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Invited Review

Recycling and recovery of spent copper–indium–gallium–diselenide (CIGS) solar cells: A review

Xiang Li^{1,2}, Baozhong Ma^{1,2},, Chengyan Wang^{1,2},, Die Hu^{1,2}, Yingwei Lü^{1,2}, and Yongqiang Chen^{1,2}

1) State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China

2) School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

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Abstract: Copper–indium–gallium–diselenide (CIGS) is a fast-evolving commercial solar cell. The firm demand for global carbon reduction and the rise of potential environmental threats necessitate spent CIGS solar cell recycling. In this paper, the sources and characteristics of valuable metals in spent CIGS solar cells were reviewed. The potential environmental impacts of CIGS, including service life, critical material, and material toxicity, were outlined. The main recovery methods of valuable metals in the various types of spent CIGS, including hydrometallurgy, pyrometallurgy, and comprehensive treatment processes, were compared and discussed. The mechanism of different recovery processes was summarized. The challenges faced by different recycling processes of spent CIGS were also covered in this review. Finally, the economic viability of the recycling process was assessed. The purpose of this review is to provide reasonable suggestions for the sustainable development of CIGS and the harmless disposal of spent CIGS.

Keywords: spent solar cells; recycling technology; valuable component separation; metallurgy progress; urban mining

1. Introduction

In recent decades, the global photovoltaic (PV) industry has grown tremendously, and the rise of this clean energy is changing the traditional fossil energy mix [1]. The copper–indium–gallium–diselenide (CIGS) solar cell is an important constituent in PV technologies, with a sharp rise in its use. Excellent photoelectric conversion efficiency and less raw material consumption are major contributors to its extreme competitiveness [2–3]. Fig. 1(a) [4] presents the variation in CIGS efficiency over time. The CIGS efficiency has continued to increase in recent decades [5]. Since 2008, the efficiency change has been more intense because of the attractiveness of CIGS development to researchers. In addition, CIGS is based on using flexible substrates, such as Polyimide (PI), which confers it with lighter weight and longer life [6] and thus has more extensive application space. Fig. 1(b) [7] shows the global production of CIGS in the past ten years. The global CIGS solar cell production presently accounts for nearly one-third of all thin-film solar cells and will have an estimated production value of 4.37 GW by 2023 [8–9]. The market size should increase further as the demand for clean energy increases.

The development of CIGS faces problems; for example, many crucial metals, including indium and gallium, are used in CIGS production [8,10]. These elements are sparse on Earth and are complicated to extract [11–13]. The shortage of critical raw materials limits CIGS development to some ex-

tent [14–15], and because CIGS contains heavy metals and toxic selenides, the potential environmental effects of toxic selenides should also be considered. Hence, high-value scattered metals are mixed with other potentially hazardous waste materials in spent CIGS, and the need to recycle the valuable components in spent CIGS solar cells is inevitable. CIGS solar cells that are already in use will need to be recycled in the future, so reasonable and harmless disposal processes of spent CIGS must be proposed. Furthermore, extensive commercial applications produce a large amount of CIGS process waste and scrap products. The recycling of CIGS should focus more on obsolete product waste in the production process. Currently, the main technologies for preparing CIGS solar cells include sputtering [16–17], chemical deposition [18], and evaporation [19]. Limited by the CIGS preparation process, much waste containing valuable elements is generated during CIGS production. In the sputtering process to produce CIGS films, the utilization rate of the initial target material is only approximately 30wt%, which means that nearly 70wt% of the unqualified target material must be recovered [20]. According to incomplete statistics, in the production process of solar cells, approximately 34% of the raw materials are lost as waste [21]. Therefore, although CIGS solar cells have not yet reached the period of mass scrap, the recovery of valuable components from the waste produced in the CIGS solar cell production process has become a vital issue. The composition of the CIGS solar cell is depicted in Fig. 1(c), and the crystal structure of the CIGS

 Corresponding authors: Baozhong Ma E-mail: bzhma_ustb@yeah.net; Chengyan Wang E-mail: chywang@yeah.net

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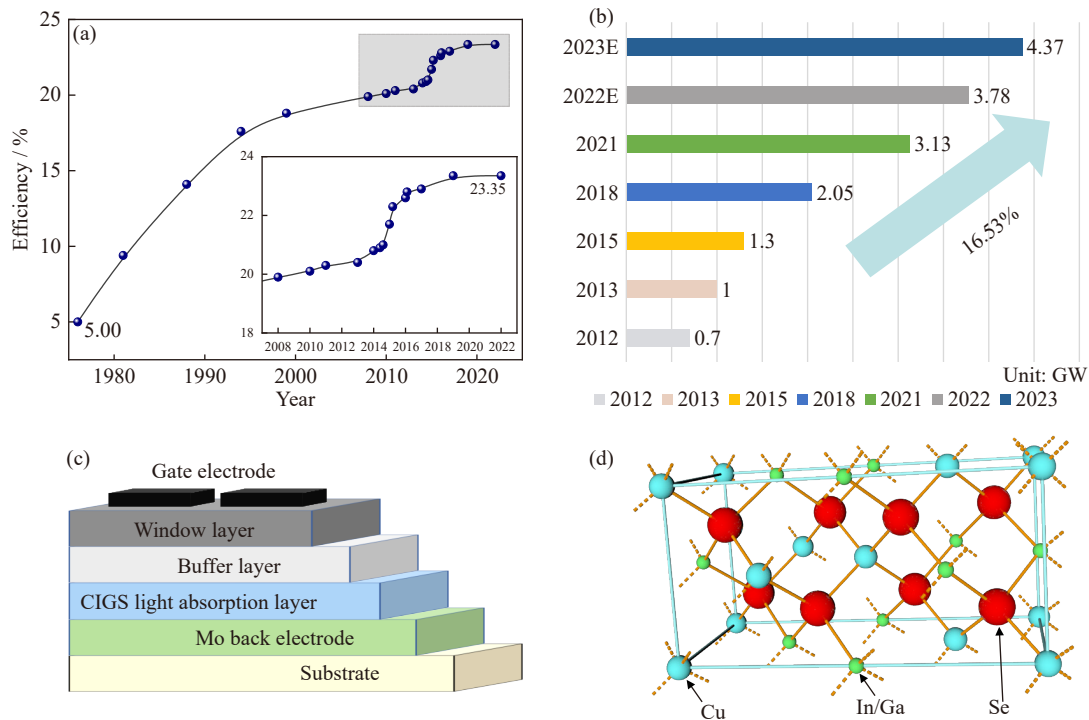


Fig. 1. (a) CIGS photoelectric conversion efficiency vs. year [4]; (b) annual CIGS global production (the data for 2022E and 2023E are estimates) [7]; (c) structure and composition of the CIGS solar cell; (d) the crystal structure of the CIGS light-absorbing layer.

light-absorbing layer is shown in Fig. 1(d) [22–23]. The composition and structure of these process wastes are basically identical to that of CIGS, so these methods and technologies can also be applied to the recycling of spent CIGS solar cells.

Secondary e-waste can be considered an important urban mine [24]. As an important energy storage material, the recovery of spent CIGS is of great importance for urban mining. This process has ecological importance and economic value, and at the same time, it has certain reference importance for similar secondary resource recovery, including indium, gallium, and other scattered metals. It provides a broader vision of the multidimensional, comprehensive, and sustainable mining of urban mines. This comprehensive review is summarized as follows: First, the structure and materials of CIGS are introduced. Second, the possible environmental impact of spent CIGS is examined in detail, the existing spent CIGS recovery technologies are summarized, and the mechanisms of different recovery processes are compared and discussed. Additionally, the challenges of different recycling processes are also covered. Finally, a possible development direction of CIGS recycling is given. The aim is to guide the research exploration of spent CIGS and to reduce its environmental impact.

