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Original Review Article

PROGRESS IN THE RECYCLING AND REUSE OF METALS IN END-OF-LIFE PHOTOVOLTAIC MODULES: A REVIEW

Fei LI[1,2,*], Liuxu SHI[1]
[1]School of Metallurgy and Environment, Lanzhou University of Technology, Lanzhou, China
[2]State Key Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Lanzhou, China

A b s t r a c t
The expansion of photovoltaics (PV) creates an increasing end-of-life management challenge. Retired modules contain recoverable materials alongside hazardous and critical elements. This critical review evaluates recycling and metal-recovery routes, focusing on crystalline silicon modules and relevant thin-film technologies. Mechanical, thermal, hydrometallurgical, pyrometallurgical, electrochemical, deep eutectic solvent and bioleaching routes are compared for recovery, purity, selectivity, resource demand, environmental risk and industrial readiness. High laboratory recoveries alone do not establish industrial feasibility. Scale-up remains constrained by hazardous reagents, wastewater, off-gases, residues, heterogeneous feeds, product quality and uncertain economics. Future recycling should combine high recovery with transparent mass balances, life-cycle assessment, techno-economic analysis, closed-loop reagent management and verified pilot- or commercial-scale performance.

Keywords: photovoltaic module recycling, separation, metal recovery, hydrometallurgy, pyrometallurgy, electrochemical processes

1. PHOTOVOLTAIC MODULE DEVELOPMENT HISTORY AND POTENTIAL RESOURCE VOLUME

1.1 Development history of solar panels and valuable metal content

PV technology has rapidly advanced as a prominent clean energy solution due to its high efficiency in harnessing solar energy and zero emissions during power generation. After the invention of the bipolar transistor in 1948, solar cell technology evolved quickly, and PV cells are now categorized into first-, second-, and third-generation cells. The first generation refers to crystalline silicon (c-Si) solar cells,

[1] Corresponding author: [1]School of Metallurgy and Environment, Lanzhou University of Technology, Lanzhou, China,
[2]State of Laboratory of Advanced Processing and Recycling of Non-ferrous Metals, Lanzhou, China, Fei LI, Liuxu SHI, li.fei@hotmail.com, 18153964392@163.com,

which use p-type or n-type doped crystalline silicon wafers (~200 μm thick) as the light absorber. c-Si cells include monocrystalline and polycrystalline silicon types [1]. In the current photovoltaic manufacturing and market, crystalline silicon still dominates, but the mainstream has shifted to technical routes such as single crystals and n-type / TOPCon, rather than polycrystalline replacement of single crystals.Crystalline silicon PV cells dominate the market because of their high efficiency, low cost, stability, and low toxicity. According to reports [2], in 2024 the installed capacity of c-Si PV modules exceeded 400 GW, accounting for ~95% of the PV market, with a cumulative installation over 1300 GW.

Table 1 (adapted from literature) lists the typical composition of a first-generation c-Si PV module. Glass constitutes about 70-75% of module mass, aluminum (mostly the frame) 10-18%, and the polymer encapsulant EVA (ethylene-vinyl acetate) around 5-6.5%. Silicon itself is ~3.5%, while the backsheet (e.g., Tedlar® PVF film) contributes ~1.5-3.5%. Copper (primarily in ribbons) is about 0.6%, and trace metals like tin, zinc, lead, and silver amount to 0.1% or less. Despite silver's tiny fraction (≈0.005-0.06%), it is a high-value metal in c-Si modules.

Table 1. Typical material composition of first-generation c-Si PV modules [3,4]

Component	Content (% by weight)
Glass	70-75%
Aluminum	10-18%
EVA	5.0-6.5%
Silicon	3.35-3.65%
Tedlar	1.5-3.5%
Copper	0.6%
Tin	0.12%
Zinc	0.12%
Lead	0.06%
Silver	0.004-0.06%

Thin-film PV technologies, including amorphous silicon (a-Si), cadmium telluride (CdTe) and copper indium gallium selenide (CIGS), have a much smaller market share than c-Si modules but are relevant to recycling because they contain critical or hazardous elements such as In, Ga, Se, Cd and Te[3-7]. Therefore, this review treats thin-film modules as a secondary but necessary scope, especially for strategic-metal recovery and hazardous-material control[8].

