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Review

Advancements in sodium production and slag recovery techniques: A comprehensive review

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ABSTRACT

Sodium is an important light non-ferrous metal with special properties and is widely applied in various fields of pharmaceutical intermediates, airbags metallurgy and nuclear coolants. However, the high energy consumption, low current efficiency of the sodium industry, coupled with the substantial sodium slag byproduct and inefficient sodium slag recovery technology, have greatly hindered the further development of the metallic sodium industry. Although many research papers and new patents continue to emerge, there are very few reviews on the preparation of metallic sodium and the disposal of sodium slag which affects the exchange and development of new technologies in the sodium industry. Herein, this review summarizes the progress in sodium production technology and sodium slag recovery. Based on the ion migration mechanism and the competition discharge mechanism of different cations, constructing suitable electrolyte components containing sodium and selecting appropriate membrane materials can significantly improve current efficiency and reduce the reduction of impurity metals, while sodium slag recovery methods like mechanical separation, solvent leaching, and melting substitution have been developed, enabling the recycling of valuable components. Furthermore, this review explores sodium applications in energy storage, inorganic/organic synthesis, metal smelting, and nuclear reactors. It emphasizes the need for further technological advancements to address energy efficiency, slag recovery, and chlorine gas utilization challenges in sodium production.

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1. Introduction

Metallic sodium is a crucial light non-ferrous metal, commonly found in the form of sodium salts in both terrestrial and marine environments. Its exceptional ductility, electrical conductivity, and thermal properties make it widely utilized in diverse applications such as nuclear energy, sodium batteries, dyes, and pharmaceutical intermediates in Fig. 1(a). In the 1980s and 1990s, the primary application of metallic sodium was predominantly in metallurgical processing, with less stringent requirements for sodium yield and purity. Then, as the energy industry has experienced exponential growth, the utilization of metallic sodium has expanded into advanced fields, including sodium-nickel salts batteries and sodium-ion batteries [1,2], medical intermediates [3], and nuclear sodium potassium alloy coolant [4–6]. These high-tech industries demand higher yields and purity of sodium, necessitating urgent reforms in the sodium industry.

High-temperature electrolysis of molten salt is the dominant process of produce metallic sodium now, which utilizes NaCl as the electrolyte under the operation temperature around 620 °C, and the nitrogen is employed as an inert atmosphere to protect metallic sodium [7]. The high demanding electrolytic conditions for sodium production are significant challenges for industrial-scale operations, leading to a limited number of countries, including China, USA, Russia, Japan, Germany, France, and the United Kingdom, possessing the capability to produce metallic sodium [8]. The United States once held the distinction of being the leading producer and consumer of sodium, with an annual production capacity peaking at 170000 t. With the escalated labor costs and environmental regulations on leaded gasoline usage became more stringent (Sodium was once a key raw material to produce tetraethyl lead as a leaded gasoline additive), the production capacity of

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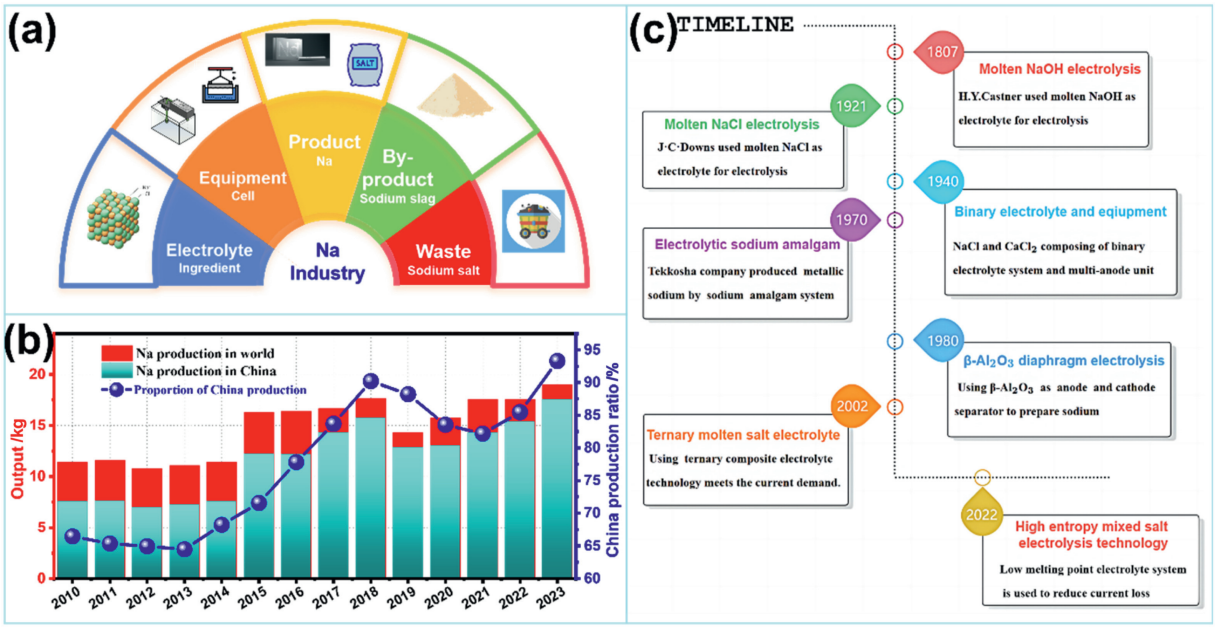

Fig. 1. (a) Industrial classification diagram of metallic sodium. (b) Production of metallic sodium in world and China, and the production proportion in China from 2010 to 2023. (c) The development timeline of sodium production technology.

metallic sodium in the United States experienced a steady decline, eventually being overtaken by China [8]. Fig. 1(b) illustrates the fluctuating trend in sodium production capacity in China and worldwide over recent years. The global and Chinese sodium yields have seen variable increases from 2010 to 2023. The production capacity of China has constituted over 65% of the global total, reaching 92% in 2023, being a foremost producer of metallic sodium in the world.