2. Environmental assessment

Existing authoritative and common environmental assessments of devices such as CIGS are usually provided by a life cycle assessment (LCA) study, which follows the International Standards Organization (ISO) 14040 series [25]. On the basis of certain input conditions and boundary factors, an

LCA assesses the possible environmental impacts of the complete life cycle of products, from raw materials to finished products and waste recycling. For the PV industry, thousands of LCA reports have provided much LCA information since their commercial application. The vast majority of LCAs are about the earliest and most sophisticated silicon-based solar cells. Although the technology may likely continue to dominate the market, CIGS-led thin-film solar cells with lower cost requirements and better performance are likely to gain a larger market share in the future. The existing LCAs for CIGS focus on extracting raw materials such as copper, indium, gallium, and selenium, preparing CIGS, and evaluating the environmental impact during service [26]. Studies show that CIGS has the second lowest impact after cadmium telluride in terms of global warming potential and other impact categories. Overall, CIGS showed relatively positive environmental impact results [27]. However, the CIGS recycling process has received less evaluation because CIGS is in the early stages of commercialization. The environmental impact of the recovery of CIGS after decommissioning is of concern. In this paper, the need to recycle spent CIGS is assessed in terms of service life, critical materials, and toxic effects (Fig. 2).

2.1. Service life and stability

Because it is related to the cost of manufacturing, the mature commercial application of solar cells depends not only on their photoelectric conversion efficiency but also on their stability during long-term service [28]. As for the research on the stability of CIGS solar cells, most existing studies focus on unencapsulated cells. At the micro level, it is like other layered cells. The instability and defects of the two-layer in-

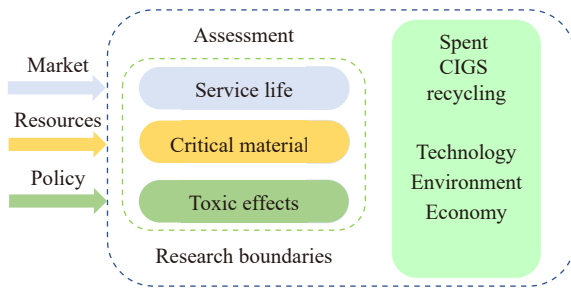


Fig. 2. Research boundaries of spent CIGS recycling assessment.

interface structure of CIGS solar cells, including the molybdenum back electrode/absorption layer, absorption layer/buffer layer, and buffer layer/window layer, where harmful interface reactions may occur, pose a major challenge to their stability [29]. The copper in the absorption layer diffuses to other layered structures as positive ions, which affects their stability. Understanding the relationship between the growth mechanism, morphology, and device characteristics of the thin films in different layered structures of CIGS cells is vital for further improving CIGS cell stability [30]. From the macro perspective, better packaging technology is required, including better adhesion, durability, lower moisture permeability, and better heat resistance, to minimize moisture and oxygen entry. Good encapsulation performance is a common requirement for all solar cells. In summary, the improvement in the micro interface and the continuous maturation of commercial encapsulation technology enable CIGS to have a more stable and continuous service life [31]. The current commercial CIGS has not yet reached its retirement date, and studies indicate that the service life of CIGS is between 20 and 40 years [32–33].

2.2. Critical materials for CIGS

The concept of critical materials has been developed by many countries to describe materials that are scarce, at supply risk, and difficult to replace during application. For the definition and classification of critical materials, each government organization has important differences according to its characteristics. Such as lithium, which is widely used in ternary batteries, and tellurium used in semiconductors [34]. The European Union's list of critical materials even includes rubber.

In the case of CIGS solar cells, the absorption layer contains four elements: copper, indium, gallium, and selenium. Globally, copper resources are widely distributed, according to the global copper production data from the U.S. Geological Survey in 2019, and the countries with the bulk of copper production are Chile, Peru, and China, with copper production in these three countries accounting for nearly half of global production. Copper has strong reproducibility; the global copper resources will be dominated by secondary copper in the future [35]. Most selenium is distributed in China, Canada, and the United States. Global selenium resources are low and mostly associated with sulfide minerals. The industrial enrichment of selenium mainly comes from copper anode slime [36]. High-purity selenium is listed as a critical

material in terms of its important role in metallurgy, semiconductors, and other fields. Among these materials, indium and gallium are globally recognized as critical materials [37]. Indium and gallium have no independent deposits of their own but are produced as by-products of the metallurgical industry. Indium and gallium mainly come from the hydrometallurgical zinc industry [38] and the aluminum extraction industry [39], respectively. The abundance of indium and gallium in these minerals is low, ranging from tens to hundreds of parts per million, which means that the extraction and enrichment processes are cumbersome. Therefore, the global production of virgin indium and gallium is affected by their primary minerals. China is the world's leading producer of primary indium and gallium. Its performance in the global market is price fluctuation and unstable supply. All of this may affect CIGS production. Because indium and gallium are expensive and scarce, some researchers are trying to develop cheaper and more readily available CZTSe solar cells based on metals such as zinc and tin as an alternative to CIGS [40–41]. In fact, indium and gallium play an important role in CIGS because of their unique characteristics [42], so CZTSe under the existing research has difficulty achieving the photoelectric conversion efficiency and stability of CIGS [43]. A good option is to recover indium and gallium from spent CIGS, where the indium and gallium content can reach tens to hundreds of times higher than the mineral content [44]. Non-ferrous metals, such as aluminum and nickel used in electrodes and molybdenum used in back electrodes, are widely used in the industry [45–46]. Therefore, the supply chain of these metals must be considered in CIGS development [47].

2.3. Toxic effects

In the layered structure of CIGS solar cells, the buffer layer is usually composed of n-type CdS and ZnS [48]. Cadmium is the main toxic element in CIGS. Cadmium and its compounds were added to the first list of toxic and hazardous water pollutants as early as 2019. Cadmium compounds are not easily absorbed by the intestinal tract but can be absorbed by the body through breathing, accumulate in the liver or kidneys, and cause harm, as well as osteoporosis and softening of the bones [49]. The metal elements in the CIGS light-absorption layer exist as metal selenides. The steam and dust produced by sputtering and co-evaporation may cause chronic selenium poisoning [50]. Although indium and gallium are relatively less toxic, the effects of their compounds on human health have been reported [51–52]. In addition, the disposal of the waste generated at the end of the life cycle of numerous CIGS solar cells and the process waste generated during CIGS production remain critical issues [53]. Therefore, reasonable recycling technology should be developed for CIGS waste.

3. Recycling and recovery technologies of CIGS waste

The treatment of spent CIGS solar cells can be divided into two parts: the pretreatment of CIGS solar cells and the re-

covery and separation of valuable metals in spent CIGS.

3.1. CIGS absorption layer element composition

The valuable components of spent CIGS (copper, indium, gallium, and selenium) are concentrated in the light-absorption layer. Table 1 [54–60] shows the chemical composition of several typical spent CIGS. Various elements in CIGS exist as selenides, and selenium is the most abundant element in CIGS, accounting for approximately half of the total, while

gallium, which is mainly used to adjust the band gap width in the light-absorption layer, is relatively scarce. The contents of copper and indium are similarly small, accounting for approximately 20wt% of the total. In Ref. [59], selenium was volatilized from the components during treatment, so the selenium content was not reported. The valuable components in CIGS process waste and retired CIGS solar panels show a high enrichment state, and their separation and recovery from spent CIGS are of great importance.

