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Review

The Extraction and Separation of Scarce Critical Metals: A Review of Gallium, Indium and Germanium Extraction and Separation from Solid Wastes

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Abstract: Gallium (Ga), indium (In), and germanium (Ge) play an important role in the modern high-tech material field. Due to their low content and scattered distribution in the crust, and the increasing demand for these metals in recent years, their supply risks have sharply increased. Therefore, the recycling of these metals is of great significance. In this work, a systematic review was performed using the Web of Science, Scopus, MDPI, Elsevier, and Springer Link databases. The combined terms used for the search were Ga/In/Ge, extraction, separation, and recycling. After a careful evaluation of the titles, abstracts, and full texts, a total of 106 articles were included. This paper briefly describes the resource features of Ga, In, and Ge. After that, the chemical principles, technical parameters, and metal recovery in various extraction and separation methods from monometallic and polymetallic resources are systematically reviewed. Leaching followed by solvent extraction or ion exchange is the main process for Ga, In, and Ge recovery. Although many attempts have been made to separate multiple metals from leaching solutions, highly selective solvents and resins are still the research priority. This review can provide theoretical and technical guidance for the separation of Ga, In, and Ge from various resources.

Keywords: Ga, In, and Ge; extraction and separation; hydrometallurgy and pyrometallurgy; technical routes; mechanism

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1. Introduction

Gallium (Ga), indium (In), and germanium (Ge), as rare metals, are the key materials for contemporary high-tech new materials, and they play an important role in the development of high technology and future energy. Ga, In, and Ge have a wide range of applications in the computer, communication, aerospace, energy, medicine, and health industries (Figure 1a) [1–3]. According to USGS statistics, shown in Figure 1b–d, the global Ga, In, and Ge products are mainly manufactured in China, Russia, Korea, and Japan, and among these countries, China accounts for the majority of the production of these three metals. However, these metals are difficult to extract since the average contents of Ga, In, and Ge in the crust are only approximately 15–19 ppm [4], 50–200 ppm [5], and 1.6 ppm [6], respectively. None of these metals have independent deposits. They are usually associated with other metal minerals. According to the relevant literature, it is expected that the production of Ga will increase by approximately 224% in 2050 compared to that in 2010 [7]. Currently, there is a high demand for Ge in fiber optic communications and new energy sectors, and it is predicted that the cumulative global Ge demand during 2020–2050 will reach 6838.6 tons [8]. The demand for In is huge in electronic products, and it is forecasted

that the demand will increase by 610–859% in 2050 [9]. Due to their relative scarcity and highly heterogeneous distribution, these metals have a high risk of supply shortages. In recent years, many major industrial countries have regarded them as strategic materials of the 21st century [10].

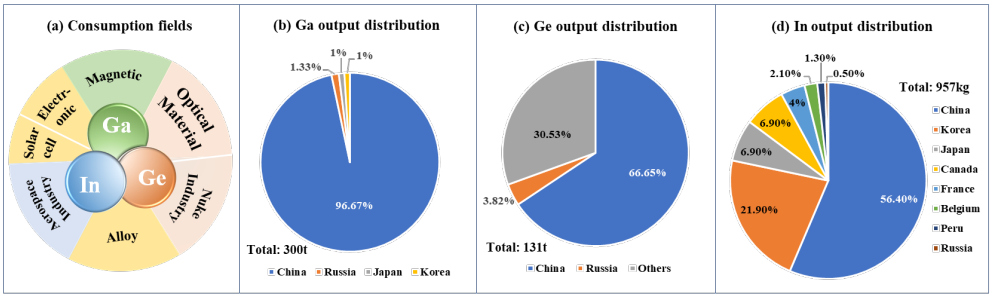

Figure 1. (**a**) Consumption fields of Ga, In, and Ge in global and (**b**,**c**) global refinery production distribution; (**b**) Ga; (**c**) Ge; and (**d**) In. (data from USGS, 2021).

With the continuous expansion of the demand for Ga, In, and Ge products, the extraction and recovery of these metals from various resources have been extensively studied. Figure 2 shows the overall material flow analyses of Ga, Ge, and In. It has been found that these metals are usually combined with Zn, Al, Pb, and Sn in bauxites, zinc concentrates, and fly ash used for coal combustion [11]. In primary resources, 90% of Ga comes from the aluminum oxide production process [12]. In addition, leaching residues from zinc hydrometallurgy and fly ash from coal combustion are also primary resources for Ga production. Waste semiconductor materials, fiber optic products, and light-emitting diodes (LEDs) are secondary resources with high Ga content. Approximately 95% of global In comes from the by-products in the zinc refining system [13], while In is enriched to varying degrees due to the different smelting methods. In is mainly concentrated in the furnace slag, flue dust, anode mud, and leaching residues [14]. Waste indium tin oxide (ITO) targets, solar cells, and alloys are secondary resources of In. Most of the Ge also comes from the zinc smelting process and fly ash. Waste fiber optics and some electronic solar components are other potential resources for Ge and In recovery [15]. Due to the complexity of these solid waste resources, there is a need to develop efficient recycling technologies for Ga, In, and Ge.

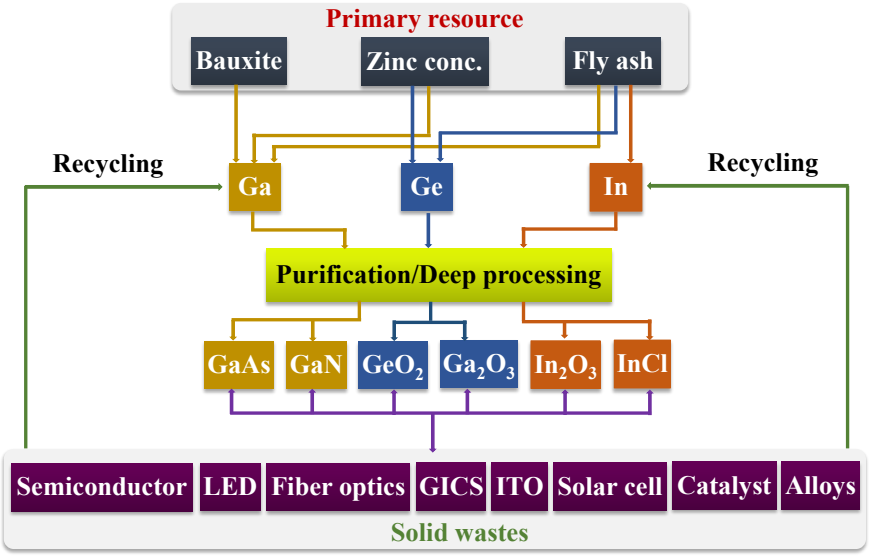

Figure 2. Overall material flow analyses of Ga, In, and Ge.

Over the past several decades, many approaches have been explored for the recovery of Ga, In, and Ge from various source materials. A small fraction of raw materials containing Ga, In, and Ge exists in the form of a liquid state (such as Bayer solutions), while the majority exists in the form of a solid state. For Ga, In, and Ge extraction from solid waste, leaching pretreatments should be conducted to transfer these critical metals into solutions [16,17]. Subsequently, the target metals are further separated, concentrated, and recovered from the leaching solution. Previous studies are mainly focused on the extraction and recycling of one of the metals. However, some metallurgical residues, coal fly ashes, waste alloys, and electronic components contain two or more of these metals. For comprehensive utilization, many researchers have shifted their attention toward the extraction, separation, and recovery of multiple metals from polymetallic resources [18]. Nevertheless, there are few reviews regarding the comprehensive separation and recovery of Ga, In, and Ge.

In this paper, a systematic search was conducted using the Web of Science, Scopus, MDPI, Elsevier, and Springer Link databases. The combined terms used for the search were Ga/In/Ge, extraction, separation, and recycling. After a careful evaluation of the titles, abstracts, and full texts, a total of 106 articles were included. Most studies focus on the methods of extracting and recycling these metals from different metal smelting by-products and related waste products in the past five years. This paper first reviews the product consumption of Ga, In, and Ge; resource characteristics; and critical metal existence forms in solid wastes. Then, the technical principles, separation efficiency, and advantages and disadvantages of the extraction and separation technologies from monometallic and polymetallic resources are summarized. Finally, based on the resource characteristics and technology differences, future research directions for the separation and recovery of Ga, In, and Ge from solid wastes are discussed.