Fig. 1(c) illustrates the historical progression of the metallic sodium industry. It is evident that sodium has garnered significant research interest since the 19th century. However, most sodium research was focused on the broadening applications of downstream sodium products while fewer on enhancing the sodium preparation technologies. Industrial sodium production mainly relies on the NaCl molten salt electrolysis technology developed in the last century, which suffers from low current efficiency and high energy consumption. During the production of sodium, chlorine gas is typically produced and emitted. If not properly managed, the release of chlorine gas into the atmosphere can result in air pollution, which poses risks to both the ecosystem and human health. The Environmental Protection Law of the People's Republic of China set clear requirements for environmental protection measures in the sodium metal production process. It is essential to control and mitigate the environmental impact through rigorous environmental impact assessments and effective environmental protection measures. Additionally, the substantial generation of by-product sodium slag leads to a considerable waste of sodium resources, thereby restricting the potential for further scale expansion in production. Clean and efficient recycling sodium slag during the production process is also an important part of the development of the sodium industry [9–12]. In this review, we systematically collected the existing literature to summarize the preparation technologies for metallic sodium, the recovery of sodium slag and the major application domains of metallic sodium, which will highlight the prevailing challenges in industrial production and provide guidance for the future development of the sodium industry.

2. Advancements in Sodium Production Techniques

Recently, the demand and production of metallic sodium has grown steadily, spurring a surge in related research [13]. The predominant production technology of metallic sodium in China is molten salt electrolysis of NaCl-based ternary electrolyte. This method requires extensive types of equipment to be installed throughout the production process [14], and the crude sodium product must undergo separation and purification in a refining tower [15]. These intricate procedures have imposed limitations on the industry scale expansion. Moreover, due to the high reactive nature of sodium [16], it is imperative to maintain an inert atmosphere throughout each process to prevent the oxidation and potential explosion risk of sodium [17]. Therefore, enhancing the production flow and equipment of the existing process is of utmost importance [18]. Depending on the difference in electrolytes, electrolysis methods can be categorized into three main types: NaCl melt electrolysis [19], NaOH melt electrolysis [20], and sodium amalgam electrolysis [21]. With the advancement of β-Al_2O_3 ceramic materials, electrolysis techniques using β-Al_2O_3 as a diaphragm have progressively gained application [22]. Recently, Pan group [23–25] has proposed the high-entropy molten salt method to obtain metallic Na under the decreased temperature of 550°C-580 °C by increasing coulombic efficiency, and this method has been successfully industrialized in Inner Mongolia RUI XIN Chemical Co., Ltd.

2.1. Evolution of salt melting electrolysis for sodium production

Due to easy operation and valuable chlorine gas by-product, NaCl was first used as the primary electrolyte employed in the electrolytic production of metallic sodium. In 1924, J.C. Downs introduced the “Downs electrolysis method”, with NaCl as an electrolyte for sodium production [26]. He also developed the corresponding equipment, termed as the “Downs Cell.” To mitigate safety risks during production, an iron-based separation was installed between the anode and cathode within the electrolytic

cell. During the electrolysis process, Na^+ are obtained electrons and reduced into Na at the cathode, while chloride ions are oxidized into chlorine gas at the anode. Due to the high melting point of NaCl (801 °C), the industry production process necessitates an electrolytic working current of approximately 20000 A to sustain high temperatures within the cell. The substantial electricity consumption notably elevates production costs. Furthermore, the square configuration of the single anode pool results in low spatial efficiency during the production process. The limited electrode surface area restricts the electrode surface reactions, thereby leading to low current efficiency. Additionally, the high voltage also increases the electrolyzer's energy loss and concurrently affects the current efficiency. The principal chemical reaction equation for this technology is presented as:

$$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g) + Q$$

In the 1940s, German researchers [27] revolutionized the Downs electrolysis process and the electrolytic cell design. They interconnected four sets of parallel cathodes to create a large-scale electrolytic unit and positioned a steel chlorine collector above the graphite anode to efficiently collect chlorine gas. This configuration effectively prevented the chlorine gas from re-entering the electrolytic cell and reacting with the liquid sodium to form NaCl. Moreover, they strategically placed barbed wire between the anode and cathode to minimize the transport of impurities to the cathode side. The innovative electrolytic device is depicted in Fig. 2(a). To address the issue of high melting point of NaCl, they developed a binary electrolyte system comprising 50% NaCl and 50% $CaCl_2$. This mixture greatly reduced melting point of electrolyte from 801 °C to 700 °C, thereby enhancing current efficiency. Industrial pilot demonstrated that this approach successfully overcame the drawbacks of high energy loss and the unstable electrolytic process associated with using pure NaCl electrolyte, achieving stable and continuous operation at high industrial currents (24–32 kA). Following electrolysis, the crude sodium product was collected from the receptacle adjacent to the cathode. Due to the significantly higher melting point of metallic calcium (840 °C) compared to sodium (97.81 °C), the refining process allowed for collecting 99.7% pure liquid sodium in the upper layer while impurities, including