Table 1. Typical spent CIGS components

| Spent CIGS | Element content / wt% | | | | References |
|--------------------------|-----------------------|-------|-------|-------|------------|
| | Cu | In | Ga | Se | |
| Spent CIGS targets | 17.68 | 28.19 | 6.71 | 47.42 | [54] |
| Spent CIGS targets | 25.78 | 26.28 | 4.80 | 43.09 | [55] |
| Spent sputtering targets | 17.00 | 30.20 | 5.00 | 47.80 | [56] |
| CIGS chamber waste | 19.78 | 19.00 | 9.26 | 49.77 | [57–58] |
| Spent CIGS panels | 23.26 | 18.90 | 15.99 | | [59] |
| Spent CIGS panels | 24.00 | 41.00 | 6.00 | 29.00 | [60] |

3.2. Spent CIGS pretreatment

The purpose of CIGS solar cell pretreatment is to separate the different components, to recycle the cover glass that encapsulates the solar cell, and, most importantly, to enrich the high-value metals as much as possible to facilitate the subsequent separation, recovery, and purification. The most common pretreatment methods for solar cell recovery include physical treatment, thermal treatment, and chemical treatment [61]. Mainly mechanical treatment (crushing, grinding, etc.) and ethylene-vinyl acetate copolymer (EVA) treatment are used to achieve mechanical separation of solar cell components [62]. First, metal supports and wires are removed, and then the glass caps of commercial CIGS solar cells are removed by a combination of heat treatment (softening the EVA) and mechanical treatment (mechanical push-off and manual disassembly). Then, the CIGS component after separation is leached to make the residual EVA, ZnO-based window layer, and buffer layer dissolved in acetic acid solution. After drying, the CIGS metal layer and the glass base are separated by mechanical scraping. The CIGS absorption layer is obtained as metal mixture powder. Finally, the base glass is treated with a nitric acid solution to remove the Mo coating and a few residual CIGS after scratching. The recycled base glass can be reused for CIGS solar cells, while the cover glass becomes raw material for the glass industry, and the CIGS powder is left to be separated and recycled by subsequent processes. The method is relatively simple to use to preprocess all parts of the CIGS solar substrate. However, it has limitations. To keep the number of impurities in CIGS powder as low as possible and facilitate subsequent separation and recovery, the dissolution of acetic acid on the ZnO base window layer and the CdS buffer layer should be sufficient. Because the absorption layer of CIGS is very thin, it is difficult to avoid rotating off the Mo coating on the glass substrate in subsequent CIGS separation and recovery. In addition,

the rotary scraping separation equipment should have high-precision requirements. Furthermore, in contrast to the pretreatment of other thin-film solar cell methods, the application of CIGS on flexible substrates is very promising. Most of the current pretreatments are based on rigid substrates, and their applicability is worth considering when recycling flexible CIGS. Therefore, developing suitable pretreatment methods for CIGS flexible solar cells is an interesting topic.

3.3. Recovery and separation of valuable metals in spent CIGS

Copper, indium, gallium, and selenium are the main metals in spent CIGS after pretreatment. These four valuable metals are present as mixed selenides. Separating and recovering valuable metals in spent CIGS are mainly achieved by pyrometallurgy, hydrometallurgy, and combined methods.

3.3.1. Pyrometallurgy separation and recovery of valuable components

Pyrometallurgy is the process of treating spent CIGS at high temperatures to separate and recover different components. Gustafsson *et al.* [63] conducted a detailed study on the separation of valuable components in CIGS by pyrometallurgy. The detailed separation process is shown in Fig. 3 [63–64]. First, spent CIGS targets were oxidized and roasted in a tubular furnace. Studies showed that the selenium in CIGS targets could be separated when the roasting temperature exceeded 500°C, and almost all the selenium in CIGS targets was separated when the roasting temperature was 800°C for 1 h. The selenium dioxide obtained by volatilization and condensation can be reduced to high-purity selenium. The reduction effects of the Riley reaction (an organic molecule was used as the reducing agent) and sulfur dioxide were compared, and the yield of selenium was 90.7% and 93.8%, respectively. The specific reactions are shown in Fig. 3. The reduction effect of sulfur dioxide was more substantial, and the purity of selenium can reach 5N [56]. This approach should

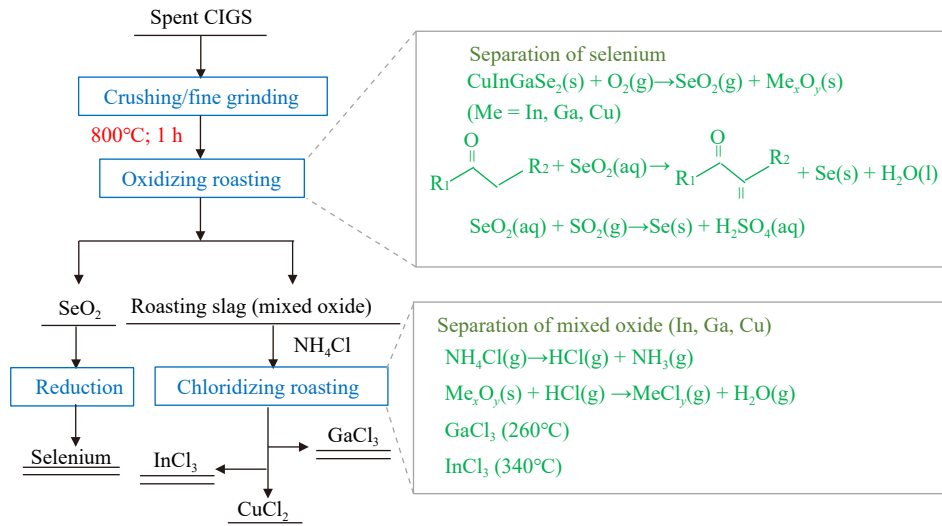


Fig. 3. Spent CIGS pyrometallurgy flowchart.

be reapplied in preparing solar-level materials.

Subsequently, Gustafsson *et al.* [64] explored the feasibility of high-temperature chlorination separation of copper, indium, and gallium using the mixed oxide obtained after selenium separation as raw material. The influence of chlorine, hydrogen chloride, and ammonium chloride on the separation effect was studied. The results show that ammonium chloride as a chlorinating agent has a good separation effect on the three metals. When the chlorination temperature is 260 and 340°C, gallium and indium can be separated as chlorides, and the separation rates are 97% and 93%, respectively [63]. Copper remains in the roasting slag. This method achieves the separation of indium, gallium, and copper from spent CIGS.

Selenium accounts for approximately half of the total amount of the four metals in spent CIGS. Compared with the other three metals, selenium has different physical properties; that is, its gaseous oxide (SeO₂) is volatile, and separating the gas–solid phase is more thorough after thermal treatment [65–66]. Therefore, the separation effect of selenium in CIGS by gas-phase roasting is optimal. The higher reactivity of chloride and its unique physical characteristics (soluble and volatile) mean that chlorination roasting can be performed at a lower temperature to separate the components [67–68]. The difference in chloride volatilization temperature among copper, indium, and gallium makes the separation process selective. The thermal recovery process for the spent CIGS is brief and has a good separation effect, but the energy consumption of thermal separation is still high. Meanwhile, the reactants (NH₄Cl) and intermediate products (Cl₂, SeO₂) in the roasting process are volatile and toxic. Therefore, the process has problems such as the coexistence of toxic gas absorption and equipment anti-corrosion in large-scale industrial applications.

3.3.2. Hydrometallurgy separation and recovery of valuable components

In contrast to the pyrometallurgy separation process, the hydrometallurgy recovery of spent CIGS valuable components usually comprises leaching and separation. The leaching

process realizes the conversion between the solid and liquid phases of the valuable components in spent CIGS. Methods such as precipitation and extraction are used to separate the valuable components from polymetallic leachate.

(1) Direct leaching of valuable components.

CIGS has a chalcopyrite-like crystal structure, which is inspired by the leaching process of chalcopyrite. The commonly used leaching agents of chalcopyrite include acid leaching agents such as hydrochloric acid [69], sulfuric acid [70], and organic acid [71]. In different leaching media, the leaching effects of indium and gallium in spent CIGS are shown in Fig. 4 [60]. This figure shows that in the absence of a catalyst, inorganic acids, including sulfuric acid, nitric acid, and hydrochloric acid, show a good leaching effect on indium. When using citric acid, the leaching rate of indium in CIGS is only half of that of an inorganic acid. The leaching effect of indium in CIGS is worse in an alkaline medium than in an acidic medium. For gallium, the leaching effect shows little difference among media, except for being slightly higher in nitric acid, reaching 40%.