2. Resource Features of Ga, In, and Ge

2.1. Ga-Bearing Resources

Currently, Ga is mainly derived from residues generated in the production process of Al or Zn. The average contents of Ga in bauxites are 50 ppm. For the alkaline leaching process, approximately 70% of Ga leaches into a caustic soda solution from bauxite, while the remaining portion accumulates in Bayer red mud (BRM). For the hydrometallurgical zinc production process, over 98% of Ga can enter the leach residue.

Additionally, fly ash, industrial dust, and e-waste containing Ga can be utilized as potential sources for Ga recovery (shown in Table 1). During the thermal yellow phosphorus production process, Ga exists in the form of Ga_2O_3 in the electrostatic precipitator dust. Ga is also found in the roasting process of bauxite for corundum production. The Ga content in waste LEDs can reach up to 100 ppm. Meanwhile, a significant amount of dust is generated during the production process of LEDs, and this dust contains a substantial amount of GaN.

Table 1. Ga contents and other major elements in different resources.

Ga-Containing Resources	Content (wt.%)	Major Elements	Ref.
Red mud	0.0033	Al, Ca, Fe, Na, Si, Ti	[19]
Zinc residue	0.043	Ca, Fe, Na, Pb, S, Si, Zn	[20]
Bauxite residue	0.0115	Al, Ca, Fe, Na, Si, Ti	[21]
Corundum flue dust (high silica)	0.15	Al, Ca, Fe, K, Mg, Na, Si,	[22]
Corundum flue dust	0.162	Al, K, Na, Si, Zn	[4]
Phosphorus dust	0.045	P, K, Si, Ca, Zn, Pb, Al, Na, Mg, Fe	[23]
Yellow phosphorus dust	0.058	P, K, Si, Ca, Zn, Al, Na, Pb, F	[24]
Coal fly ash	0.00671	Al, Si, Ca, Ti, Fe	[25]
Used smartphones	0.0116	Ag, Al, As, Au, Cu, Fe, Si, Sn, Zn	[26]

2.2. In-Bearing Resources

For Zn hydrometallurgy, over 98% of In is enriched in zinc leaching residues. Table 2 lists the indium content and main element composition of some materials. In is widely applied in liquid crystal displays (LCDs). LCDs are primarily composed of polarizing films, glass substrates, ITO thin films, and liquid crystals. The indium-containing part of the LCD screen mainly includes an ITO layer, glass, and polarizing film. Depending on the separation method, the main materials commonly used to recover indium include waste ITO glass (including glass and the ITO layer), waste LCD screen (glass with polarizing film and the ITO layer), and waste ITO targets (containing only the ITO layer). ITO consists of 90% In_2O_3 and 10% SnO_2 [27]. Therefore, scrapped ITOs are also a promising secondary resource for indium recovery.

Table 2. In contents and other major elements in different resources.

In-Containing Resources	Content (wt.%)	Major Element	Ref.
Sphalerite	0.0577	Zn, Fe, S, Cu, Pb, Sn	[28]
Zinc residue	0.0635	Zn, Fe, S, Pb, Ca, Cu, Si	[29]
Hard zinc slag	0.49	Zn, Fe, Pb, Al, Sn, As, Ca, Bi, Cu, Sb	[30]
Lead smelting dust	0.053	Zn, Pb, Cu. Cd, As, Fe, S, Ca	[31]
Waste LCD screen	0.036	Al, As, Ca, Si, K	[32]
Waste ITO glass	0.0108	As, Al, Cu. Cd, Ca, Fe, K, Mg, Sr	[33]
Waste ITO targets	72.16	Sn, Fe, Cu, Pb, Si	[34]

2.3. Ge-Bearing Resources

The main Ge sources are the smelting residues of lead–zinc ore and fly ash used for coal combustion (shown in Table 3). Usually, Ge exists in the form of GeO_2 and GeS_2 in fly ash. It can be enriched to tens or even hundreds of times than raw coal.

Table 3. Ge contents and other major elements in different resources.

Ge-Containing Resources	Content (wt.%)	Major Element	Ref.
Germanium residue	1.34	Zn, Mg, Fe, As, Ca	[35]
Zinc oxide dust	0.062	Zn, Pb, S, Fe, As, Si	[6]
Secondary zinc oxide	0.0593	Zn, Pb, As, Si, Cd, Fe	[3]
Coal fly ash	0.042	Si, Al, Fe, K, Ca	[36]
Coal fly ash	0.025	Si, Al, Fe	[37]
Optical fiber scraps	1.48	Si, Fe, Al, Ca	[38]

Additionally, as products such as semiconductors, catalysts, and optical devices are continuously being upgraded and replaced, a considerable amount of Ge-containing waste is generated. At the same time, during the production process of these products, certain amounts of by-products containing Ge will be generated. For example, during the production process of optical fibers, the conversion rate of GeCl to GeO_2 is only 15–30%, and the rest is lost in the form of wastewater. The proper treatment of these wastes can not only reduce environmental pollution but also realize the recovery of Ge.

2.4. Polymetallic Resources

Residues from zinc smelting and coal fly ash contain two or three metals of Ga, In, and Ge [39]. In and Ge are naturally enriched in sulfide zinc mineral sphalerite (ZnS), and pregnant leaching solutions are generated by the bioleaching of ore materials composed of sphalerite, galena (PbS), and pyrite (FeS_2). Significant quantities of polymetallic metals (two or three metals of Ga, In, and Ge) also exist in the fourth-generation LEDs, commercial thin-film solar cells based on CIGS, indium gallium zinc oxide (IGZO) targets used in

display panels, and in some alloys. The contents of Ge, In, and Ga in different resources are shown in Table 4.

Table 4. Ge, In, and Ga contents and other major elements in different resources.

Resources	Content		Major Element	Ref.
Pregnant leaching solutions	Ge: 5 μg/L	In: 760 μg/L	Zn, Fe, Cu, Cd, Pb	[40]
Pregnant leaching solutions	Ge: 1 mg/L	In: 1 mg/L	Zn, Fe, Cu	[17]
PbSnCuGeIn alloys	Ge: 6.9 wt.%	In: 1.74 wt.%	Sn, Pb, Cu, Zn, Sb, As	[41]
Waste LEDs	Ga: 0.04 wt.%	In: 0.01 wt.%	Fe, Sn, Cu, Al, Pb, Zn,	[42]
Zn smelting residue	Ge: 0.5 wt.%	Ga: 0.4 wt.%	Cu, Zn, Si, Pb, Al	[43]

3. Extraction and Separation Technologies from Monometallic Resource

3.1. Ca Extraction

3.1.1. By-Products of the Aluminum Industry

Hydrothermal alkaline leaching was used to leach Bayer red mud to achieve Ga/Fe separation and Ga enrichment [44]. Under the optimal conditions, the leaching rate of Ga was 91.4%, and the Ga_2O_3 concentration in the leaching solution reached 73.44 mg/L. However, the alkaline leaching method results in the excessive loss of the leaching agent and aluminum, which increases the operating cost. Acid leaching is usually applied to leach Ga from the by-products of Al. The concentration of H^+ can affect the leaching efficiency of Ga to a certain extent, and the specific reaction is shown in Equations (1) and (2). The leaching efficiency of Ga in Bayer red mud using different inorganic acids (HCl, H_2SO_4, and HNO_3) was evaluated. The results demonstrated that HCl leaching had the highest Ga leaching rate of 94.77% [19].

$$Ga_2O_3 + 6H^+ \rightarrow 2Ga^{3+} + 3H_2O \quad (1)$$

$$Ga(OH)_3 + 3H^+ \rightarrow Ga^{3+} + 3H_2O \quad (2)$$

Bioleaching can also be used as a green alternative to Ga extraction. Metal can be released from a variety of solid substances with the help of cells under mild conditions. Jia Wang et al. [45] first used inexpensive sulfur (Thiobacillus acidophilus thiooxidans) to leach Ga^{3+} from aluminum smelting slag. Under the optimal conditions, the leaching efficiency of Ga was 100%, and the release concentration was 505 mg/L.