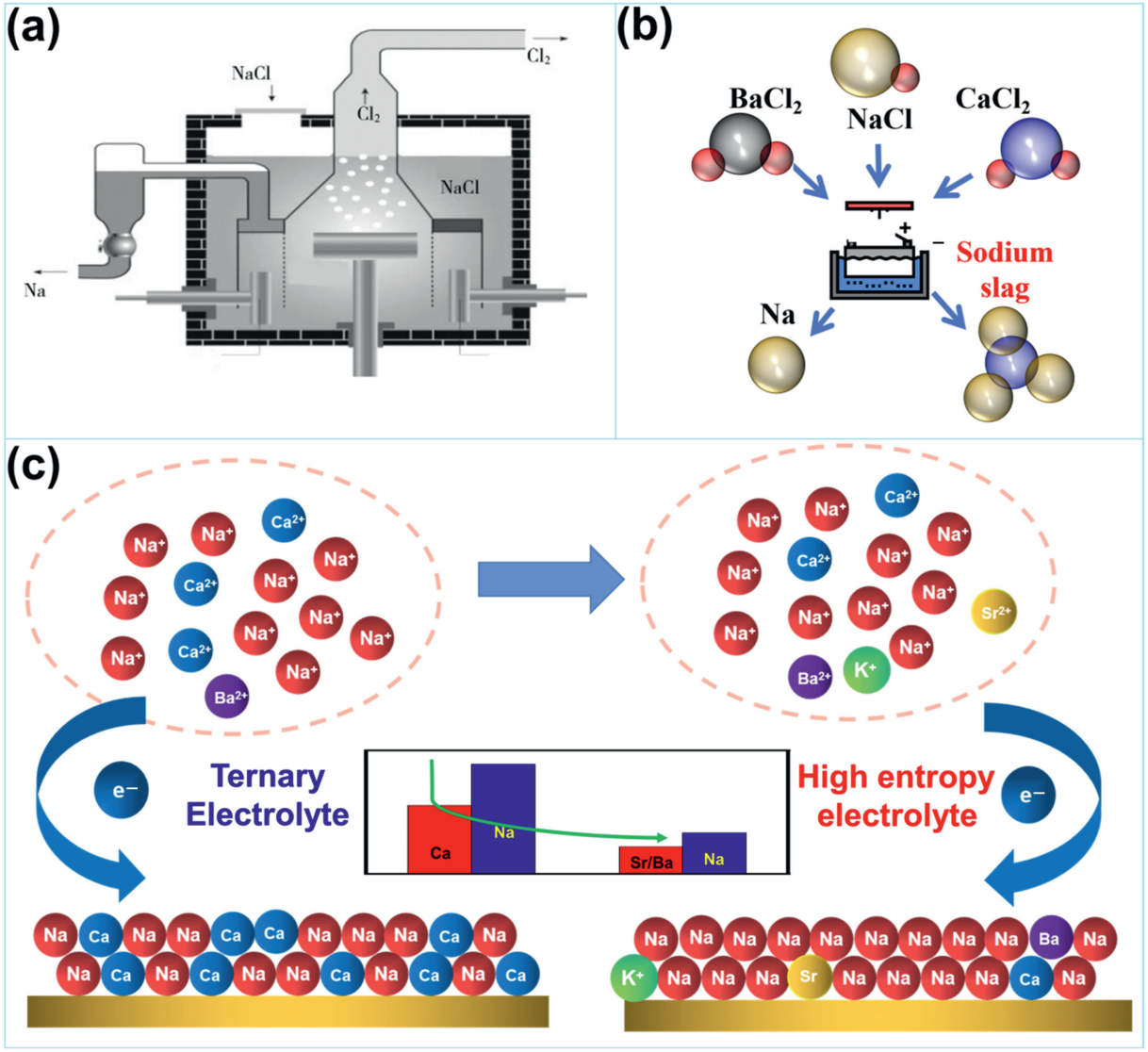

Fig. 2. (a) Equipment diagram of Binary molten salt electrolysis process, (b) mechanism schematic, (c) mechanism schematic of high entropy molten salt electrolysis, reproduced with permission from Ref. [21].

calcium, settled to the bottom. Refined sodium was subsequently collected in the sodium outlet pipe [28–32]. This technology significantly reduced the operating temperature of the electrolytic process, thereby improving industrial safety and becoming the prevailing method in the industry. However, the close reduction potential of Ca^{2+} to Na^{+} [33,34] led to the easy reduction of calcium chloride at the cathode with the average current efficiency of about 70%, resulting in an elevated impurity content of calcium in the product sodium [35] and rapid consumption of electrolyte calcium chloride.

Currently, the sodium production industry predominantly employs an enhanced salt electrolysis technology developed by the DuPont Company. Building upon the binary electrolyte system, a ternary electrolyte system was established by incorporating barium chloride eutectic salt, consisting of 28% NaCl, 24% $CaCl_2$, and 48% $BaCl_2$ (Fig. 2(b)). This innovative approach has lowered the electrolytic temperature from 700 °C to approximately 600–620 °C [35,36], increasing the average current efficiency from 75% to 80% with reduced power consumption of 2% to 3%.

Recently, Pan's group [37] has developed a novel technology based on the transfer mechanism of sodium ion discharge and the principles of high-entropy molten salt structure. This innovation has been integrated into the electrolytic sodium production process and has already been applied in industrial production in 2023. Building upon the existing ternary electrolyte, $SrCl_2$ and KCl were introduced as the eutectic salt component. The electrolyte components were then re-optimized with $SrCl_2$, $BaCl_2$ and KCl, which possess high reduction potentials to replace calcium chloride in large quantities. This substitution greatly reduced the co-reduction of metallic calcium at the cathode, thus diminishing the impurity content of calcium in the crude sodium and the generation of sodium slag by-products. This technology has been successfully scaled up to industrial levels in Inner Mongolia RUI XIN Chemical Co., Ltd. with an annual output of 3000 t, and has achieved international leading standards. Industrial experiments indicate that the average daily yield of metallic sodium in a single tank has increased by 12.9%, from 722 kg to 815 kg. The average current efficiency has risen from 76% to 87.5%. The average power consumption for producing one ton of sodium has decreased by 15%, from 10709 to 9102 kW h. Additionally, the average weekly profit has increased by CNY 17000. The mechanism schematic, process flow, and equipment diagram of this method are illustrated in Fig. 2(c).

In summary, the electrolytes in salt-melting electrolysis systems have evolved from a single NaCl to a high-entropy molten salt system. The comparison of compositions, melting points, and current efficiencies of different electrolyte systems is provided in Table 1. Among them, the high-entropy system will be the focal point of future advancements with significantly reduced melting point, enhanced current efficiency, and optimized sodium production and power consumption.

2.2. Sodium electrolysis with alternative electrolytes

In addition to NaCl, other sodium-containing compounds can also be employed as electrolytes in electrolytic processes. In 1807, the British chemist H.Y. Castner utilized a binary mixture of NaOH (60%) and Na_2CO_3 as the electrolyte to produce sodium through electrolysis at 300 °C with an applied voltage of 4–5 V [39]. Then the obtained crude sodium was transferred to a refining machine at 110–120 °C for refining after precipitation and separation. The electrolytic apparatus employed in this process is depicted in Fig. 3(a), featuring nickel as the anode, iron as the cathode, and a nickel net as separator. The chemical reaction for this method is presented as:

$$4NaOH(l) \rightarrow 4Na(l) + 2H_2O(l) + O_2(l)$$

The metallic sodium is successfully produced via this method with the current efficiency of 50% due to the readily secondary reaction of sodium and water to form NaOH and H_2. Consequently, this technology is limited to specific enterprises or small-scale production operations. In the 1970s, Tekkosha Company [41–43] developed a sodium amalgam electrolysis technology for sodium production. This technology uses sodium amalgam prepared from saltwater as the anode material. The electrolyte consisted of NaOH, NaI, and NaCN, and Na was collected at the cathode. The technical device is illustrated in Fig. 3(b). The electrolytic temperature is much lower than other electrolytic processes, and the current efficiency is up to approximately 95%. However, this technology was quickly phased out due to the highly toxic Hg vapor used in the production process, which seriously threatened the health of employees and the environment.