Table 2. Cumulative material quantities of CdTe panel waste in 2040 and 2050 (tons) [9]

Year	Glass	Al	Steel	Si	EVA	Cu	Te	Cd	Pb	Ni	Cr
2040	37181	367	4876	1223	14669	12231	488	488	17.1	17.1	73.5
2050	879640	869	11536	2893	34705	28937	1154	1154	40.6	40.6	174

Table 3 summarizes typical metal distributions in spent CIGS-related materials. Selenium (Se) accounts for the highest average fraction (43.53%), followed by indium (In, 27.26%) and copper (Cu, 21.25 wt.%), while gallium (Ga) accounts for 7.96 wt.%. These data illustrate why CIGS recycling should be assessed not only by total mass recovery, but also by the selective recovery and safe handling of critical elements.

Table 3. Metal content in typical waste CIGS components [10]

Element / wt% Spent CIGS	Cu	In	Ga	Se	Refs
Spent CIGS targets	17.68	28.19	6.71	47.42	[11]
Spent CIGS targets	25.78	26.28	4.80	43.09	[12]
Spent sputtering targets	17.00	30.20	5.00	47.80	[13]
CIGS chamber waste	19.78	19.00	9.26	49.77	[14,15]
Spent sputtering panels	23.26	18.9	15.99		[16]
Spent sputtering panels	24.00	41.00	6.00	29.00	[17]
Average	21.25	27.26	7.96	43.53	-

Third-generation and emerging PV technologies are mentioned only where they affect end-of-life management. For example, perovskite modules raise specific concerns regarding Pb recovery and solvent management, whereas III-V or multi-junction cells may contain high-value but low-volume elements. These technologies are not the main focus of this review because they are not yet the dominant source of PV waste.[18-22]

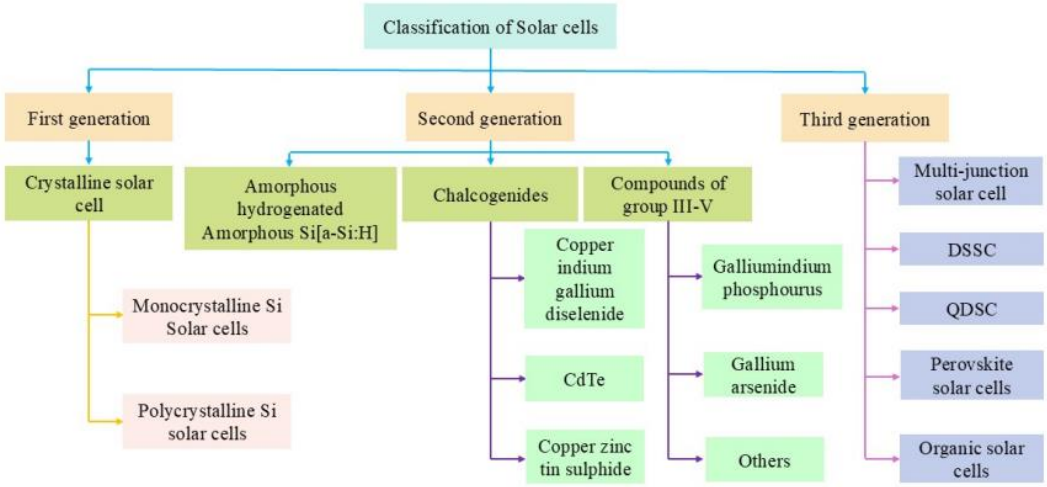


Fig. 1. Classification of solar cells (Adapted from An integrated hybrid lifecycle assessment and review in comparison with other photovoltaic technologies. and comply with copyright requirements)[23]

1.2 PV module structure

As shown in Figure 2a, a standard PV module is composed of a frame, front glass, encapsulant, solar cells, backsheet, and a junction box. The frame protects the panel and provides mechanical support for installation. The front glass is a low-iron tempered glass with high transmittance and strength to withstand outdoor exposure. The encapsulant, usually EVA (ethylene-vinyl acetate) polymer, encases the cells to provide electrical insulation and mechanical cushioning. The backsheet is often a multilayer fluoropolymer (e.g., TPT, with PVF and PET layers) that protects the module's backside Solar cells within the module are interconnected by tinned copper busbars. Edge sealants (butyl rubber, silicone, or adhesive tapes) prevent moisture ingress, and the junction box (typically made of PET plastic) on the back houses wiring and bypass diodes for safe electrical connections. In crystalline silicon cells, the

front metal electrodes are printed with silver, and the rear contact is usually aluminum. An anti-reflective (AR) coating (e.g., silicon nitride) on the cell surface maximizes light absorption. Figure 2b schematically illustrates a c-Si solar cell structure, including the silver front grid, AR coating, doped p-n junction, and aluminum back contact.