The most traditional processes for recovering Bayer solutions include chemical precipitation, solvent extraction, and electrochemical deposition. However, in practical applications, many techniques have certain limitations. The chemical precipitation method improves the purity of Ga by adding alkali for selective precipitation, but the coprecipitation of Ga and Al is very serious. Electrochemical deposition methods are banned due to the high toxicity of mercury. The use of solvent extraction in Bayer solutions is limited by cost-effectiveness.

Ion exchange is a highly effective method for recovering Ga from Ga-containing leaching solutions. Cross-linking amidoxime-functionalized PAN fiber (C-PAO) can improve the efficiency of Ga extraction from Ga/V-containing solutions [46]. This is mainly because C-PAO has more content of functional groups. Among them, the amidoxime group has a high affinity for Ga. An ion-exchange chromatographic column using 8-HQA-functionalized hybrid chitosan–silica (CS) as the stationary phase can completely separate Ga^{3+} from Al^{3+} in a high-alkaline aluminosilicate matrix in Bayer waste liquid samples [47]. After seven cycles of adsorption/desorption, the reusability efficiency was higher than 97%.

3.1.2. By-Products of the Zinc Industry

Because Ga exists as a homogeneous form in zinc ferrate ($ZnO{\cdot}Fe_2O_3$), for the zinc industry's by-products, SO_2 was used as a reducing agent to assist sulfuric acid to leach 91% of Ga from zinc slag [20].

Then, solvent extraction was used to recover Ga from different leaching liquids. For a strong acidic sulfate leaching solution, the new phosphoric acid extractant (H_2R) is suitable for Ga recovery. Through continuous extraction tests, the extraction efficiency of Ga reached 98.54% [48]. Zhang et al. [49] carried out the stepwise separation of Zn, Ga, and Fe using N235 and Cyanex 272 as the extractants. The main chemical reactions involved in the extraction process are shown in Equations (3)–(6):

$$3\overline{HA} + Ga^{3+} \rightarrow \overline{GaA_3} + 3H^+ \quad (3)$$

$$\overline{GaA_3} + 4H^+ + 4Cl^- \rightarrow 3\overline{HA} + GaCl_4^- + H^+ \quad (4)$$

$$2\overline{HA} + GaCl_4^- + H^+ \rightarrow \overline{HGaCl_4 \cdot 2HA} \quad (5)$$

$$\overline{HGaCl_4 \cdot 2HA} \rightarrow Ga^{3+} + 2\overline{HA} + 4Cl^- + H^+ \quad (6)$$

3.1.3. Dust

According to the properties of various types of dust, different acid-leaching methods are adopted. The overall technical route (leaching and recovery processes) is also applied for the separation and recycling of Ga. A mixed acid solution of H_2SO_4 and HF was used to leach Ga from high-silicon corundum dust [22]. The addition of HF corroded the silica phase, which promoted the full release of Ga from the silica phase. The leaching rate of Ga increased significantly from 38% to more than 90%. The main reactions in this process are shown in Equation (7):

$$Ga_2O_3 + 6HF = 2GaF_3 + 3H_2O \quad (7)$$

Ultrasonic waves can quickly disperse solids and speed up the reaction. For the treatment of corundum dust, ultrasonic wave technology is used to assist H_2SO_4 leaching, as shown in Figure 3a [4]. Under optimum conditions, the leaching rate of Ga increased from 62.78% to 82.56%. The Na_2CO_3 calcination–water leaching is used to enrich Ga from phosphate dust, and the specific process is shown in Figure 3b,c [23]. At high temperatures, Na_2CO_3 reacts with phosphate rock powder to encapsulate Ga in sintered minerals. This method can effectively enrich Ga and is simple to operate.

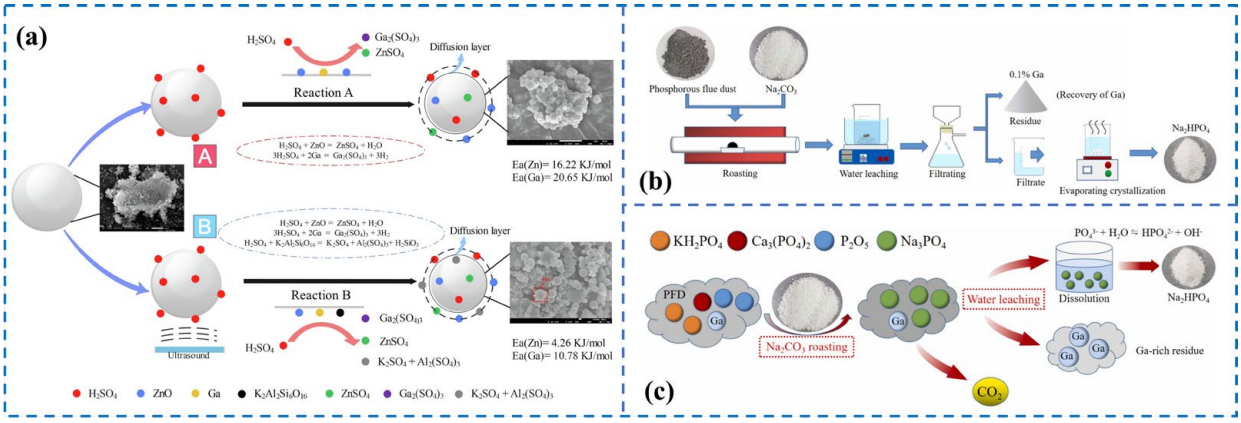

Figure 3. (**a**) The ultrasound−assisted leaching mechanism of Ga (Wei et al. [4]); (**b**) schematic diagram; (**c**) mechanism diagram of Na_2CO_3 roasting−water leaching process for Ga enrichment (Ji et al. [23]).

The alkali leaching–carbonation–acid leaching–solvent extraction process was used to recover Ga from high silica fume, and the specific flowchart is shown in Figure 4a [50]. The carbonation process can reduce the concentration of silicon, which is conducive to the subsequent Ga leaching. The overall recovery of Ga was more than 90%. Ji et al. [24] used cheap activated carbon powder for the recovery of Ga using vacuum carbothermal reduction technology (Figure 4b–d), achieving a Ga recovery rate of 92.5%. This process

does not produce harmful gases or substances. The reaction of Ga_2O_3 with C is shown in Equations (8)–(11).

$$Ga_2O_{3(s)} + C_{(s)} = 2GaO_{(g)} + CO_{(g)} \quad (8)$$

$$Ga_2O_{3(s)} + 3C_{(s)} = 2Ga_{(l)} + 3CO_{(g)} \quad (9)$$

$$Ga_2O_{3(s)} + 2C_{(s)} = 2Ga_2O_{(g)} + 2CO_{(g)} \quad (10)$$

$$Ga_2O_{3(s)} + C_{(s)} = 2Ga_2O_{2(g)} + CO_{(g)} \quad (11)$$

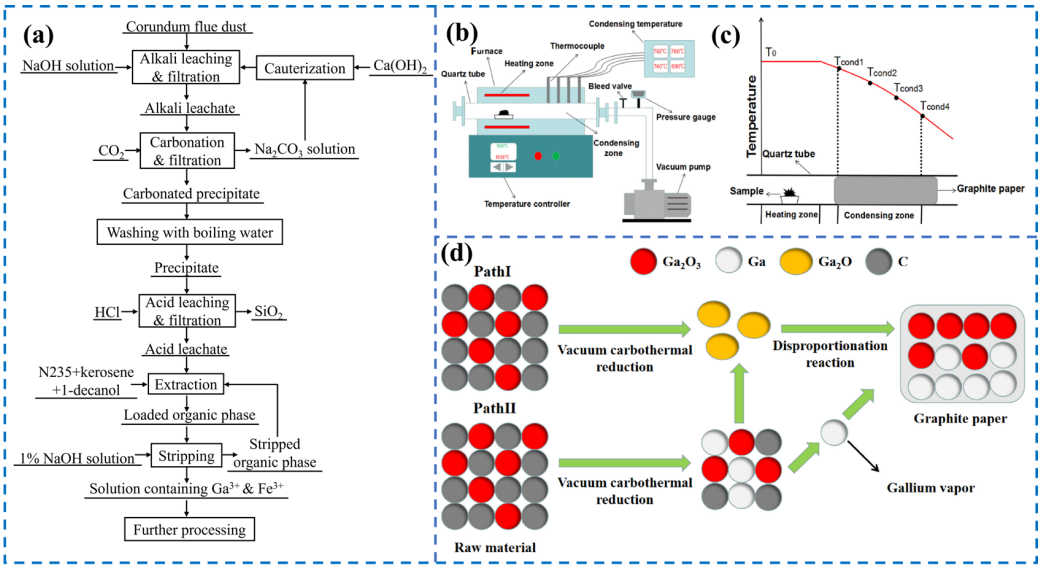

Figure 4. (**a**) Process flowchart of Ga recovery from corundum flue dust (Wen et al. [50]) and schematic diagrams of (**b**) vacuum quartz tube furnace, (**c**) condensation zone, and (**d**) recovering Ga by vacuum carbothermal reduction (Ji et al. [24]).