In summary, the mentioned technologies can use other sodium-containing substances to produce Na with certain advantages of lower operation temperature and high current efficiency. However, these methods also carry significant safety risks that hinder their scalability and are largely eliminated from industrial production.

2.3. Na-β-Al_2O_3 diaphragm electrolysis technology

Na-β-Al_2O_3 is a specialized ceramic material [40,44] with a high selectivity towards sodium ions which has been extensively utilized as a separator for sodium-ion batteries. In the 1960s, Ford Motor Company adopted it as a separator in sodium-sulfur batteries [45]. During the discharge process, the β-Al_2O_3 diaphragm selectively allows Na^{+} to pass through while restricting the passage of other ions. This selectivity ensures that only Na^{+} gathers at the cathode, enhancing the purity of the product when used in the electrolytic sodium production process. Furthermore, Na-β-Al_2O_3 can also serve as a solid electrolyte with a low melting point from 300 °C to 400 °C, thereby circumventing the high electrolytic temperatures typically associated with traditional molten salt electrolysis technology and reducing energy consumption. Based on this theory and previous experimental tests, researchers have conducted industrial pilot tests using β-Al_2O_3 diaphragms to validate their practical feasibility.

Chen [23] developed a Na-β-Al_2O_3 membrane electrolysis method, employing a NaCl and $ZnCl_2$ mixture as the anodic liquid, a β-Al_2O_3 tube as the diaphragm, steel as the cathode, and liquid sodium as the cathodic liquid for the electrolytic process. The DC

Table 1
Comparison of electrolytic effect of different components in molten salt electrolysis process.

Models	Component	Melting point/°C	Current efficiency/%	Ref.
Mono electrolyte	NaCl	801	75	[26]
Binary electrolyte	NaCl, $CaCl_2$	710	76	[27]
Ternary electrolyte	NaCl, $CaCl_2$, $BaCl_2$	600	78	[35,36]
Quaternary electrolyte	NaCl, $CaCl_2$ $BaCl_2$, $SrCl_2$	530	85	[37]
High entropy electrolyte	NaCl, $CaCl_2$, $BaCl_2$, $SrCl_2$, KCl	515	87	[38]

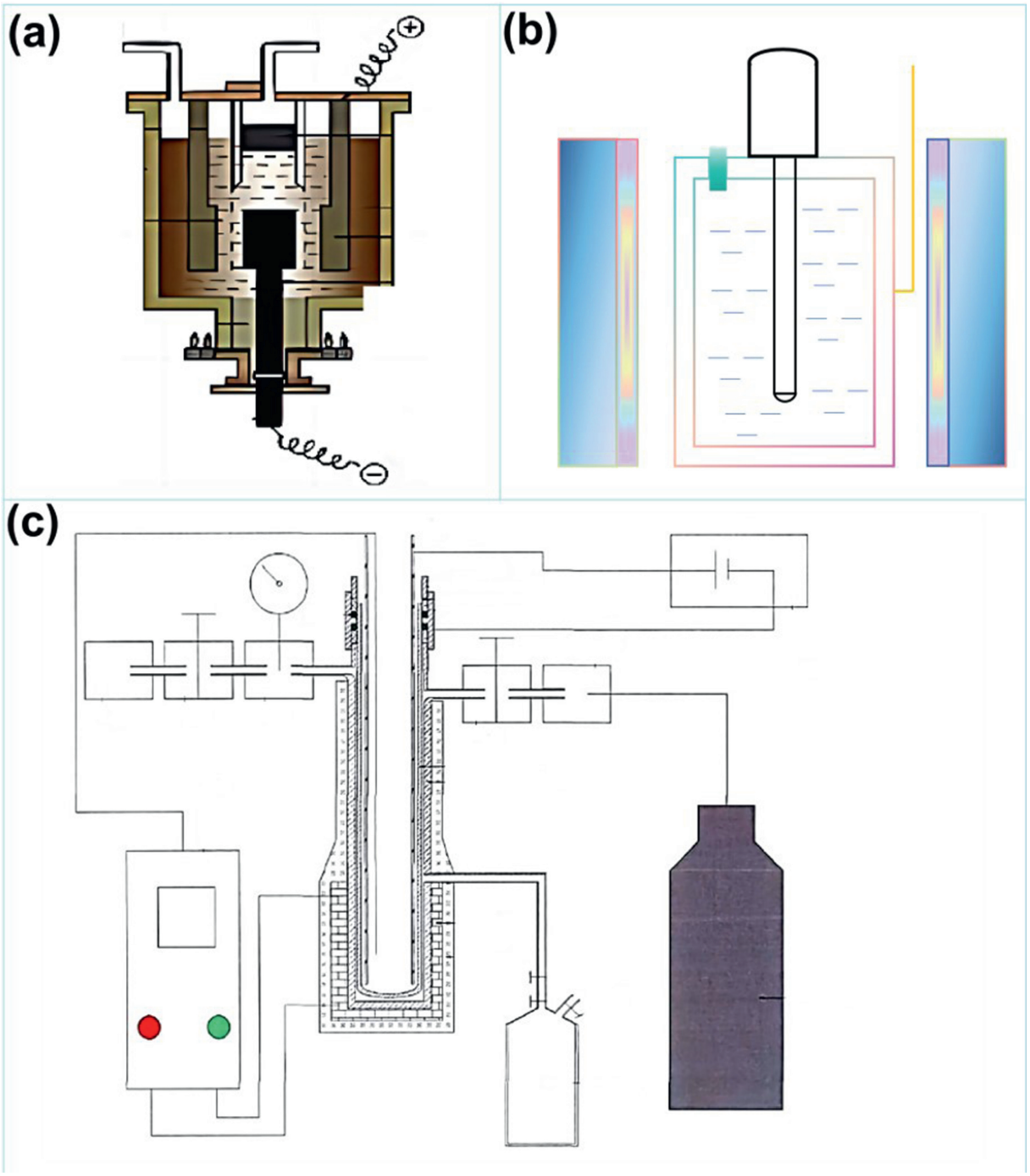

Fig. 3. Equipment diagrams of (a) melting NaOH electrolysis process. (b) Sodium amalgam process. (c) Electrolytic equipment diagram of Na-β-Al_2O_3 ceramic diaphragm melting caustic electrolytic method, reproduced with permission from Ref. [40].