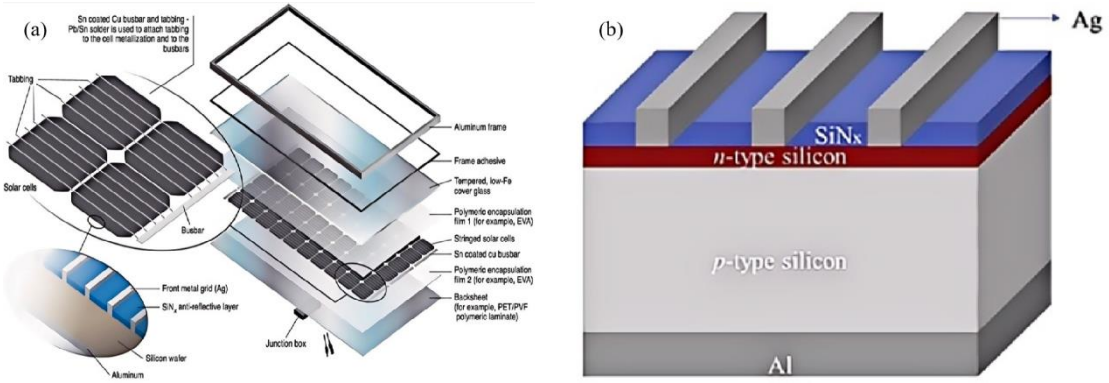


Fig. 2. (a) Components of photovoltaic modules (b) schematic structure of crystalline silicon photovoltaic solar cells [24,25]

1.3 Projected waste volumes and metal resources

1.3.1 Accumulation of end-of-life PV modules

The first large-scale deployments of c-Si PV modules began around 2000. Thanks to falling costs and global green growth initiatives, PV installation has accelerated dramatically in recent years. In 2024 alone, global PV installed capacity reached 1,865 GW. China, now the country with the largest PV capacity, hit 886 GW by 2024. Given a typical module lifespan of 20-25 years, the world faces an impending wave of PV module waste. The issue of module end-of-life is becoming increasingly prominent. Assuming an average module of 300 W weighs ~18 kg, China's installed PV capacity by 2024 corresponds to over 16 million tonnes of future electronic waste. The European Union is projected to generate >2 million tonnes of PV waste by 2028, and by 2030 the global PV waste could reach ~8 million tonnes [26] .As shown in Figure 3a, the new PV installed capacity in China and the world shows a continuous growth trend, and the growth rate of the Chinese market is significantly higher than the global average. The International Renewable Energy Agency (IRENA) [27] estimated that by 2050, China 's annual cumulative retired photovoltaic installed capacity will be ~ 20 GW, the United States is 10 GW, Japan is 7.5 GW, Germany is 7.5 GW, and India is 4.3 GW (Fig.3b). This is equivalent to tens of millions of tons of waste modules (it is predicted that by 2050, China alone will have ~ 20 million tons of photovoltaic waste, about 2000 times the weight of the Eiffel Tower). Obviously, end-of-life PV modules represent an imminent waste management challenge.

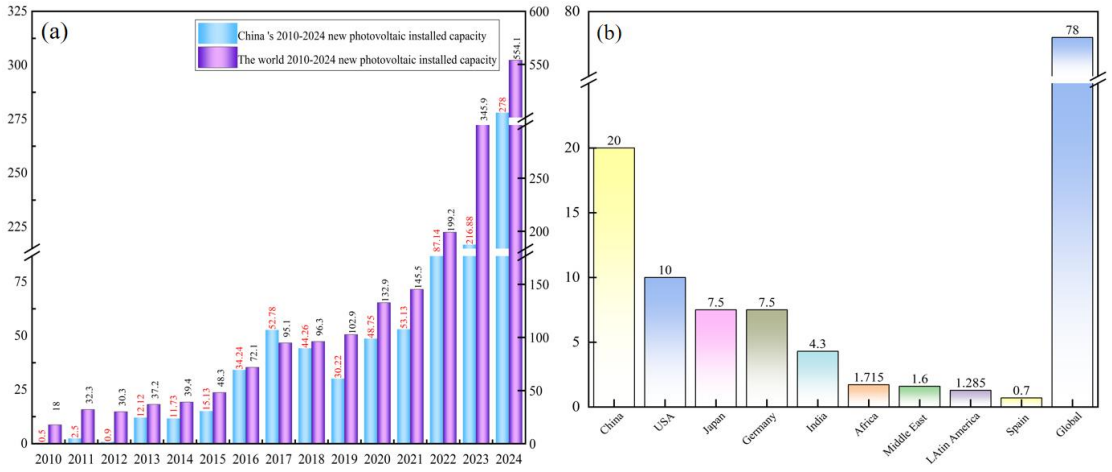


Fig. 3. (a) New PV installed capacity in China and the world from 2010 to 2024 (b) Estimated amount of PV modules scrapped in 2050 (unit : GW) [28]