3.1.4. Electronic Wastes

For electronic wastes, acid leaching and bioleaching methods are used for the leaching of Ga. Ga in the leaching solution can be recovered by solution extraction or nanofiltration.

Table 5 shows the various methods and specific experimental conditions of Ga leaching from different e-wastes. The leaching effect of $H_2C_2O_4$ on Ga was significantly better than that of other acids (HCl, citric acid, and malic acid) through the selection of lixiviant experiments [51]. $H_2C_2O_4$ has a high dissociation constant and forms ferrous oxalate with iron ions, which promotes the generation and maintenance of H^+. The composition of electronic waste is complex. Thus, auxiliary methods are often used to improve the leaching rate of Ga. As shown in Figure 5a, high-temperature oxidation treatment can convert insoluble gallium nitride to soluble gallium oxide [52]. Under optimum conditions, the Ga leaching rate reached 91.4%. The specific reactions are shown in Equations (12) and (13).

$$4GaN(\text{hexagonal}) + 3O_2 = 2Ga_2O_3(\text{monoclinic}) + 2N_2 \quad (12)$$

$$Ga_2O_3 + 6HCl = 2GaCl_3 + 3H_2O \quad (13)$$

Bioleaching relies on substances metabolized by microorganisms to leach Ga from Ga-containing wastes, as shown in Figure 4b. Related studies have investigated the leaching capacity of various strains, such as Thiobacillus ferrooxidans [42] and Acidithiobacillus [53]. Moreover, different leaching processes can also improve the efficiency of bioleaching [54,55].

Cyanex 272 is a commonly used extractant for Ga recovery [56]. The combination of acid leaching and nanofiltration can optimize the leaching process and the recovery of Ga from waste LEDs [57]. The results showed that 96.79% Ga could be leached using HNO_3, and 85% Ga could be recycled via nanofiltration.

Table 5. Various gallium leaching processes from gallium-containing resources.

Secondary Resources	Leaching Method	Leaching Condition	Recovery Rate	Ref.
Waste LEDs	Oxalic acidic leaching	90 °C, Pulp density:10 g/L, 0.7 M $H_2C_2O_4$, particle size: 48–75 μm;	90.36%	[51]
Waste LEDs	Oxidation and subsequent leaching	4 M HCl, 93 °C, 120 min	91.4%	[52]
Waste LEDs	adaptation of Acidithiobacillus ferrooxidans	—	60%	[42]
Waste LEDs	The multistep noncontact bioleaching method	Sulfuroxidizing bacteria Acidithiobacillus thiooxidans	75%	[53]
Waste LEDs	Stepwise indirect bioleaching	Pulp density: 20 g/L, 15 d;	84%	[54]
Waste LEDs	Novel green hybrid acidic–cyanide bioleaching	pH = 7, $C_2H_5NO_2$ 2.5 g/L, L. methionine 10 g/L, 15 mg/L cyanide was produced by B. megaterium in 14 h, 10 g/L bio-pretreated;	84%	[55]
Smartphones	Oxidative alkaline pressure leaching	180 °C, 5 g/L NaOH, 5 MPa O_2;	82%	[26]

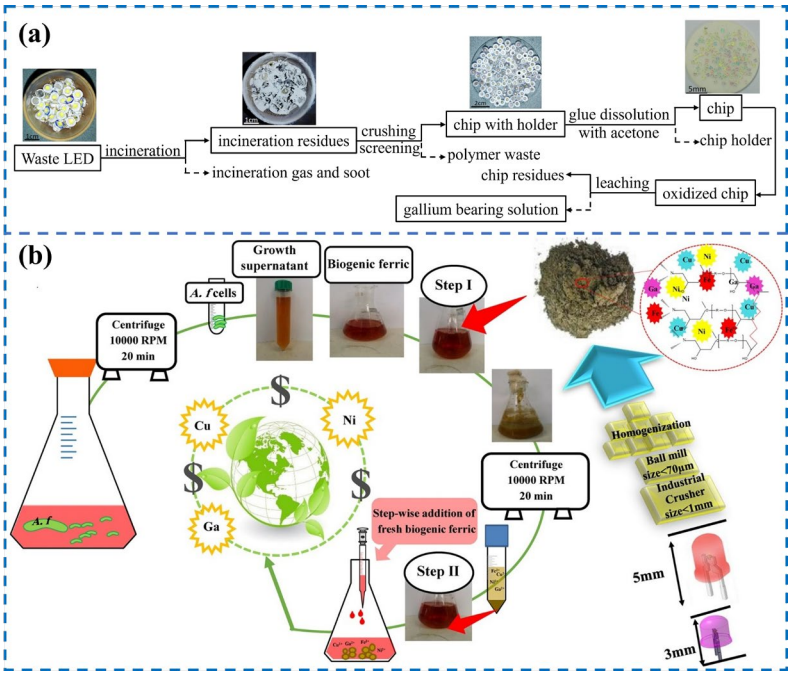

Figure 5. (**a**) Process flowchart of Ga recovery from waste LEDs (Maarefvand et al. [52]) and (**b**) a schematic diagram of the recovery of valuable metals from waste LEDs by bioleaching (Pourhossein et al. [54]).

3.2. In Extraction

3.2.1. By-Products of the Zinc Industry

H_2SO_4 is a common leaching agent for indium extraction from the by-products of the zinc industry. To better leach In, adding reducing agents (galena [29], SO_2 [58], and $H_2C_2O_4$ [59]) as leaching aids in the leaching process of H_2SO_4 is an effective extraction method. SO_2, as a reductant, provided a reductive atmosphere to accelerate the decomposition of indium-bearing zinc ferrite. As the partial pressure of SO_2 increased, the indium leaching efficiency increased from 77.70% to 93.17%.

Solvent extraction can effectively separate indium from other metals, and N503 can recover indium from a high-concentration HCl solution [11]. Microfluidic extraction involves a combination of microfluidic technology and extraction [60], which can change the flow mode of fluid. Compared with conventional extraction, microfluidic extraction can reduce the contact time by half and effectively improve the separation coefficient of indium and other metals [61]. An ionic liquid (PJMTH + HSO_4^-) synthesized by combining an amine with sulfuric acid can be used to extract indium from an acidic H_2SO_4 solution, and the

reaction is shown in Equation (14). The supported ionic liquid phase (SILP) synthesized by impregnating Amberlite XAD-16N with the iodized form of quaternary ammonium salt Aliquat 336 was used to separate and purify indium from an iron-rich matrix solution [62]. It was found that indium and iron were well separated in the validation of the actual hematite slag leaching solution. The IL + TBP + P204 extraction system was found to prevent the cyclic enrichment of iron ions in the organic phase [63]. Under the optimal extraction conditions, the extraction rate of indium reached 100%.

$$p\left(PJMTH^{+}HSO_4^{-}\right)_{q_{org}} + In_2\left(SO_4\right)_{3_{aq}} \leftrightarrow \left(\left(JMTH^{+}HSO_4^{-}\right)_p\right)_q\left(In_2\left(SO_4\right)_3\right)_{org} \quad (14)$$

The two-stage countercurrent pressure H_2SO_4 leaching–solvent extraction process can extract indium from the harmful dust generated during lead smelting [31], as shown in Figure 6a. Under the optimal conditions, the leaching rates of indium exceeded 99%. Finally, more than 98% of indium was recovered by three-stage D2EHPA solvent extraction. For the treatment of zinc leaching residue, the pH of the solution is adjusted with limestone. Then, indium is enriched by hydrolysis [64], as shown in Figure 6b. Indium mainly exists in the form of gypsum in the precipitate. The recovery rate was more than 98%.