power consumption of this method is only about 2750 to 2900 kW·h, much lower than that of traditional salt melt electrolysis. The purity of the metallic sodium exceeds 99.8% [46,47] with nearly 100% of current efficiency. Yang [48] and Dang [49] *et al.* reported β-Al_2O_3 as a membrane for the electrolysis of NaOH. The electrolytic device features a nickel sheet as the anode and corundum as the electrolytic cell material, as illustrated in Fig. 3(c). Following electrolysis, metallic sodium with a purity higher than 99.7% is collected at the cathode. The purity of the sodium product met the national first-class product industry standards. The DC power consumption for producing sodium per ton is only 3450 kW·h at around 350 °C, and the current efficiency approaches 100%. These technologies have achieved advanced domestic standards due to superior product purity, reduced power consumption, and high current efficiency [50]. The β-Al_2O_3 film electrolysis technology for sodium production exhibits substantial industrial application potential. However, its high initial investment cost stems from the requirement for precision equipment and costly raw materials, including hydroxyl alumina and sodium carbonate. Additionally, operating expenses are elevated due to the necessity

of high-temperature operation during the electrolysis process and the need for proper treatment and utilization of the generated chlorine gas. On the safety front, the use of solid electrolytes enhances operational safety by minimizing leakage and corrosion issues. The limited lifespan of the β-Al_2O_3 film and the instability of the solid electrolyte pose significant challenges to its industrial application, necessitating further research and development to address these limitations.

A comparison of various electrolytic processes is presented in Table 2. The sodium chloride electrolysis method has been adopted as the predominant position for industrialization than other methods after gradual improvements. Further optimization of its electrolytic conditions represents the key direction for future research. As for β-Al_2O_3 method, how to increase the lifespan of separator, address the problems of hydrolyzing of solid-state electrolyte, and manufacture large size β-Al_2O_3 tubes to promote industrial application. These advancements will also shape the future trajectory of the metal sodium electrolysis production industry.

Currently, metallic sodium is increasingly used in high-tech sectors, the presence of 0.2% to 0.3% Ca impurities in the product sodium significantly impacts its further applications [51]. To align with national energy-saving initiatives and meet green factory standards, the sodium industry urgently needs new electrolysis technologies to improve product purity, save energy consumption, and recycle sodium slag, leading to competitive costs.

3. Advancements in Sodium Slag Recovery Techniques

In the current mainstream ternary electrolysis technology [52], the co-reduction of Ca^{2+} at the cathode [53] results in the incorporation of Ca into the product Na, which should be refined in a refine tower to remove Ca impurities and form about 2% sodium slag [49,54,55]. Sodium slag contains 70% to 85% metallic sodium, 15% to 30% metallic Ca, trace amounts of Mg, Ba, K, and other impurities. It easily reacts and burns easily with water in the air and is classified as a hazardous chemical with high risk. The disposal fee of sodium slag is 4000–6000 CNY·t^{-1}, which wastes valuable sodium metal resources and greatly increases production costs. Therefore, the recovery of sodium slag has emerged as a significant challenge for the sodium production industry [55–58]. In this section, we summarize the typical sodium slag recovery technologies developed in recent years to provide new insights into recycling waste sodium resources.

3.1. Mechanical separation for sodium slag recovery

Metallic sodium has a low melting point of 97 °C and low density of 0.968 g·cm^{-3}, Ca has a much higher melting point of 842 °C and a density of 1.55 g·cm^{-3}, making them easily separate from crude sodium an applied force field, without introducing additional chemical components.

Huang [59] described a melt extrusion separation process. In this method, hot sodium slag about 110 °C was placed in a specialized heating tank. Then, the mixed components are filtered into a treatment device with a constant temperature piston, where the molten liquid sodium is forced into a bottom collector to achieve solid-liquid separation (Fig. 4(a), (b)). The recovery rate of Na from sodium slag by this method can reach 70% to 80%, and approximately 1 ton of sodium slag can be processed daily, which generally meets the needs of small enterprises. However, the piston extrusion equipment is prone to corrosion by Na, resulting in short service life and high maintenance costs. Cui *et al.* [60] reported a vacuum distillation process for separating sodium and calcium from sodium slag by employing stage temperature control, leveraging the different freezing points of sodium and calcium vapor. Initially, sodium slag is evaporated into gas under vacuum conditions and sent to the separation device. When the first condensation temperature is reached through gradient cooling, calcium vapor with a higher freezing point condenses into metallic calcium and drops into the vacuum tank, while the sodium vapor continues through the pipeline and condenses into metallic sodium in the collection tank at the second condensation temperature. The oxidation slag, white oil, and other residues remain in the distillation sodium storage tank. The recovery rates of sodium and calcium are 96% and 95% respectively, with purities of 99% and 97%. This method can simultaneously recover metallic sodium and solid calcium and has advantages in terms of environmental protection, high efficiency, and resource yield. However, the process conditions are demanding, involving a vacuum steam environment and a large temperature gradient in the different evaporation chambers of the device, which is not conducive to large-scale industrial production.

Pan *et al.* [62,63] proposed a simple technique for refining sodium and recovery of Na from sodium slag through super-gravity separation method (Fig. 4(c)). Approximately 60% of the metallic sodium in the sodium slag is efficiently recovered within 3–10 min, and its purity reaches 99.9%, exceeding the requirements of Industrial Metal Sodium (GB/T 22379–2017) for first-class products. However, the safety problems of high temperature centrifugal equipment hinder the further application of this technology.

