mud not being utilized on a large scale; (2) vortex technology is used to suck the raw material powders directly into the smelting reaction zone and strengthen the smelting reaction process to realize clean feeding, rapid dispersion, and uniform distribution of reducing agent powder; strengthen the smelting multiphase reaction process; and lastly realize the efficient and rapid reduction of calcified slag; and (3) the utilization efficiency of calcium oxide is improved through the new mode of “one calcium oxide used three times” (in
the process of calcified transformation, calcium oxide is used for dealkalization; in the process of vortex reduction, calcium oxide is used to modify the basicity of the slag; in the process of cement preparation, calcium oxide is used as the main component of cement).

This method eliminates the “grinding-calcination” processes in the conventional cement preparation process of “grinding-calcination-grinding” and considerably reduces the carbon dioxide emissions from limestone decomposition and fuel combustion during the traditional cement preparation process. Low-carbon cement clinker is prepared directly from molten reduction slag by high-temperature modulation and water quenching. The novel method realizes the tandem coupling and integration innovation of nonferrous metals, steel, and cement industries and has important guiding significance for the harmless, resource, and slag-free comprehensive utilization of high-iron red mud.

Wang et al. (2020) carried out direct smelting reduction experiments of mixed powders with high-iron red mud, coking coal, and additive and studied the reaction mechanism of iron extraction from high-iron red mud. It was disclosed that the reduction sequence was $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$, and the needed theoretical C/O mole ratio was 1:1. The recovery rate of iron in high-iron red mud reached 92.8% after smelting reduction for 30 min at 1500 $^\circ\text{C}$. The sodium oxide content in the reduction residue was 1.9%, which limited its further use. Li et al. (2022a) surveyed the advantages of the vortex smelting reduction method in treating high-iron red mud, calcified slag and aluminum leached slag. The effects of different adding methods, impeller stirring

![Diagram](image)

**Fig. 9** Comprehensive utilization of high-iron red mud by the “calcified transformation–vortex smelting reduction-cement preparation” method

![Graph](image)

**Fig. 10** Iron recovery with different reduction time (a) and water-quenched slag (b)
speeds, and reaction times on iron recovery were investigated. Mechanical stirring increased the feeding speed and promoted the reduction reaction and directional iron deposition, which was profitable to the separation of slag and molten iron.

To decrease the harm of high-iron red mud and widen its application, Wang et al. (2022) extracted iron from calcified slag and prepared a low-carbon cement clinker utilizing molten reduced slag. The effects of different conditions on iron recovery were systematically investigated, and the properties of cement samples prepared by water quenching slag were analyzed. Under the optimum process conditions, the recovery of iron achieved 97.6%, and the obtained metal met the industrial standard of pig iron for steelmaking. The vitreous content of water-quenched slag was 99%. The activity of pozzolanic ash was comparable to that of S95 grade mineral powder, and the doping amount of water quenched slag in cement was 50%. Yang et al. (2022) carried out mineral phase reconstruction experiments by adding an additive into molten reduced slag during the smelting reduction process. With a basicity of 1.1, a carbon/oxygen mole ratio of 1.1 and an amount of calcium fluoride of 3%, the iron recovery of calcified slag was 90.06% after reduction at 1550°C for 30 min, and the content of sodium oxide in the reduced slag was 0.48%. By XRD detection, the main phases of the reduced tailings were 2CaO·Al2O3·SiO2 and CaTiO3, which could be used to prepare aluminite cement.

Vortex smelting reduction experiments with ten thousand tons of high-iron red mud have been completed. The results of the vortex smelting reduction experiments with pilot scale are shown in Fig. 10. As shown in Fig. 10a, the iron recovery rate was higher than 95% when the reduction time was longer than 15 min, and the iron recovery reached 97% after vortex smelting reduction for 30 min. After being water quenched, the water-quenched slag presented a bright black vitreous state with vitreous content of 99% in water quenched slag. The chemical composition of reduced pig iron was detected, and the results are shown in Table 2. As can be seen from Table 2, the content of sulfur and phosphorus in the reduced pig iron is meager, and the composition meets the pig iron L03 standard for steelmaking. Moreover, the water-quenched slag can be utilized to prepare low-carbon cement directly with a doping amount of 30–50%.

### Conclusions and prospects

The key to achieving the clean production of alumina is red mud, and the key to treating red mud is dealkalization. In future research, there are two main research directions for the treatment of red mud. First, treat from the source, break the equilibrium solid phase of Bayer red mud, establish a new structure of red mud without alkali and aluminum, and develop disruptive technology. The second is the end treatment. The principles of red mud treatment should be established, that is, harmless, resource, slag-free, large-scale, and low-cost absorption of red mud.

The application of red mud in building materials is a direct and simple method. However, due to the strong alkalinity, the building materials produce a continuous “frost” phenomenon, weakening the service life of the building. In the field of waste gas treatment and waste water treatment, red mud has achieved good results. Nonetheless, after treatment, new waste slag is formed, which does not achieve the purpose of reducing red mud. For dealkalization and aluminum extraction, most methods are still in the laboratory research stage, and there is no method with obvious effects of dealkalization and aluminum extraction and good industry economy. In the extraction process of rare metals, a large amount of wastewater is produced and new waste is generated, which increases the difficulty of environmental protection treatment. Although it is not problematic to recover iron from high-iron red mud from a technical perspective, optimizing the process to reduce resource waste, energy consumption, and recovery cost is crucial for industrial implementation.

The calcification-carbonization method is effective and economical for treating red mud. For CCM, sodium alkali, alumina, and iron can be effectively recovered from red mud, and the final low-alkali tailings can be used to prepare cement clinkers or for soil treatment. Both laboratory and industrial experiments have achieved good results. This method realizes the large-scale, harmless, and comprehensive utilization of red mud and fundamentally solves the problem that red mud cannot be used on a large scale because of its alkali content.

### Author contribution

Wang and Li provided conceptualization and first draft preparation; Dou, Liu, Lv, and Zhang reviewed and edited.
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