(2) Enhanced leaching of valuable components.

Considering the compact chalcopyrite-like crystal structure of CIGS, passivation films may be formed on the surface of the material during leaching, which may deteriorate the leaching effect [72–74]. Therefore, it is feasible to use enhanced leaching methods, including adding reinforcing oxidizer and pressurization in the leaching process of spent CIGS. In the aforesaid direct leaching process, sulfuric acid, hydrochloric acid, and nitric acid, three inorganic acids, show a better leaching effect. At the same time, inorganic acid has more economic advantages in large-scale industrial applications. Therefore, the enhanced leaching processes of spent CIGS in inorganic acid media are of great importance. Enhanced leaching of spent CIGS in inorganic acid media (H₂SO₄, HCl, and HNO₃) and its mechanism is shown in Fig. 5 [54–55,75].

Hsing *et al.* [54] used sulfuric acid to leach CIGS in an autoclave for 4 h at 140°C and found that much CIGS phase remained in leach residue after leaching. This finding is re-

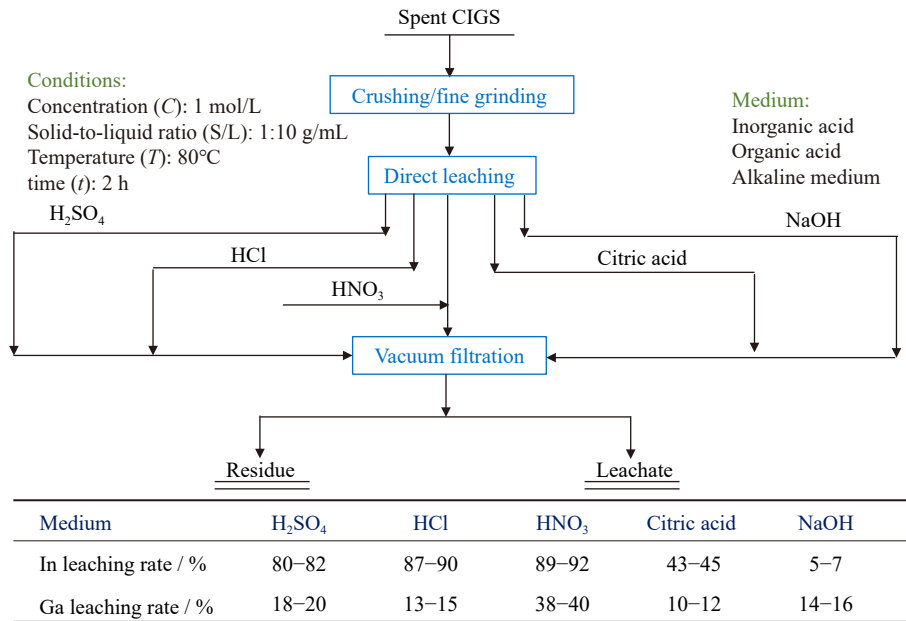


Fig. 4. Direct leaching rates of valuable components from spent CIGS with different media.

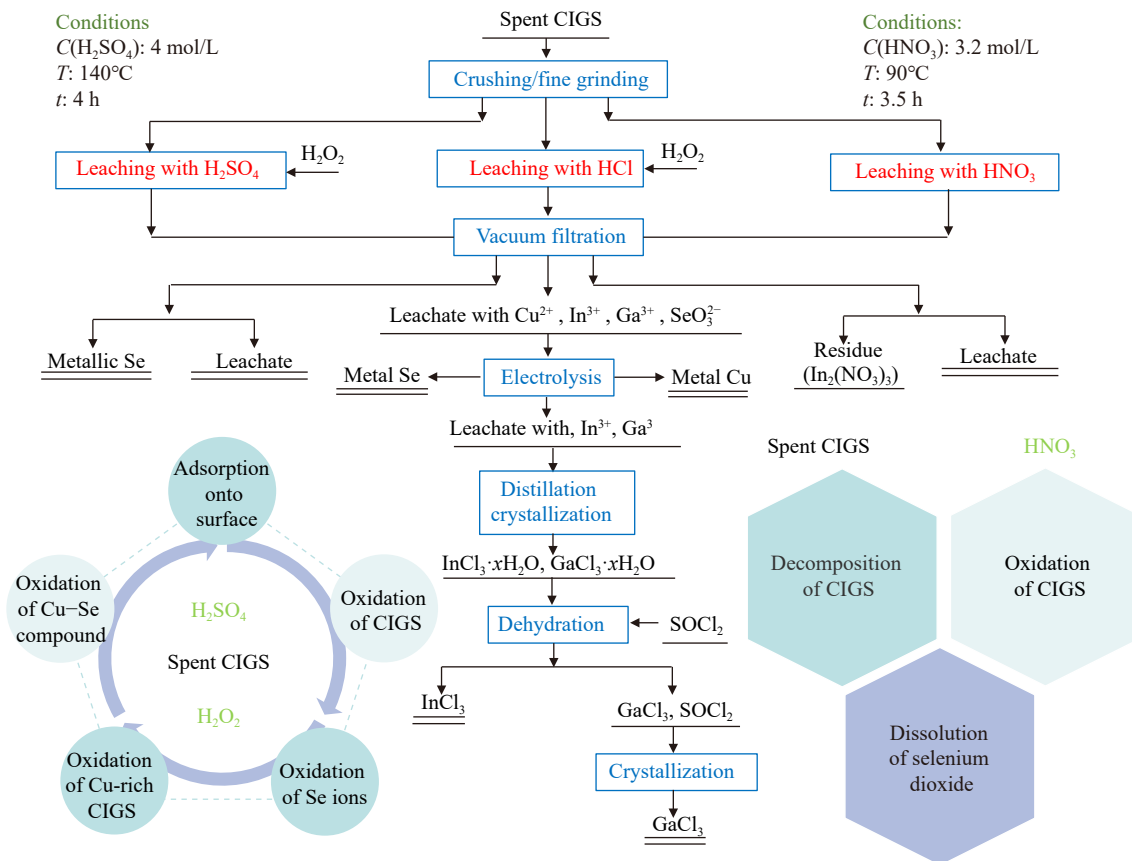


Fig. 5. Enhanced leaching of spent CIGS in inorganic acid media and the leaching mechanism.

lated to the compact crystal structure of CIGS materials. H₂O₂ was added in the leaching process. With increasing dosage of H₂O₂, the main phase of CIGS in the leaching residue changed to metal selenium. Finally, the optimal leaching conditions were determined as follows: 0.15 g CIGS powder, 30 mL of 3 mol/L H₂SO₄, and 1 mL of 1 mol/L H₂O₂ for 4 h. Under the optimal leaching conditions, the indium, gallium, and copper in CIGS were almost completely

leached, and the selenide in CIGS was oxidized to elemental metal selenium.

Gu *et al.* [55] recovered valuable components from spent CIGS by combining hydrometallurgy and electrochemical technology. Hydrochloric acid is selected as the medium for the leaching process, and under optimal leaching conditions (HCl solution containing 5vol% H₂O₂ with 5 mol/L acid concentration, a solid–liquid ratio of 5 g/L, a leaching temperat-

ure of 40°C , and a leaching time of 1.5 h), more than 99.9% of copper, indium, gallium, and selenium were leached. Notably, a mixture of Cu²⁺, In³⁺, Ga³⁺, and SeO₃²⁻ was obtained by leaching a spent CIGS target with hydrochloric acid and H₂O₂. Unlike the sulfuric acid, selenium is present in the leaching solution as selenic acid instead of solid metal selenium. Metal selenium and copper were obtained through electrolysis according to the different electrochemical properties of components in the leaching solution. Indium and gallium in the electrolytic solution were obtained by distillation with InCl₃ and GaCl₃, respectively. Then, indium and gallium were separated by their different solubilities in SOCl₂. The results showed that the separation rate and purity of indium and gallium reached 99.99%.