In summary, the mechanical method has significant promise for the sodium slag recovery industry, so subsequent research should focus on further optimizing production conditions and reducing safety hazards in the production process.

3.2. Solvent leaching for sodium slag recovery

Sodium is more chemically reactive than calcium, allowing it to react more efficiently with specific leaching agents to separate target elements more readily. In the present study, the solvent leaching method primarily focuses on selecting suitable solvents and designing an optimal leaching process.

Liu [61] employed alcoholysis with methanol as the leaching agent to recover sodium slag and the process flow is shown in Fig. 4(e). The sodium slag was immersed directly in a methanol solution within the reaction kettle, where the sodium component reacted to form sodium methanol. Subsequently, chloroform was

Table 2
Summary of different electrolytic processes for sodium production.

Models	NaOH electrolysis	NaCl-based electrolysis	HgNa electrolysis	β-Al_2O_3 diaphragm
Electrolyte	NaOH	NaCl and other chloride	NaOH, NaI	NaOH, NaCl
Temperature/°C	300–350	500–800	200–240	300–350
Energy/kW·h	22000	9000–11000	11000	2750–3500
Current efficiency/%	50	75–90	95	100
Purity of product Na	>99.0%	>99.3%	>99.7%	>99.8%
Degree of industrialization	Specific enterprise	Mainstream technology	Elimination	Laboratory stage
Ref.	[39]	[26,27,35–38]	[41–43]	[23,48]

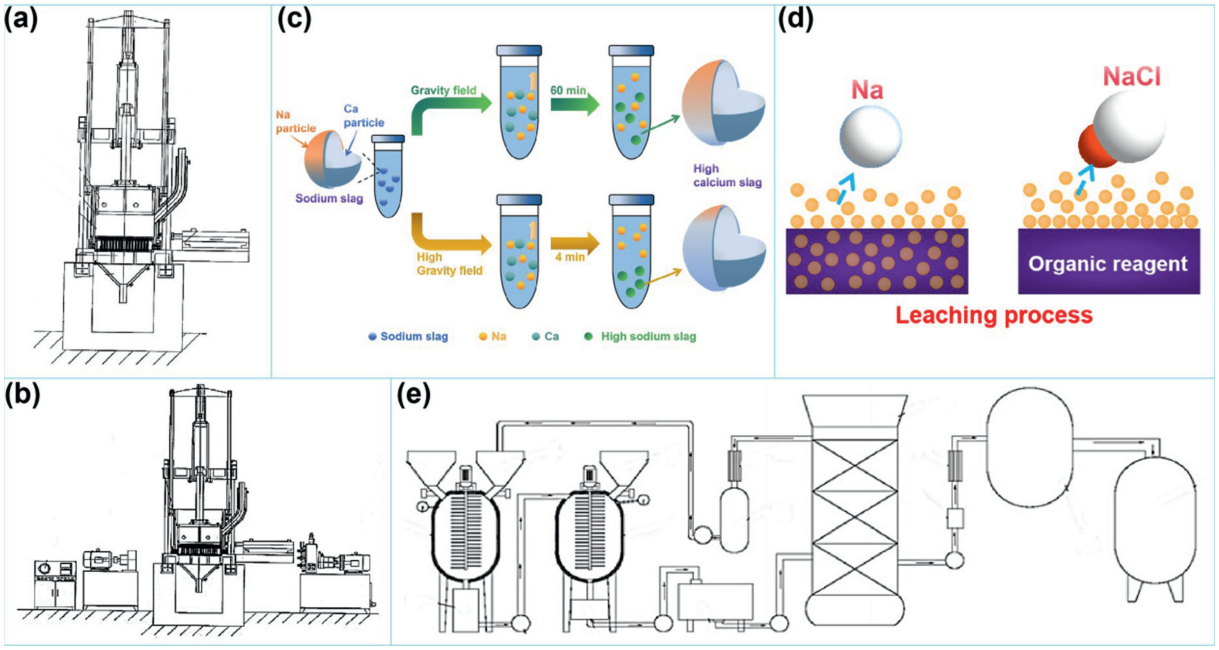

Fig. 4. (a), (b) Thermostatic piston extrusion process reaction device diagram, reproduced with permission from Ref. [59]. (c) Super-gravity separation process mechanism diagram. (d) Mechanism diagram and (e) reaction device diagram of sodium slag recovery by alcohol hydrolysis reproduced with permission from Ref. [61].

added to the mixture, forming trimethyl orthoformate and NaCl. After cooling, the reaction products were centrifuged and filtered to obtain NaCl. The trimethyl orthoformate product was recovered by fractionation with a purity greater than 99.8%. The technical process flowchart and device diagram for this method are depicted in Fig. 4. The chemical reactions involved in the process are outlined in the following Formulas.

$$2CH_3OH(l) + 2Na(s) \rightarrow 2CH_3ONa(l) + H_2(g)$$

$$3CH_3ONa(l) + CHCl_3(l) \rightarrow HC(OCH_3)_3(l) + 3NaCl(l)$$

Furthermore, continuous production was achieved by integrating the reaction unit with subsequent centrifugal equipment and a rectification tower, ensuring a comprehensive recovery rate of sodium slag up to 90%. However, this technology requires a large amount of toxic and explosive organic reagents, producing waste liquid containing unreacted reagents, by-products and salts, which increases the safety risks associated with the disposal of sodium slag and imposes higher safety standards on enterprises. If these wastes are not treated properly, they may cause pollution to water bodies and soil. Biobased solvents or water-soluble solvents can be used to replace toxic organic solvents, in order to remove harmful substances in the waste liquid and recycle useful substances.