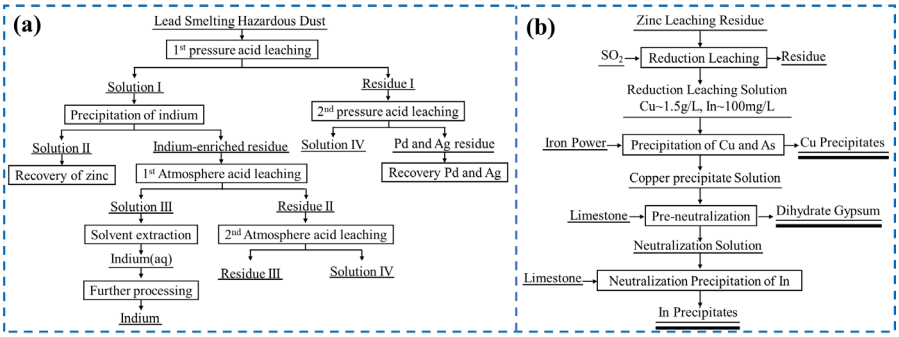

Figure 6. (**a**) Flowchart of selective recovery of indium from LSHD (Zhang et al. [31]) and (**b**) from zinc leaching residue (Deng et al. [64]).

3.2.2. Electronic Wastes

Wet leaching and bioleaching methods were applied to recover indium from electronic waste. The influence of different strains on the indium leaching rate was studied using the bioleaching method. Solvent extraction, membrane separation, electrodeposition, and combined processes were used to study the indium recovery.

After the preliminary treatment of the discarded LCDs, different inorganic acids were used as leaching agents. Among them, H_2SO_4 leaching was the most effective [32]. The H_2SO_4 concentration and reaction temperature are considered to be the main factors [33]. However, Cui et al. [65] found that $H_2C_2O_4$ was superior to inorganic acid as a leaching agent, and the leaching rate of indium reached 100%. $H_2C_2O_4$ can maintain an appropriate H^+ concentration and reduce acid consumption by other impurities. The main reaction is shown in Equations (15) and (16):

$$In^{3+} + 3H_2O \Leftrightarrow 3H^{+} + In(OH)_3 \downarrow \quad (15)$$

$$2In^{3+} + 3C_2O_4^{2-} \Leftrightarrow In_2(C_2O_4)_3 \downarrow \quad (16)$$

In recent years, researchers have attempted to carry out the bioleaching of indium from waste LCDs, such as sulfur-oxidizing bacteria [66], acidophilic iron-oxidizing bacteria [67], Aspergillus niger fermentation broth [68], Eleocharis acacularis [69], etc. In addition, different bioleaching approaches (as shown in Figure 7a) have an impact on the leaching efficiency of indium [70]. Thiobacillus acidophilus thiooxidans could completely develop indium leachate from waste LCDs under S-mediated conditions. Cui et al. [71] optimized the fermentation system of Aspergillus niger and elucidated its bioleaching mechanism

(as shown in Figure 7b). The fermentation broth of Aspergillus niger can secrete organic acids and proteins and release a large amount of H^+. H^+ can react with indium-containing substances in waste LCDs.

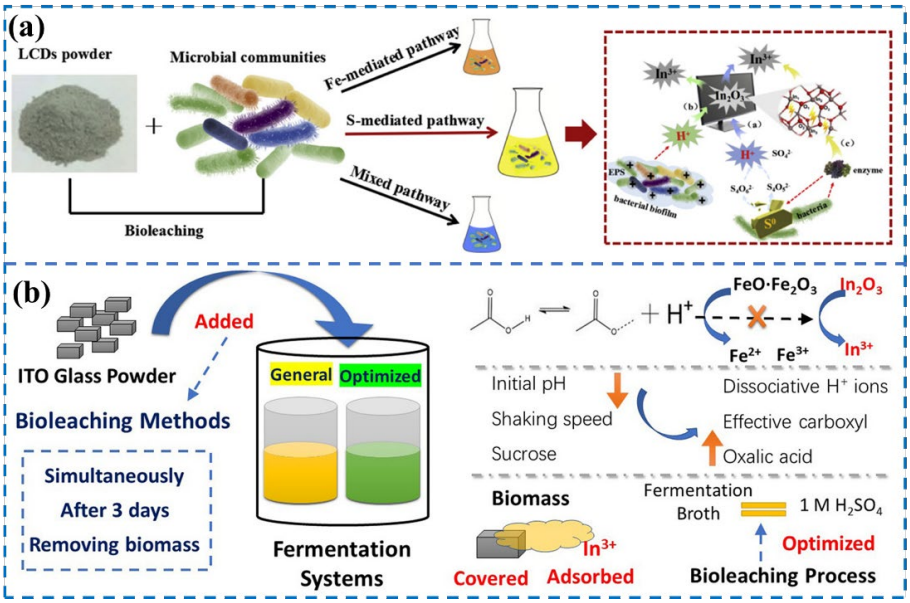

Figure 7. Method optimization and mechanism analysis of bioleaching: (**a**) Acidithiobacillus thiooxidans (By three methods: S-mediated pathway, Fe-mediated pathway and Mixed pathway of S- and Fe-mediated) (Xie et al. [70]) and (**b**) Aspergillus niger (Cui et al. [71]).

Table 6 summarizes the indium recovery methods using different extractants. A common extraction agent of recovering indium is D2EHPA. Under optimum conditions, the recovery rate of indium can reach 97.25% [72]. Takemura et al. [73] used ethylenediamine tetraacetic acid (EDTA) as a chelating agent to recover indium by bipolar membrane electrodialysis (BPED). Indium can form an anionic chelate with EDTA(Y_4^-), while aluminum ions exist as cations. Taking advantage of differences in chelation stability, the indium recovery rate of 91.8% was achieved under the best conditions. The specific process is shown in Figure 8.

Table 6. Summary of various indium solvent extraction processes.

Secondary Resources	Extraction Agent	Extraction Condition	Extraction Rate	Recovery Condition	Recovery Rate	Ref.
Waste LCDs	D2EHPA	20% D2EHPA, O/A = 1:10, 3 min	100%	4 M HCl, O/A = 10:1, 10 min	97.25%	[72]
Waste LCDs	Nylon 6 nanofibers were modified DEHPA	DEHPA 30%, pH = 0.5, 7.5 min, S/L = 1:300	74%	1.5 M HCl, S:L = 1:20, 5 min	92%	[74]
Waste LCDs	(Hbet)(Tf2N)	50% ionic liquid/$C_6H_8O_6$, S/L= 20 g/L, 90 °C, 24 h	99.75%	— —	— —	[75]
Waste LCDs	(PIL)cyphosil 104	A/O = 3/2, 0.1 mol/L Cyphos IL 104	98.9%	O/A = 3/2, 4 mol/L HNO_3	— —	[76]

As shown in Table 7, many adsorbents have been used for the recovery of indium from solutions. Layered double-hydroxide magnesium iron ore and natural montmorillonite can selectively adsorb indium through an ion-exchange reaction [77]. UiO-66 metal–organic frameworks (MOFs) can be used as acid-resistant adsorbents for indium recovery [78]. UiO-66 can keep its structure unchanged at a strong acidity of pH = 1.