Hu et al. [75] studied the separation and leaching effect of spent CIGS in a nitric acid system. Under a nitric acid concentration of 3.2 mol/L, liquid-to-solid ratio of 9 mL/g, leaching temperature of 90°C, and leaching time of 3.5 h, the leaching rates of copper, indium, gallium, and selenium in the spent CIGS were 98.74%, 95.55%, 60.22%, and 3.18%, respectively. The phase of leaching residue is indium selenate. A leaching solution rich in copper, gallium, and selenium was precipitated by magnesium oxide at pH 5.5. The precipitation rates of Cu, Ga, and Se were 99.23%, 98.08%, and 98.43%, respectively. The precipitated solution was magnesium nitrate solution, and the leaching reagent nitric acid could be regenerated through pyrolysis and absorption. Exploiting the volatile property of selenium, high-purity selenium was obtained from precipitation residue and leaching

residue by roasting.

The enhanced leaching of spent CIGS in an inorganic acid medium showed that adding an oxidizing agent, increasing leaching system pressure, increasing temperature, and increasing acidity can substantially increase the extraction rate of valuable components. A mechanism comparison of the enhanced leaching of spent CIGS in inorganic acid media is shown in Table 2. In a sulfuric acid and hydrogen peroxide system, the adsorption of hydrogen peroxide on CIGS particles occurred first, followed by CIGS decomposition and Se oxidation in CIGS. The indium and gallium of CIGS were leached first, while the selenide of copper residue was leached slowly. In the oxidation reaction, the –2-valence selenium in CIGS was oxidized to metallic selenium. In the hydrochloric acid system, almost all the components were leached by adding hydrogen peroxide, and the valence state of selenium in the leached solution was +4 selenite. The leaching reaction of CIGS in the nitric acid system showed that low-valence nitrogen oxides were discharged during the leaching process. The researchers used a closed-cycle leaching process in which selenium dioxide gas and nitrogen oxides produced during the oxidation leaching process were absorbed by the leaching solution. In the subsequent process, approximately 40wt% of the produced selenic acid was combined with indium to form indium selenate, which was insoluble in acid. Indium was separated during leaching. Therefore, during enhanced leaching, the valence and forms of selenium and the reaction pathways of selenium oxidation in CIGS vary greatly between leaching media, which directly affects the subsequent extraction and separation effect.

Table 2. Reaction comparison of the enhanced leaching of spent CIGS in inorganic acid media

| | |
|--|---|
| Spent CIGS + H ₂ SO ₄ + H ₂ O ₂ [54] | |
| Surface adsorption of H ₂ O ₂ | CuInGaSe ₂ + H ₂ O ₂ → CuInGaSe ₂ [H ₂ O ₂] _{ads} |
| Decomposition of CIGS | CuInGaSe ₂ → Cu _{1-x} (InGa) _{1-y} Se ₂ + xCu ²⁺ + yIn ³⁺ + yGa ³⁺ + Se ²⁻ |
| Oxidation of Se ions | 2Se ²⁻ + H ₂ O ₂ + 2H ⁺ → Se ₂ ²⁻ + 2H ₂ O, Se ₂ ²⁻ + H ₂ O ₂ + 2H ⁺ → 2Se ⁰ + 2H ₂ O |
| Oxidation of Cu-rich CIGS | Cu _{1-x} (InGa) _{1-y} Se ₂ → Cu _{1-x-z} Se ₂ + zCu ²⁺ + (1-y)In ³⁺ + (1-y)Ga ³⁺ |
| Oxidation of Cu–Se compound | Cu _{1-x-z} Se ₂ → (1-x-z)Cu ²⁺ + Se ⁰ |
| Spent CIGS + HCl + H ₂ O ₂ [55] | |
| Surface adsorption of H ₂ O ₂ | CuInGaSe ₂ + H ₂ O ₂ → CuInGaSe ₂ [H ₂ O ₂] _{ads} |
| Decomposition of CIGS | CuIn _{0.5} Ga _{0.5} Se ₂ → Cu ⁺ + 0.5In ³⁺ + 0.5Ga ³⁺ + 2Se ²⁻ |
| Oxidation of Se ions | Se ²⁻ + 3H ₂ O ₂ → SeO ₃ ²⁻ + 3H ₂ O |
| Spent CIGS + HNO ₃ [75] | |
| Oxidation of CIGS | 2CuIn _{0.5} Ga _{0.5} Se ₂ + 36H ⁺ + 26NO ₃ ⁻ → 2Cu ²⁺ + In ³⁺ + Ga ³⁺ + 4SeO _{2(g)} + 18H ₂ O + 26NO _{2(g)} |
| Dissolution of SeO ₂ | SeO _{2(g)} + 2H ₂ O → SeO ₃ ²⁻ + 2H ⁺ |
| Formation of In ₂ (SeO ₃) ₃ | 2In ³⁺ + 3SeO ₃ ²⁻ → In ₂ (SeO ₃) ₃ (insoluble) |

3.3.3. Comprehensive treatment processes

Studies on the direct leaching and enhanced leaching of spent CIGS showed that large amounts of inorganic acids and oxidants are needed to destroy the stable chalcopyrite structure. In the leaching process, Se in spent CIGS is oxidized. Se shows different characteristics in different media and leach-

ing conditions, which makes the subsequent separation of the four valuable components uncertain. Considering the phase structure and component characteristics of CIGS, it is more beneficial to destroy the phase structure of CIGS before leaching. Therefore, some researchers combine methods to treat spent CIGS. The separation process is shown in Fig. 6

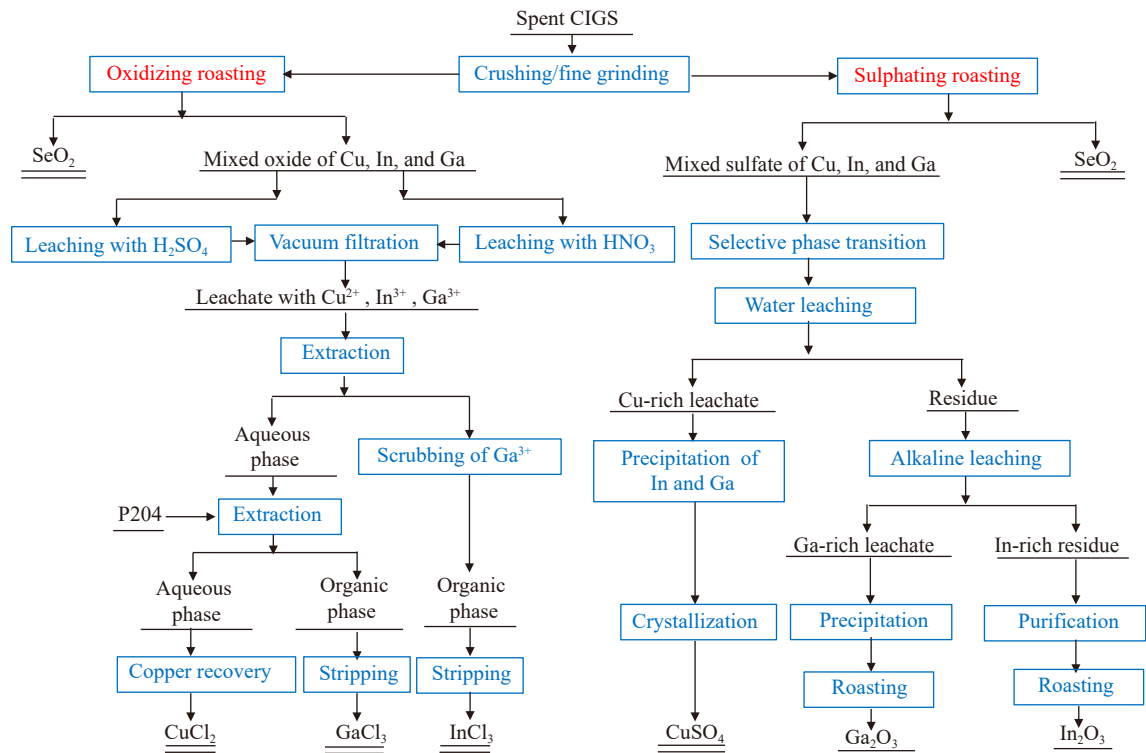


Fig. 6. Process flow chart of combined processes for spent CIGS treatment.