Pan *et al.* [64] reported a method of alkaline solution to atomize leaching sodium slag and recovery system. Firstly, the sodium slag was roasted into the corresponding oxides by controlled atmosphere of N_2 and O_2. The oxides were contacted with atomized alkaline solution to form NaOH solution and $Ca(OH)_2$ solid, respectively. Finally, a small amount of CO_2 was pumped into the separated NaOH solution to convert the slightly dissolved $Ca(OH)_2$ into $CaCO_3$ solid, thereby purifying the NaOH solution. In this process, the recovery rates of Na and Ca components in the sodium slag both reach 98%. This atomized leaching method significantly increases the contact area between reactants, accelerates the leaching rate, and makes the reaction process gentler, resulting in a more efficient and safer recovery process. The production of 30% NaOH solution and 98% $Ca(OH)_2$ can increase the profit of 4500 yuan per ton sodium slag processed, indicating a promising application prospect. However, alkaline solutions are used in the process, resulting in a high concentration of alkaline substances in the waste solution. These wastes may cause damage to the acid-base balance of the water. The waste liquid needs to be treated and recycled effectively to reduce the emission of pollutants. The harmful substances in the waste liquid can be removed by neutralization, precipitation, adsorption and other methods, and the useful substances can be recycled.

In summary, the solvent leaching method has significant research value within the sodium slag recovery industry. The selection of leaching agents and the recovery methodology are pivotal determinants of the safety and economic viability of the recovery process, which must be carefully considered for further improvement of this method.

3.3. Melting substitution method for sodium slag recovery

For the Ca components in sodium slag, it is more valuable to convert it into $CaCl_2$, which can be used to supplement the original electrolyte, thus achieving the recycling of the calcium component. Hai *et al.* [65] described a method for recovering NaCl and $CaCl_2$ from sodium slag through a melting substitution process. In this process, the sodium slag and NaCl are transformed into metallic sodium and $CaCl_2$ through a melting substitution reaction at 630–650 °C in the reactor. The produced $CaCl_2$ can be returned to the electrolytic cell as an electrolyte component by separation, while the liquid sodium is refined further into metallic sodium with a purity of 99.7%. However, this method requires operation at high temperatures above 600 °C with a very slow reaction rate and limited recovery rate due to

tiny potential difference of Na and Ca. Building upon this, Pan *et al.* [66] explored new approaches to enhance the displacement process. By substituting NaCl with a pre-treated multi-component molten salt in the electrolytic process, the reaction temperature for the substitution reaction is reduced to 500 °C. Additionally, the reaction rate is greatly increased by additional power supply, thus achieving a new balance of calcium chloride in the electrolytic cell. However, the separation and purification of the sodium product from two chambers and electrolyte is challenging, which require further optimization.

The various sodium slag recovery processes are summarized in Table 3. The most effective approach to recover sodium slag involves obtaining high-purity metallic sodium and recycled calcium products through the atomic economic method, establishing a balance between electrolyte reduction and regeneration, and achieving the complete recycling of all valuable components. Moreover, reducing the amount of sodium slag produced at the source is crucial, which can be achieved by reducing the migration rate of calcium ions at the cathode and strengthening the desorption separation of metallic sodium and calcium by the new high entropy electrolyte and efficient separation method.

4. Applications of Metallic Sodium

Metallic sodium has high energy density and chemical activity, along with excellent conductivity and thermal conductivity, making it an ideal metal for the following applications: metal smelting, energy storage devices, inorganic salts, organic intermediates, and nuclear coolants (Fig. 5). Diverse industrial applications are driving the need for enhanced performance characteristics in sodium-based products, particularly regarding product purity , ionic conductivity, thermal stability, and environmental compatibility (Table 4). This section will offer a concise overview of its applications to generate new insights for future research and advancement of the upstream metallic sodium preparation industry.

4.1. Energy storage applications of metallic sodium

The purity of metallic sodium significantly impacts the performance of sodium-ion batteries. High-purity metallic sodium minimizes impurities within the battery, thereby enhancing its cycle life and energy storage efficiency [67]. Typically, the purity of metallic sodium must exceed 99.9%, and in some cases, it should reach 99.99% (4 N) or even higher to ensure the battery's stability and safety [68]. As compared with lithium-based batteries, sodium exhibits a higher resource abundance, lower potential of −2.71 V with considerable specific capacity (1166 mA $h \cdot g^{-1}$), making it well-suited to construct new batteries with good price competitive and energy density [69–73]. At present, Na-S and Na-$NiCl_2$ batteries have reached commercial availability [72,74]. β-Al_2O_3 is used as the electrolyte for both batteries. During electrolysis process, the sodium anode loses electrons and the Na^+ transfers through the solid electrolyte to the cathode, where they combine with S_x^{2-} to form sodium polysulfide. The corresponding reaction [75] is represented by as:

$$2Na + x\,S \rightarrow Na_2S_x\ (x \geq 3)$$

β-Al_2O_3 can maintain high conductivity only at temperatures above 250–300 °C, which is higher than the melting points of sodium and sulfur. The high operating temperature exacerbates the corrosion of the electrode plate materials, enhancing the corrosion resistance of batteries and developing new solid electrolyte materials the primary focus areas for future research [75–81].

Table 4
Summary of sodium slag application.

Application	Purity of Na material	Ref
Energy storage	>99.9%	[67–81]
Hydrogen storage material	>99.9%	[82–88]
Sodium organic matter	>99.9%	[89–94]
Smelting auxiliary	>99.999%	[95,96]
Nuclear reactor coolant	>99.9%	[97–101]

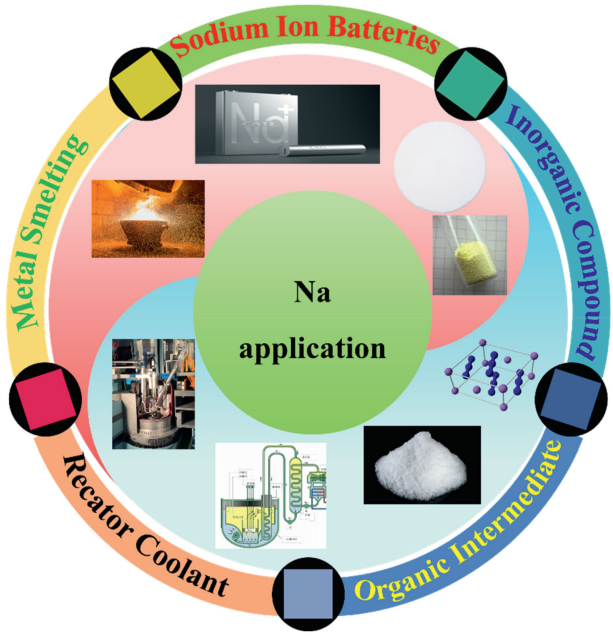

Fig. 5. The application fields of metallic sodium.