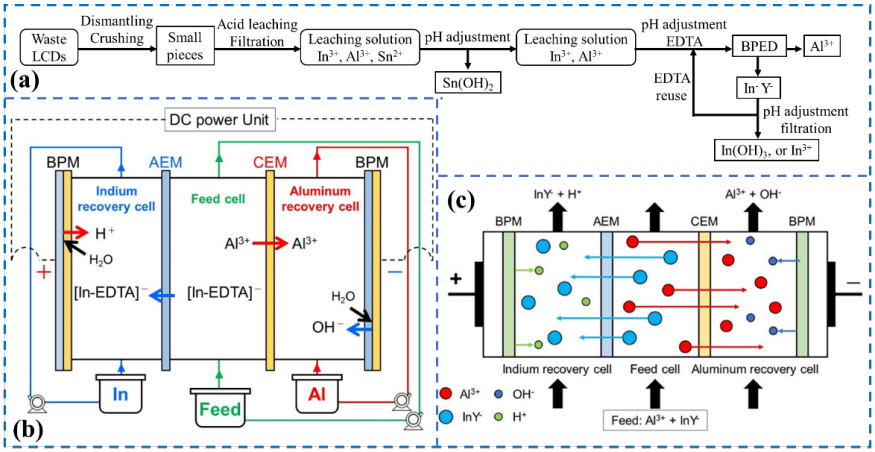

Figure 8. (**a**) Schematic diagram of the process of BPED separation of In and Al, (**b**) schematic diagram of electrodialysis device, and (**c**) mechanism diagram (Takemura, Y et al. [73]).

Table 7. The adsorption capacity of indium by different adsorption materials.

Absorbent Material	Optimum Condition	Adsorbing Capacity	Ref.
SiO_2@GO-PO_3H_2 composite	pH = 2.5, 303 K, 50 min	149.93 mg/g	[79]
Hydroxyl- and amine-rich poly network (PAN-FA)	30 °C, pH = 4–6	206.3 mg/g	[80]
Phytic acid–hyperbranched polyethyleneimine–oxidized carbon fiber (PA–HPEI–OACF)	pH = 3.5, T = 298 K	34.21 mg/L	[81]
Microalgae	pH = 2	0.14 mmol/g	[82]

Fan et al. [34] proposed a closed-circuit hydrometallurgical process (as shown in Figure 9a). The indium leaching percentage could reach 99.13% using the ammonium bisulfate leaching process. Then, after selective precipitation of Sn, the indium oxide product was finally obtained through hydroxide precipitation and calcination. The main reaction in the leaching process is shown in Equations (17) and (18):

$$In_2O_3 + 6NH_4HSO_4 \rightarrow 2NH_4In(SO_4)_2 + 2(NH_4)_2SO_4 + 3H_2O \quad (17)$$

$$In_2O + 6NH_4HSO_4 + O_2 \rightarrow 2NH_4In(SO_4)_2 + 2(NH_4)_2SO_4 + 3H_2O \quad (18)$$

Moreover, the specific process of recovery of indium by microwave extraction–nitrogen pyrolysis–vacuum reduction is shown in Figure 9b [83]. The recovery of indium was realized by vacuum reduction, and the conversion rate of indium was as high as 99.92%.

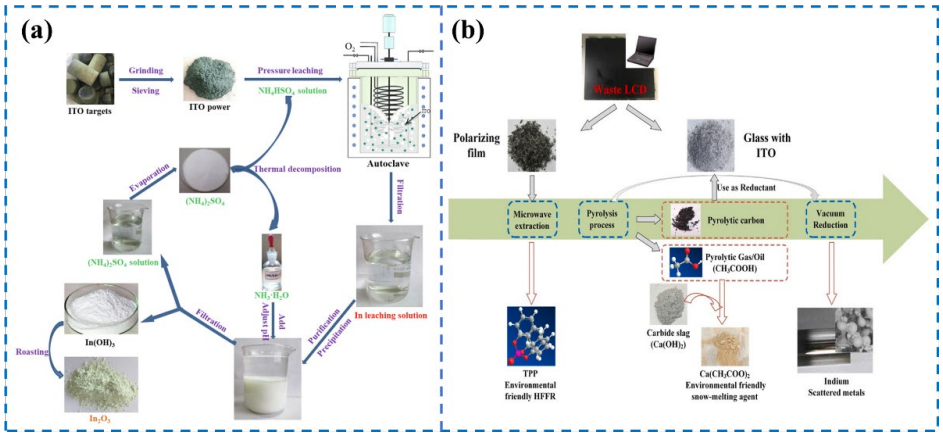

Figure 9. Flowchart of indium recovery from (**a**) waste ITO targets (Fan et al. [34]) and (**b**) LCDs (Wang et al. [83]).

3.3. Ge Extraction

3.3.1. By-Products from the Lead and Zinc Industries

Acid leaching is the main method for recovering Ge from the by-products in the lead and zinc industries. In order to improve the leaching rate, various auxiliary means such as oxidants, complexing agents, pressure, and ultrasound have been studied. Solvent extraction is the main method for recycling Ge from a leaching solution, and different combinations of extractants have been explored for extraction methods.

In comparative experiments between conventional pickling (RP) and ultrasound-assisted pickling (UAP), UAP could accelerate the breaking of complex bonds and improve the removal efficiency of impurities [35]. The specific flowchart is shown in Figure 10a. For the treatment of germanium slag dust, ultrasound was also used to assist the H_2SO_4 leaching process in an oxygen-enriched environment [6]. Ultrasound and O_2 have a good synergistic effect. Under the optimal conditions, the leaching rate of Ge reached 92.96%. The main reaction occurring in the solution is shown in Equation (19):

$$GeO_2 + 2H_2SO_4 = Ge(SO_4)_2 + 2H_2O \quad (19)$$

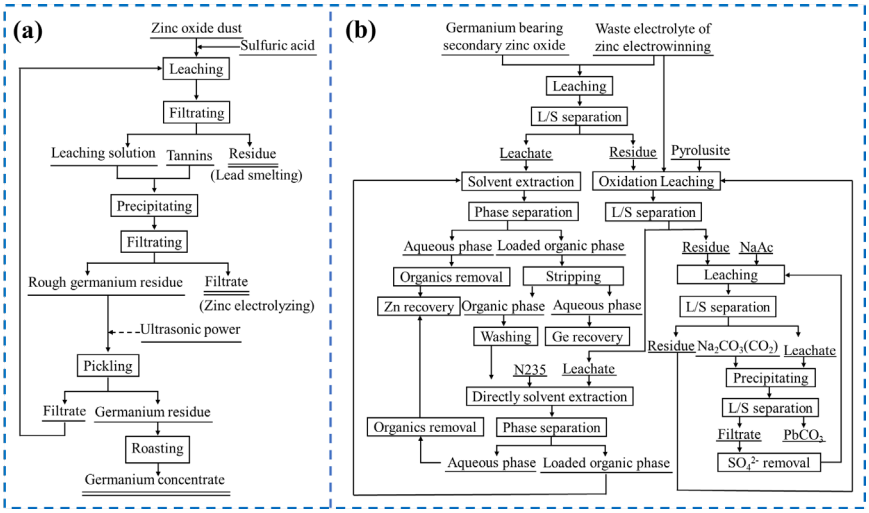

Figure 10. Flowchart of recycling Ge from (**a**) purifying germanium−tannin residue (Di et al. [35]) and (**b**) secondary zinc oxide (Jiang et al. [3]).

To further recover Ge from the leaching solution, extractants are widely used, including P204, LIX6, Kelex 100, H10, and YW100. For the selective recovery of Ge, Van Roosendael et al. [84] put forward a supported ionic liquid phase (SILP) synthesized through the impregnation of Amberlite XAD-16N and methyltrioctylammonium chloride. The effective separation of Ge(IV) and Fe can be achieved through the coordination of the citrate ligand with Ge(IV). Ge(IV) exists in electroneutral form in both acidic and neutral sulfate solutions. In order to extract Ge(IV), relevant studies have investigated the N235/TOP/tartaric acid system [85], the N235/tri-n-butyl phosphate/sulfonated coal oil system (non-reacidified) [3] (Figure 10b), and the tertiary amine (N235/TOP)/tartaric acid system [86]. In these three acidic systems, the hydroxide of Ge is converted into the anionic complex by adding tartaric acid (H_4T), and the complexation reaction is shown in Equations (20) and (21).

$$Ge(OH)_4 + H_3T^- = Ge(OH)_2(HT)^- + 2H_2O \quad (20)$$

$$Ge(OH)_4 + H_2T^{2-} = Ge(OH)_2(T)^{2-} + 2H_2O \quad (21)$$

3.3.2. Coal Fly Ash

During the recycling process of Ge from coal fly ash, a solution containing tartaric acid was used as the leaching agent, and a leaching rate of 86% was achieved [36]. In addition,

the sodium salt roasting–organic acid leaching method was used to extract Ge from coal fly ash. $NaCO_3$ and citric acid were used as roasting and leaching agents, respectively. This method resulted in the leaching of 98.15% of Ge from coal fly ash [37].