1.3.2 Valuable metal reserves in PV waste

Waste PV modules contain a variety of materials with significant recycling value. These include common metals like aluminum, silicon, copper, and solder (lead-tin alloy), as well as precious metals such as silver [29,30]. For instance, c-Si PV cells use silver in their front electrodes and solder that contains lead. Thin-film modules consume strategic elements like gallium (in GaAs or CIGS cells), indium (CIGS), tellurium (CdTe), etc., which are considered critical materials. Many of these materials (aluminum, glass, semiconductor metals) can be recycled and reused, underscoring the circular economy opportunity. By 2030, the cumulative recoverable materials from PV waste are estimated at 5.76 million tonnes of glass, 1.16 million tonnes of aluminum, 0.48 million tonnes of polymers, 0.27 million tonnes of silicon, 48,000 tonnes of copper, and 4,000 tonnes of silver. This highlights the dual strategic value of recycling both high-volume materials (glass, aluminum, etc.) and low-content but high-value metals (e.g., Ag) from PV waste. Special recycling processes will be required for hazardous substances (e.g., Cd, Pb) and strategic metals (In, Te) to achieve a closed-loop recovery. In China, industry estimates by 2030 predict that recycling retired PV modules could yield about 550 tonnes of silver, 1.45 million tonnes of steel, 1.10 million tonnes of glass, 0.54 million tonnes of plastic, 0.26 million tonnes of aluminum, 0.17 million tonnes of copper, and 50,000 tonnes of silicon [31]. Such resource recovery not only has economic value (e.g., 420,000 tonnes of cumulative copper from c-Si modules by 2050 is valued around US$4.5 billion), but also reduces the need for virgin material production. In sum, the resource potential in end-of-life PV modules is enormous, providing strong motivation for developing efficient recycling technologies.

2. RECYCLING INDUSTRY DEVELOPMENT STATUS

In the context of today's global low-carbon transition, PV module recycling has become a key breakthrough for a green circular economy. Worldwide, the PV recycling industry is developing with regional differences (see Table 4). European companies have taken the lead in large-scale and high-value recycling: for example, France's Rosi Solar and Germany's Reiling have each built demonstration recycling plants with capacities on the order of 10,000 tons/year. Rosi Solar focuses on recovering high-purity silicon, while Reiling specializes in processing CdTe modules. Japan has pursued low-cost

dismantling techniques led by NEDO, developing low-temperature thermal decomposition methods to streamline module disassembly. China's PV module recycling industry began systematic R&D around 2017 and has rapidly progressed. Multiple companies built pilot or demonstration lines between 2018-2021; After 2022, China's photovoltaic module recycling industry has entered a stage of accelerated development. The maturity of physical separation and chemical purification technology has been improved, and the metal recovery rate can reach more than 95%. From 2020 to 2050, China's photovoltaic waste is projected to increase markedly. In 2020, photovoltaic waste was below 200,000 tons. This figure is expected to rise substantially to 3.2 million tons by 2030 and to 23 million tons by 2050[32]. For instance, State Power Investment Corporation (SPIC) launched a 30 MW pilot line in 2021, and Jinko Solar established a >12 MW/year pyrolysis-based line. Since 2021, China has gradually scaled up to commercial production, annual processing capacity is about 20,000-30,000 tons (30% -40% of the decommissioned components of the year). The current mainstream process in China combines thermal delamination and mechanical separation, supplemented by hydrometallurgical refining. This hybrid approach achieves overall material recovery rates around 90-95%, with critical elements like silver and silicon >95% recovery. Some enterprises (e.g., Shanghai JH-JY) have even realized full recovery of silicon material at 6N purity (see Table 5).