[57–59].

Lv *et al.* [57] separated the components in spent CIGS by combining oxidizing roasting with leaching, precipitation, and extraction. First, the selenium was separated by oxidizing roasting. The separation rate of selenium reached 99.9% after roasting the CIGS chamber waste at 1000°C for 3 h. The mixed oxide roasting residue was obtained after selenium separation and leached it with 4 mol·L⁻¹ sulfuric acid at a liquid-to-solid ratio of 10 mL·g⁻¹ and a leaching temperature of 90°C for 4 h. The leaching rates of copper, indium, and gallium were 98.81%, 97.80%, and 98.22%, respectively. These results show that almost all the metal go into the solution. Indium, gallium, and copper were then separated by precipitation. When the pH was 3.5, indium and gallium were almost completely precipitated (99.60% and 99.51%, respectively) with ammonia water as the precipitant. The resulting precipitate was calcined at 800°C to obtain mixed oxides of indium and gallium. The obtained indium–gallium mixed oxide was dissolved in hydrochloric acid and then extracted with a P204 extraction agent. When the O/A ratio was 1:3, the acidity was 1 mol·L⁻¹, and the mixing time was 5 min, the indium extraction rate was 91.5%, while the gallium extraction rate was only 0.4%. The copper remaining in the submerged solution was extracted using Lix984. The separation rate of copper was 99.83%. Copper sulfate crystals could be obtained by evaporation crystallization.

The recent research work of Hu *et al.* [76] showed that the three components of copper (99.98%), indium (93.40%), and gallium (96.86%) can be completely dissolved by leaching the roasting residue after oxidative roasting to separate selenium with hydrochloric acid (conditions: concentration (*C*), 4 mol/L; Temperature (*T*), 80°C; time (*t*), 3 h; liquid-to-solid

ratio (L/S ratio), 10 mg/L). Under low acidity, extractant P204 has a better extraction ability for indium and gallium but can barely extract copper. Indium has a higher complexation ability than gallium. Therefore, indium, gallium, and copper can be separated theoretically through extraction. Thus, the ions of indium, gallium, and copper in the leachate were separated by extraction. The study by Hu *et al.* [76] showed that almost all the In (99.92%) in the leachate obtained from spent CIGS was extracted (conditions: *C*(HCl), 0.7 mol/L; 30vol% P204 (in sulfonated kerosene); aqueous phase to organic phase ratio (A/O), 1; *t*, 5 min with three-stage extraction). The extraction rate of gallium in the residual extract of indium can reach 99.4% under an acidity of 0.1 mol/L, 30vol% P204, and an extraction time of 5 min. During the extraction process, copper remains in the aqueous phase and can be recovered by extraction or precipitation.

Liu *et al.* [59] combined the methods of oxidative roasting–acid leaching–extraction–precipitation to treat waste CIGS panels. The separated CIGS waste was oxidatively roasted at 900°C for 4 h to remove selenium. The mixed oxidative roasting residue after de-selenium was leached by nitric acid (conditions: *C*, 5 mol/L; L/S ratio, 50 mL/g; *T*, 80°C; *t*, 3 h). Then, indium, gallium, and copper were extracted and separated in a nitric acid system. When the pH range was 0.5–1.0, the concentration of extractant D2EHPA was 0.05 mol/L, the extraction time was 5 min, and the A/O ratio was 4, 99% of indium could be selectively separated from the leaching solution. After separating indium, gallium was subsequently separated from the aqueous solution using D2EHPA, and under optimal conditions (conditions: pH, 2.0; *C*(D2EHPA), 0.06 mol/L; A/O, 1; *t*: 10 min), the separation of gallium was nearly complete. Stripping was applied to the

separated indium (conditions: $C(\text{HCl})$, 2 mol/L; A/O, 1; t , 10 min) and gallium (conditions: $C(\text{HCl})$, 1 mol/L; A/O, 1; t , 5 min). Then, the hydroxides of copper indium and gallium were obtained by ammonia precipitation, the corresponding oxides were obtained after calcination, and the recovery rates of copper, indium and gallium were 88.9%, 98.2%, and 97.1%, respectively.

Ma *et al.* [58] also used a combination of pyro-hydrometallurgy to separate and recover valuable elements from CIGS chamber waste. In contrast to the abovementioned oxidizing roasting, concentrated sulfuric acid was added in this study for sulfating roasting. The results showed that when acid-to-material ratio was $2.5 \text{ g} \cdot \text{g}^{-1}$, and CIGS chamber waste was calcined at 600°C for 3 h, the separation rate of selenium from CIGS chamber waste was 99.96%. After separating the selenium, a mixed sulfate of indium, gallium, and copper was obtained, and the obtained mixed sulfate was subsequently calcined a second time to complete the phase transition. The roasting temperature was controlled at 710°C , and the roasting time was 2 h, so that the indium sulfate and gallium sulfate in the roasting slag were transformed into oxides, while the copper sulfate almost did not undergo phase transformation. The leaching rate of copper was 95.90%, while the leaching rates of indium and gallium were only 5.67% and 2.89%, respectively. The separation of indium, gallium, and copper was achieved. Li *et al.* [77] conducted follow-up work related to separating indium and gallium. According to their different occurrence forms in an alkaline environment, indium and gallium were separated by alkali leaching. Under the optimal experimental conditions (conditions: C , 7 mol/L; T , 60°C ; S/L, 1:10 g/mL; t , 3 h), the leaching rate of indium and gallium was 3.37% and 97.26%, respectively. After purification, indium oxide and gallium oxide, with a purity of 96.04% and 99.83%, respectively, were obtained.

3.3.4. Component separation mechanism

The physicochemical properties of selenium in spent CIGS clearly differ from those of the other three elements. The direct leaching process of CIGS shows that the leaching effect of nitric acid is considerably higher than that of other media under the same conditions. This difference comes from the oxidizing properties of nitric acid itself. Selenides in CIGS are more susceptible to oxidation and structural damage. A thermodynamic analysis of leaching CIGS in a nitric acid system is given in Fig. 7(a) [75]. During enhanced leaching, upon adding an oxidant to treat CIGS waste, different products are generated because of the different oxidation paths and reaction modes of low-valence selenium in the oxidation process. This feature has a considerable impact on the subsequent separation process. Selenium dioxide is very volatile, so separating selenium from spent CIGS in the gas–solid phase and destroying the stable crystal structure of mixed selenides effectively recovers the valuable components in spent CIGS.

Differences in chamber waste, target material, and solar panels pertain to separating selenium during oxidative roasting. The roasting temperature is $800\text{--}1000^\circ\text{C}$, and the roasting time is 1–4 h. These differences may be related to the

structural stability of different classes of CIGS wastes. A composition equilibrium diagram of CIGS during oxidation roasting is shown in Fig. 7(b) [57]. Increasing the roasting temperature and prolonging the roasting time benefit the complete oxidation of selenium in CIGS, but it may also generate extremely stable and insoluble acid-insoluble copper–indium–gallium mixed oxides in the roasting slag. This result causes trouble in the subsequent leaching. In contrast, the temperature of sulfated roasting is substantially lower than that of oxidative roasting. The sulfated and roasted products, sulfates, and oxides are also easier to separate in the subsequent leaching process. This recovery process is disadvantageous because sulfur dioxide flue gas is discharged from the sulfation roasting, and a more complicated tail gas treatment device is necessary.