The ion-exchange resin was prepared with catechol and 8-hydroxyquinoline. It significantly improved the selectivity of Ge [87]. When pH < 4, catechol can form a complex with Ge, and the reaction is shown in Equation (22). Zhang et al. [88] proposed a vacuum reduction metallurgical process to recover Ge from coal fly ash. This process makes use of the saturated vapor pressure of metal in vacuum, which is lower than the atmospheric pressure and is beneficial to the separation of volatile metals. The practical effect of Ge recovery was evaluated through a pilot experiment, and the recovery rate of Ge was 94.64%.

$$Ge(OH)_4^0 + 3C_6H_4(OH)_2 \leftrightarrow Ge(C_6H_4O_2)_3^{2-} + 2H^+ + 4H_2O \quad (22)$$

3.3.3. Electronic Waste

For electronic waste, organic acids, phosphoric acid-based ionic liquids, and H_2SO_4 were investigated as leaching agents to extract Ge. Solvent extraction, ion exchange, and vacuum phosphoric acid reduction processes were used for Ge recovery from the leaching solution. Phosphate-based ionic liquids (ILs) were used to leach Ge directly from the waste diode [89]. Then, deionized water was used for back extraction, achieving a recovery of 94.6%. After the pretreatment of the waste fiber optic cable, 98.3% of Ge could be leached using H_2SO_4 and HF as leaching agents [90].CH_3COOH was used to treat waste semiconductor diodes, and more than 70% of Ge was extracted [91]. The reaction of the leaching process is shown in Equations (23)–(26).

$$GeO_2 + 4CH_3COO^- + 4H^+ \rightarrow Ge(CH_3COO)_4(aq) + 2H_2O \quad (23)$$

$$GeO_2 + 4H^+ \rightarrow Ge^{4+} + 2H_2O \quad (24)$$

$$GeO + 2H^+ \rightarrow Ge^{2+} + H_2O \quad (25)$$

$$Ge + 4H^+ + O_2 \rightarrow Ge^{4+} + 2H_2O \quad (26)$$

Alkali roasting–H_2SO_4 leaching resulted in the leaching of more than 99.5% of Ge from waste optical fibers [92]. Using the ion-exchange method with IRA900 as resin and citric acid as a new additive, the Ge recovery was 99%, and purity was more than 99%. Zhang et al. [38] used a low-vacuum phosphoric acid reduction process to recover Ge from waste optical fibers. Sodium hypophosphite (NaH_2PO_2) was used to reduce GeO_2 in a low-vacuum environment, and the Ga recovery rate of 90.6% was successfully achieved.

4. Extraction and Separation Technologies from Polymetallic Resource

4.1. In and Ga Separation

For the treatment of zinc ferrite reduction (ZRR), the reduction gas containing 10% H_2 was used for calcination, and then the leaching effect with H_2SO_4 and HCl was compared [93]. HCl leaching is an ideal method, and roasting can improve the leaching efficiency of Ga and In. The leaching effects of different leaching agents (H_2SO_4, HCl, HNO_3, citric acid, and NaOH) and their combinations were investigated in the treatment of waste CIGS [94]. The leaching process with the combination of citric acid and H_2O_2 had the best effect and the least impact on the environment.

The combination of tannic acid-functionalized microcrystalline cellulose (MCC-g-GMA-TA) and a fixed-bed column allowed for the effective recovery of Ga and In from a simulated leaching solution [95]. The ionic liquid synthesized by Aliquat 336 and organic phosphoric acid (Cyanex 272, D2EHPA, and PC88A) could completely separate the two metal ions [96]. During the LED production process, a large amount of Ga-containing dust (MOCVD dust) was generated. By controlling leaching agent properties and leaching conditions, the two-step recovery process (Figure 11a) led to the recovery of approximately 89.83% of Ga and 92.42% of In [97]. The main reaction involving GaN is shown

in Equation (27). For the treatment of waste generated during CIGS production [98], a phase change controlled by a two-stage sulfuric acid roasting–selective water immersion technique was used to recover valuable components (Figure 11b). The phase transformation of selenide and the separation of selenium were realized simultaneously by sulfuric acid roasting. Meanwhile, the mixed content of In_2O_3 and Ga_2O_3 in the water leaching residue was 91.09%. The chemical reaction during the vulcanization roasting process is shown in Equations (28)–(30).

$$GaN(s) + OH^-(aq) + 2H_2O(l) = Ga(OH)_4^-(aq) + NH_3(aq) \quad (27)$$

$$Cu_2Se_{(s)} + 2O_{2(g)} + 2H_2SO_{4(l)} = SeO_{2(g)} + 2CuSO_{4(s)} + 2H_2O_{(g)} \quad (28)$$

$$In_2Se_{3(s)} + 4.5O_{2(g)} + 3H_2SO_{4(l)} = 3SeO_{2(g)} + In_2(SO_4)_{3(s)} + 3H_2O_{(g)} \quad (29)$$

$$Ga_2Se_{3(s)} + 4.5O_{2(g)} + 3H_2SO_{4(l)} = 3SeO_{2(g)} + Ga_2(SO_4)_{3(s)} + 3H_2O_{(g)} \quad (30)$$

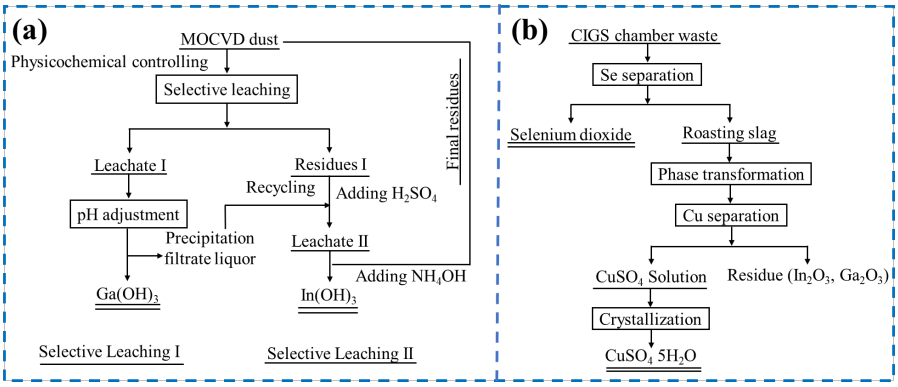

Figure 11. Flowchart of Ga and In recovery from (**a**) MOCVD dust (Fang et al. [97]) and (**b**) CIGS cavity waste (Ma et al. [98]).

For the treatment of CIGS materials, the maximum leaching rates of In and Ga were 93.40% and 96.86% by using HCl after oxidation roasting CIGS wastes [99]. Then, the extraction was carried out with P204, and the specific flowchart is shown in Figure 12a. Moreover, the recovery of valuable elements was achieved through the process of high-temperature roasting (selenium recovery)–sulfuric acid leaching–In and Ga precipitation–solvent extraction (copper recovery) [100]. The recovery rates of In and Ga were 97.74% and 97.41%, respectively. Xiang et al. [101] treated waste CIGS by selective alkaline leaching (see Figure 12b). The selective alkaline leaching led to the effective separation of In and Ga, and their comprehensive extraction rates were 97.26% and 3.37%, respectively. After the subsequent purification and hydrolysis of the leaching solution, indium oxide with purity of 96.04% and gallium oxide with purity of 99.83% were successfully prepared.