4.2. Complex compound applications of metallic sodium

In the realms of sodium organics and sodium hydrogen storage materials, the purity of metallic sodium is of paramount importance [82]. High-purity sodium metal guarantees the stability and

Table 3
Summary of sodium slag recovery methods.

Method	Advantages	Disadvantages	Benefits/CNY·t^{-1}	Ref.
Alcoholysis process	High yield	Organic solvent hazard	680	[59]
Lye leaching	NaOH product	Reaction risk	900	[60]
Thermostatic piston	Simple process	Short equipment life	330	[61]
Vacuum distillation	High product purity	High production cost	500	[62]
Gravity separation	Full use of sodium slag	Complicated process	1290	[63,64]
Melting replacement	Electrolyte regeneration	Slower reaction rate	550	[38,65]
Electrolysis	High utilization rate	Industrial difficulty	1400	[66]

safety of sodium organic compounds and sodium hydrogen storage materials, thereby enhancing their application efficacy [83]. Typically, the purity of metallic sodium must exceed 99.9%, and in certain specialized applications, it may need to reach as high as 99.99% (4 N) or even greater. In the realm of hydrogen storage materials, $NaBH_4$ is regarded as a crucial choice for hydrogen production through hydrolysis due to its high hydrogen storage capacity and stability in alkaline solutions with non-flammability. $NaBH_4$ has emerged as a promising hydrogen carrier for power sources [84] with significant economic potential [85–88]. In the domain of organic ligands, sodium nitride (NaN_3) is a cost-effective and valuable nitrogen source in organic synthesis. It is beneficial to its excellent nucleophilic anions [89] which can be used to construct *N*-heterocycles [90], amines [91], nitriles [92], and amides [93], and finds extensive application in military industry, biomedicine [94], and agriculture.

4.3. Smelting refractory metals applications of metallic sodium

In the field of smelting refractory metals, the purity of metallic sodium is of paramount importance. According to relevant information, the purity of refractory metals must reach a level of 5 N (99.999%) or even higher [95]. Additionally, the content of individual impurity elements, such as alkali metals like potassium and sodium, and radioactive elements like uranium and thorium, must be at the nanogram level (10^{-9}). This stringent requirement for high purity is essential to ensure the stable performance and safety of the final product. As for some refractory metals of Ti (melting point: 1725 °C), Zr (1857 °C), and Nb (2468 °C), which can be fabricated through sodium reduction [96]. The sodium-titanium method is particularly advantageous due to its concise process flow, high purity, and low production cost. It is well-suited for producing high-quality titanium powder and ferroalloy powder, which is important in advancing the titanium industry.

4.4. Reactor cooling systems applications of metallic sodium

A sodium-cooled fast neutron reactor is a fast neutron breeder reactor that typically uses liquid sodium-potassium alloy as a coolant [97]. The application of sodium in reactor cooling system has a high demand for purity. As a coolant, its purity directly affects the heat transfer efficiency [98]. Impurities such as oxygen, carbon, and hydrogen reduce the thermal conductivity of sodium, affecting its cooling effect in the reactor. At the same time, high purity sodium can reduce the blockage of the flow channel caused by impurities, ensure the heat transfer performance of the fuel assembly and heat exchange, and prevent system failures and accidents [99]. Therefore, the purity of nuclear grade sodium is usually more than 99.9%. Due to its advantages of low melting temperature, low capture cross-section, appropriate flow characteristics, and good compatibility with structural materials and fuels, many countries have proposed liquid metal-cooled fast reactors (LMFR) as fourth-generation reactors [100]. Compared to currently operating reactors, LMFR have a higher heat transfer velocity and temperature expected range to improve safety and economy and reduce equipment core size, significantly improving process safety and operating costs [101].

5. Conclusions and Prospect

As an important light non-ferrous metal, metallic sodium plays a pivotal role in both industrial production and daily life, making it indispensable in energy storage devices, pharmaceuticals, and nuclear energy. Through continuous research efforts, industrial sodium preparation technology has reached a point to basically meet global demand, and several areas require improvement in the future.

(1) Develop new electrolysis methods with high current efficiency.

The mainstream sodium electrolysis technology is around 80%, which leads to higher energy consumption. Therefore, it is imperative to further enhance the electrolysis technology by considering factors such as electrolyte selection, catalyst preparation for the chlorine evolution process, and optimization of membrane materials. These advancements will not only increase production capacity but also lead to energy savings.

(2) The safety treatment of sodium slag recovery technologies

There is currently no standardized technology for the disposal of sodium slag in the industry scale. Therefore, it is urgent to explore new atomic economic method to recovery sodium slag and design the new types of equipment for high separation efficiency in the future.

(3) High-value metal-coupled electrolysis technology for chlorine.

The chlorine gas generated at the anode significantly threatens the environment and human health. Therefore, developing absorbing gas method and producing high-value chloride is a practical research goal for reducing waste of by-product chlorine resources and energy consumption.

(4) Sustainable development of sodium industry

It is essential to optimize the efficiency of resource utilization, reduce waste, and improve the efficiency of raw material use. For example, by improving mining and smelting technologies, the impact on the environment is reduced and the overall utilization rate of resources is increased.

In conclusion, the development of the sodium industry should align with the concept of atomic economic reactions and maximize resource utilization to construct a continuous, efficient, and intelligent production process.

CRediT Authorship Contribution Statement

Keyu Wang: Writing – original draft, Visualization, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Qiuchen Wang: Writing – original draft, Resources, Methodology, Data curation. Man Zhao: Writing – review & editing, Visualization, Validation, Supervision, Project administration. Yanzhi Sun: Software, Methodology. Junqing Pan: Writing – review & editing, Visualization, Validation, Supervision, Software, Project administration, Funding acquisition, Data curation.

Data Availability

No data was used for the research described in the article.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the

review of, the manuscript entitled: Advancements in Sodium Production and Slag Recovery Techniques: A Comprehensive Review.

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