Roasting slag after de-selenium also completed the phase transformation. After acid dissolution, mainly a mixed solution of copper, indium, and gallium ions in the liquid phase is obtained. The methods for separating copper, indium, and gallium from liquid components mainly include precipitation and extraction. The forms of copper, indium, and gallium ions clearly differ at different pH values, so adjusting the pH can realize their gradient separation. The pH range at which copper, indium, and gallium begin to precipitate and complete precipitate in the liquid-phase system is given in Fig. 7(c) [77]. P204 extractant has strong selectivity for indium and gallium, but almost no copper is extracted [78–79]. Compared with gallium, indium shows stronger complexing ability. The difference between indium- and gallium-loaded organic phase products separated by P204 extraction is given in Fig. 7(d).

3.3.5. Other methods

In addition to complete separation and recovery of the valuable components of spent CIGS, some researchers have attempted to reapply spent CIGS directly into CIGS production. Miyazaki [80] peeled off the light-absorbing layer in the CIGS solar cell and then directly used it as a raw material for secondary deposition to prepare a new CIGS thin film. The research shows that the main phase structure of the light-absorbing layer obtained after redeposition is still chalcopyrite-like, and the surface microstructure is similar to that of the original CIGS film. Therefore, using the spent CIGS absorber layer as the deposition source of new CIGS is feasible. The excellent photoelectric conversion efficiency of CIGS comes from its high requirements for the purity of its components, and introducing trace impurities may affect its performance [81–82]. As mentioned earlier about the pretreatment of CIGS solar cells, impurity elements such as Mo are very easily introduced during the separation process. In addition, the aforementioned studies indicate that the structural components of CIGS process waste and CIGS waste solar cells may still differ, and whether the process waste is also suitable for the direct deposition regeneration of CIGS remains unknown. Therefore, much work is needed to ensure a good conversion efficiency of CIGS deposited directly from the spent CIGS absorber layer.

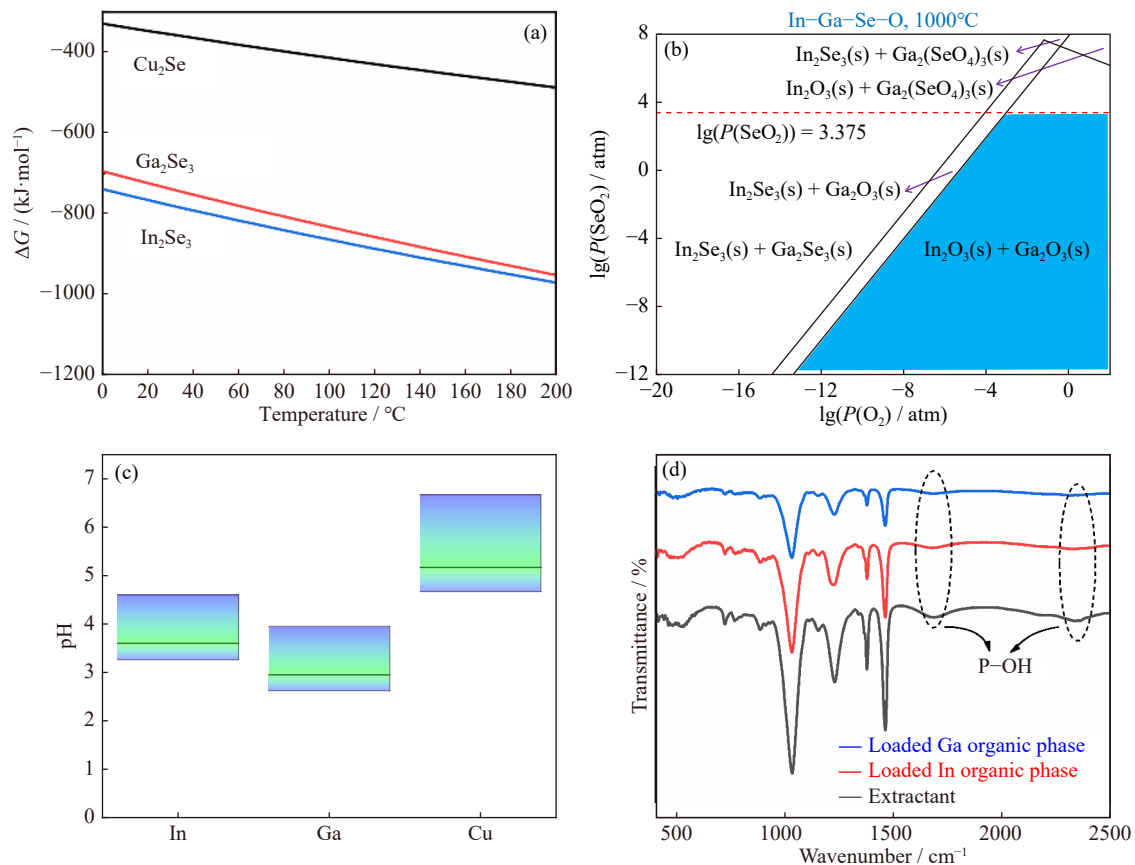


Fig. 7. Mechanism of spent CIGS recovery: (a) thermodynamic analysis of leaching CIGS in a nitric acid system; (b) composition equilibrium diagram of CIGS during oxidation roasting; (c) pH range at which copper, indium, and gallium begin to precipitate and complete precipitation in the liquid-phase system; (d) indium- and gallium-loaded organic phase products separated by P204. ΔG —Gibbs free energy; $P(\text{O}_2)$ —Vapor pressure of oxygen; $P(\text{SeO}_2)$ —Vapor pressure of selenium dioxide. (a) Reprinted from *J. Clean. Prod.*, 350, D. Hu, B.Z. Ma, X. Li, *et al.*, Innovative and sustainable separation and recovery of valuable metals in spent CIGS materials, 131426, Copyright 2022, with permission from Elsevier. (b) Reprinted with permission from Y.W. Lv, P. Xing, B.Z. Ma, *et al.*, *ACS Sustain. Chem. Eng.*, 19816–19823 (2019) [57]. Copyright 2019 American Chemical Society. (c) Reprinted from *J. Clean. Prod.*, 339, X. Li, B.Z. Ma, D. Hu, *et al.*, Efficient separation and purification of indium and gallium in spent copper indium gallium diselenide (CIGS), 130658, Copyright 2022, with permission from Elsevier.

4. Recovery process assessment

Many efforts have been made to recycle CIGS waste in hydrometallurgy as well as pyrometallurgy. Experimental details on the recovery of valuable components from spent CIGS are shown in Table 3. The merits and demerits of dif-

ferent recycling processes are compared in Table 4. In the current recovery methods, copper, indium, and gallium are recovered to more than 90%, while selenium is nearly completely recovered. Regarding the products, selenium is mainly obtained as selenium dioxide, while copper, indium, and gallium are separated in the leaching solution to obtain

Table 3. Experimental details on the recovery of valuable components from spent CIGS

| Methods | Extraction agents | Extraction conditions | Extraction efficiency | References |
|----------------------|--|---|--|------------|
| Oxidative roasting | Air | T , 800°C; t , 1 h | $\text{SeO}_2 > 99\%$ | [56] |
| Chlorinated Roasting | NH_4Cl | Gallium recovery: T , 240°C; $t > 6$ h; NH_4Cl addition (mol/mol), 9; gas flow, 400 mL/min | Ga, 97.2% | [63–64] |
| | | Indium recovery: T , 360°C; $t > 6$ h; NH_4Cl addition (mol/mol), 13.5; gas flow, 200 mL/min | In: 93.6% | |
| Enhanced leaching | $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ | T , 140°C; 0.15 g CIGS powder, 30 mL of 3 mol/L sulfuric acid, 1 mL of 1 mol/L H_2O_2 for 4 h | Leaching rate: In/Ga/Cu $> 99\%$ | [54] |
| | $\text{HCl} + \text{H}_2\text{O}_2$ | C , 5 mol/L; T , 40°C; S/L, 5 g/L; t , 1.5 h; $C(\text{H}_2\text{O}_2)$, 5vol% | Leaching rate: Cu/In/Ga/ $\text{SeO}_3^{2-} > 99\%$ | [55] |
| | HNO_3 | C , 3.2 mol/L; T , 90°C; S/L, 1:9 g/mL; t , 3.5 h | Leaching rate: Cu, 98.74%; In, 95.55%; Ga, 60.22%; Se, 3.18% | [75] |