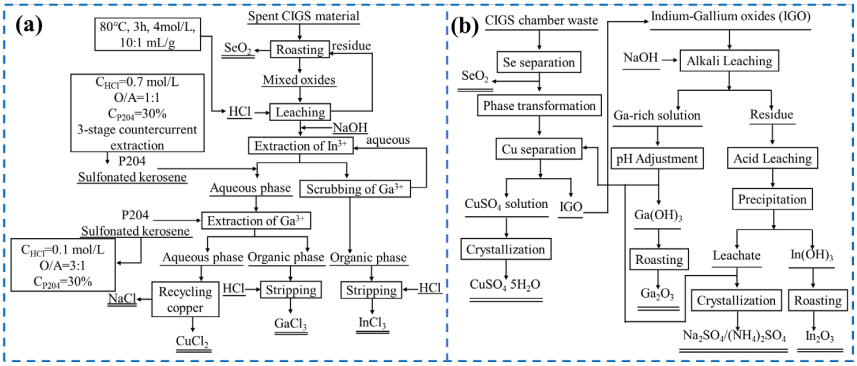

Figure 12. Flowchart of recovery of valuable metals from (**a**) spent CIGS materials (Die et al. [99]) and (**b**) IGO (Xiang et al. [101]).

4.2. In and Ge Separation

Alloys, electronic components, and scrap from their production processes contain a large amount of Ge and In. In and Ge in the form of oxide slag can be obtained through the pyrometallurgical process for treating PbSnIn and PbSnCuGeIn multicomponent alloys [41], which facilitates further hydrometallurgical treatment. In terms of the separation and recovery of Ge and In from the leaching solution, they can be successfully separated by utilizing commercially available polymer nanofiltration flat membranes (NP010 and NF99HF) while adjusting the pH of the leaching solution [102]. This is mainly caused by the electrostatic interaction and membrane charge of In^{3+} and $In(OH)_4^-$. The same method has also been verified on the actual enriched leachate of the bioleaching process [40]. When the pH was 2, In and Ge could be effectively separated in the complex model solution (containing In^{3+}, $Ge(OH)_2$, Zn^{2+}, Cu^{2+}, and Fe^{2+}). The actual sulfuric acid leaching solution (containing Ge, In, and Zn) can be treated using the solvent extraction method [16], as shown in Figure 13a. Ge and In were extracted by TOA + TBP and D2EHPA, respectively.

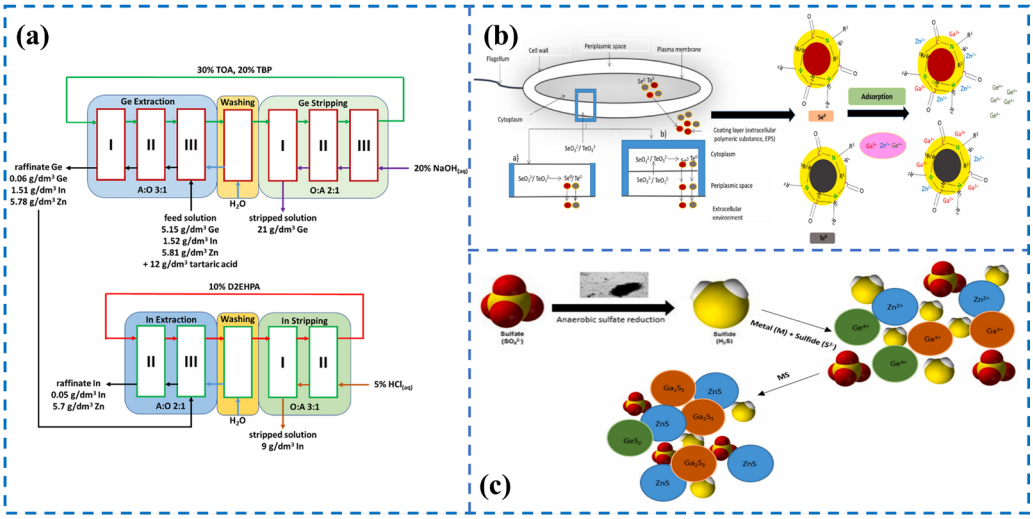

Figure 13. (**a**) Flowsheet for selective multistage solvent extraction of In and Ge (Drzazga et al. [16]); (**b**) mechanism of biosorption and (**c**) mechanism of bioprecipitation for the removal of Ga, Ge, and Zn (Saikia et al. [12]).

4.3. Ga and Ge Extraction

Tartaric acid was synergized with H_2SO_4 to leach Ge and Ga from zinc leaching slag [43]. The addition of tartaric acid promoted the decomposition of certain iron minerals, and the leaching rate of Ge increased from 63.8% to 91.7%. A two-stage acid leaching process was used to leach Ge and Ga from zinc powder replacement residue. The study was carried out at different temperatures, strong magnetic field, and ultrasonic field [103]. The temperature, magnetic field intensity, and ultrasonic field had a synergistic effect on the leaching behavior of Ge and Ga, and the leaching rates of Ga and Ge reached 95.53% and 97.11%, respectively. A crude zinc oxide generated by electric furnace dust was leached with common inorganic acids [104]. Under optimum conditions, Ga, Ge, and In were extracted at 82%, 100%, and 89%, respectively.

For the recovery of Ge and Ga, the three-dimensional layered porous structure of 3D-α-FeOOH provides more adsorption sites on the surface, which is in favor of the synergistic adsorption and rapid recovery of Ge and Ga [105]. A low sulfuric acid leaching–oxalic acid leaching–solvent extraction process was used to recover Ga and Ge from zinc refinery slag [106]. Low sulfuric acid selectively leached Zn and Cu preferentially and enriched Ga and Ge. Subsequently, oxalic acid could leach 99.32% and 98.86% of Ga and Ge. Finally, the organic system containing N235 and TBP was used to recover Ga(III) and Ge(IV). Saikia et al. [12] studied the adsorption and precipitation of Ga, Ge, and Zn using chemical sulfur

and biological sulfur (S_0). They found that bioderived adsorbents and biosulfides have good treatment effects. The mechanism diagram is shown in Figure 13b,c.

5. Conclusions

Ga, In, and Ge, as rare metals, are unevenly distributed and relatively scarce in natural resources. Currently, these metals are mainly recovered from the by-products of metal smelting industries. Some primary resources contain these metals, such as coal fly ash, smelting waste residue, and waste liquid. Recycling Ga, In, and Ge from secondary resources is of great significance.

Leaching followed by separation is the main process for Ga, In, and Ge recovery from monometallic and polymetallic resources. Acid leaching is the most used method for the extraction of Ga, In, and Ge from these resources. Some new methods have been explored to improve the leaching rate, such as alkaline leaching, ultrasonic-assisted, sodium roasting, and so on. Alkaline leaching is more conducive to the separation of Ga/Fe. Ultrasonication-assisted acid leaching has certain advantages for the extraction of Ga, In, and Ge, such as not requiring the addition of other reagents, simple operation, and a high leaching rate. Bioleaching is the most environmentally friendly method for recycling Ga, In, and Ge. At present, ultrasound-assisted leaching and bioleaching treatments are still in the exploratory stage. In the future, it is necessary to carry out in-depth research regarding the optimization of process parameters, the study of leaching mechanisms, engineering applications, etc., to promote industrial application.

Each of the methods for separating and recycling Ga, In, and Ge, such as chemical precipitation, solvent extraction, ion exchange, membrane separation, high-temperature chlorination separation, and electrodeposition, has its own advantages and disadvantages. Generally, an appropriate method needs to be selected according to the raw materials and specific circumstances. Solvent extraction is the most widely used method for the recovery of Ga, In, or Ge from acidic/alkaline solutions. However, for polymetallic resources, the highly selective membrane separation and ion-exchange methods have great advantages for multimetal recycling from the solutions. Due to the lower contents of Ga, In, and Ge in some resources, many low-concentration solutions are generated, while the commonly used separation methods are unsatisfactory. Future research should focus on developing efficient, inexpensive, and stable extractants and modifying resins or other adsorbents such as ion-imprinted polymers and polyurethane foam to enhance selectivity and cycling stability. In addition, the development of more environmentally friendly, economically applicable, and controllable reaction processes in the recovery technology route should also be a key focus.

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