Table 3 (Continued)

| Methods | Extraction agents | Extraction conditions | Extraction efficiency | References |
|-----------------|--|---|---|------------|
| | Oxidative roasting | Roasting conditions: T , 1000°C; t , 3 h | SeO ₂ > 99.9% | |
| | Acid leaching: H ₂ SO ₄ | Acid leaching conditions: C (HCl), 4 mol/L; T , 80°C; S/L, 1:10 g/mL; t , 3 h | Leaching rate: Cu, 96.45%; In, 94.06%; Ga, 96.49% | |
| | Precipitation: NH ₄ OH | Precipitation condition: pH = 3.5 | Precipitation rate: In, 99.60%; Ga, 99.51% | [57] |
| | Extraction: P204; Lix984 | Extraction condition: O/A, 1:3; C , 1 mol/L; t , 5 min | Extraction rate: In, 91.5%; Ga, 0.4%; Cu, 99.83% | |
| | Oxidative roasting | Roasting conditions: T , 1000°C; t , 3 h | SeO ₂ > 99.9% | |
| | Acid leaching: HCl | Acid leaching conditions: C (H ₂ SO ₄), 4 mol/L; T , 90°C; S/L, 1:10 g/mL; t , 4 h | Leaching rate: Cu, 99.98%; In, 93.40%; Ga, 96.86% | |
| Combined method | Extraction: P204 | Extraction condition for In: C (HCl), 0.7 mol/L; C (P204), 30vol%; O/A, 1:1; t , 5 min; extraction stage, 3 Extraction condition for Ga: C (HCl), 0.1 mol/L; C (P204), 30vol%; O/A, 3:1; t , 5 min | Extraction rate: In, 99.91%; Ga, 99.93% | [76] |
| | Oxidative roasting | Roasting conditions: T , 900°C; t , 3 h | SeO ₂ > 99.9% | |
| | Acid leaching: HNO ₃ | Acid leaching conditions: C (HNO ₃), 5 mol/L; T , 80°C; S/L, 1:50 g/mL; t , 3 h | Leaching rate: Cu, In, and Ga > 99% | |
| | Extraction: D2EHPA | Extraction condition for In: pH, 0.5–1.0; C (D2EHPA), 0.05 mol/L; A/O, 4; t , 5 min Extraction condition for Ga: pH, 2.0; C (D2EHPA), 0.06 mol/L; A/O, 1; t , 10 min | Recovery rate: Cu, 88.9%; In, 98.2%; Ga, 97.1% | [59] |
| | Sulfating roasting: H ₂ SO ₄ | Sulfating roasting condition: ratio of acid-to-material, 2.5 g·g ⁻¹ ; T , 600°C; t , 3 h | SeO ₂ > 99.9% | |
| | Phase transition | Phase transition condition: T , 710°C; t , 2 h | | |
| | Water leaching: H ₂ O | Water leaching condition: T , 60°C; t , 1 h; S/L, 1 g/10 mL | Water leaching rate: Cu, 95.90%; In, 5.67%; Ga, 2.89% | [58,77] |
| | Alkaline leaching: NaOH | Alkaline leaching condition: C (NaOH), 7 mol/L; T , 60°C; S/L, 1:10 g/mL; t , 3h | Alkaline leaching rate: In, 97.26%; Ga, 3.37% | |

Table 4. Comparison of spent CIGS disposal methods

| Recycling technologies | Methods | Merits | Demerits | Industrialization degree | References |
|------------------------|---|--|--|--------------------------|------------|
| Pyrometallurgy | Oxidation roasting | Efficient recycling of selenium; Large processing capacity | High energy demand | Laboratory | [56] |
| | Chlorination Roasting | High separation efficiency; Stable operation | Exhaust gas treatment demand | Laboratory | [63–64] |
| Hydrometallurgy | Leaching | Simple operation and low energy consumption; Short process | Consumption of a large amount of lixiviant and additives | Laboratory | [75] |
| Combined methods | Oxidation roasting–leaching–extraction | Achieved the separation of copper, indium, gallium, and selenium, high recovery efficiency | Produces organic waste | Laboratory | [59,76] |
| | Sulfate roasting–leaching–precipitation | High recovery efficiency | Requires exhaust gas treatment | Laboratory | [58,77] |
| Other methods | Direct deposition | Realize the closed loop of CIGS production | Immature technology | Laboratory | [80] |

salts or oxidation products. The selenium products have high purity, while the purity of the products of the other three metals needs further improvement.

5. Conclusions and perspectives

CIGS is a type of photovoltaic material with great market prospects. Either process waste or discarded CIGS potentially affect the environment. In this paper, the necessity to recycle CIGS waste was assessed in terms of service life, critical materials, and toxic effects. The technologies related

to spent CIGS recycling were reviewed, providing a reference for establishing a complete CIGS recycling life cycle. Some conclusions and perspectives are as follows.

(1) The recovery methods for the valuable components in CIGS mainly include pyrometallurgy, hydrometallurgy, and combined methods. The stable chalcopyrite crystal structure in spent CIGS is the key factor hindering the separation and recovery of valuable CIGS components. The physical properties of the four elements in CIGS waste are considerably different. Low-valent selenium in CIGS waste occurs in different forms during the oxidation process in different media.

Using the strong volatility of selenium dioxide to separate selenium from CIGS waste in the gas–solid phase, the separation efficiency is optimal, the purity is high, and the CIGS crystal structure is destroyed simultaneously. This separation method has industrial prospects. The copper, indium, and gallium ions in the liquid system showed obvious differences at different pH values. The extractant P204 has obvious selectivity for indium and gallium. Separating copper, indium, and gallium by precipitation and extraction in the liquid-phase system is a suitable method. Most existing recovery processes focus on the separation process of the components in spent CIGS. Product purification needs further study.

(2) CIGS waste has many types, and in the recycling process, the specific conditions of the same treatment method still differ. However, the principle of separation and recycling is similar. Being circular recycling rather than linear recycling, directly reapplying CIGS waste to CIGS production is undoubtedly the optimal recycling method. The research on this method is extremely limited, and considering the high requirement for the material purity of CIGS photoelectric conversion efficiency, this approach requires more attention and investment.

(3) Because the service life of CIGS commercial photovoltaic products has not yet ended, a limited amount of work has been reported on CIGS scrap recycling, and all the reported studies are still in the laboratory research stage. Further research needs to be conducted on the feasibility of industrial-scale recycling of CIGS. Given the development trend of flexible CIGS, the recycling method of flexible CIGS must be further considered, which may differ from general CIGS recycling.

(4) Recycling CIGS is a typical multicomponent separation process, and it can provide ideas for the similar recycling of polymetallic hazardous wastes. It should expand the scope of the reliable management of urban mines and provide a reference for recovering other secondary resources.

Overall, appropriate CIGS recycling techniques should be less energy intensive, have less potential environmental impact, and possess economic feasibility. Furthermore, as an emerging energy storage material, CIGS is rapidly updated and iterative, and more investment and real-time follow-up recycling technology are also a matter of concern. These issues are inseparable from the development of intelligent manufacturing in metallurgy [83].

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Conflict of Interest

The authors declare that they have no known competing

financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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