Table 4. Overseas examples of large PV recycling demonstration lines

Company / organization	**Location**	**Technology route**	**Capacity / scale**	**Reported recovery or performance**
Soren	France	Collection, sorting, reuse and recycling of end-of-life PV modules	A reuse-oriented production line was established in 2024 with an investment of approximately €0.5 million	Specific material recovery rate not reported; mainly focused on collection, reuse and waste management
ROSI Solar	France	High-value recovery of silicon and metals from PV waste, including silicon kerf waste	"Alps Silicon Recycling Center" launched in 2023, with a reported processing capacity of 10,000 tons/year	Recovery of high-purity silicon and valuable metals was reported, but detailed recovery efficiencies detailed recovery efficiencies were not reported.
Reiling	Germany	Physical recycling and sorting of silicon-based PV modules; CdTe module recycling also included	Recycled over 4,200 tons of PV modules in 2022; a dedicated PV recycling facility with 50,000 tons/year capacity was commissioned in 2023; CdTe recycling capacity was reported as 10,000 tons/year	Mainly focused on glass and module material recovery; specific metal recovery rates should be further clarified

Company / organization	Location	Technology route	Capacity / scale	Reported recovery or performance
PV Industries	Australia	Mechanical separation of aluminum frames, copper wires, junction boxes, glass and other module components	Operates six collection points for end-of-life PV modules across Australia	Specific recovery rate not reported; recovered fractions are supplied to downstream recycling partners

Table 5. Chinese examples of large PV recycling demonstration lines

Company / organization	Location	Technology route	Capacity / scale	Reported recovery or performance
State Power Investment Corp. (SPIC)	China; specific site not specified	Mechanical dismantling, hot-knife cutting, selective separation, pyrolysis and hydrometallurgical purification	Pilot line with an annual capacity of 30 MW, built in December 2021	Specific recovery rate not reported
Jinko Solar Co., Ltd.	China; specific site not specified	Pyrolysis combined with chemical treatment	>12 MW/year	Mass recovery >92%; energy consumption ≤27 kWh/kW; Ag recovery >95%, Si recovery >95%, Cu recovery >98%
Changzhou Ruisai Environmental Tech.	Changzhou, China	Mechanical/physical separation combined with pyrolysis	~3,000 tons/year	Material recovery >95%; overall utilization >90%
Shanghai Jinghuan Jiayuan New Energy	Shanghai, China	Wet chemical separation for EVA removal and material purification	Not reported	Production of 6N Si; PV glass purity >99.9%; complete material recovery claimed
Changsha Mining and Metallurgy Institute	Changsha, Hunan, China	Integrated thermal treatment, mechanical separation and chemical processing	16 prototype and pilot units	Specific recovery rate not reported
Nantong Riyihe New Environmental Tech.	Nantong, Jiangsu, China	Automated disassembly combined with physical separation and pyrolysis	10,000 tons/year by 2021	Module recycling rate >95%; recovery efficiency >95%

Company / organization	Location	Technology route	Capacity / scale	Reported recovery or performance
Xi'an Faherman Intelligent Tech.	Xi'an, Shaanxi, China	Mechanical crushing, pyrolytic separation and material sorting	R&D team established in 2014; capacity not reported	Specific recovery rate not reported
Jereh Environmental Tech. Co.	China; specific site not specified	Automated dismantling, thermal-phase separation, off-gas treatment and comprehensive sorting	Not reported	c-Si cell recovery rate and purity >95%
Yicheng Xinneng (Suzhou) Tech.	Suzhou, Jiangsu, China	Ambient-temperature delamination of fluorinated backsheets, lead-containing ribbons and shattered glass	Not reported	Delamination at <80 °C; no fluorine or lead off-gassing reported
Grimmie	Wuxi, Jiangsu, China	Mechanical disassembly, pyrolysis stripping and hydrometallurgy	100,000 tons/year	Recovery rates of Si, Ag, Cu and other metals >95%
Longi Green Energy	Xi'an, Shaanxi, China	Sorting and material regeneration of crystalline silicon modules	Not reported	Direct recovery and reuse rate of silicon wafers up to 90%

3. DISMANTLING PROCESSES FOR WASTE PV MODULES

As illustrated in Figure 4, dismantling a retired PV module generally involves three steps: (1) Mechanical separation of easily removable parts [31]; (2) Encapsulant (EVA) removal [33]; and (3) Chemical extraction or refining of metals [34]. First, the aluminum frame and junction box are removed and recycled. Next, the remaining laminate is crushed, and the crushed material is sieved to separate glass and semiconductor pieces. To remove the EVA encapsulant, thermal treatment is often applied - for example, incinerating the module in a muffle furnace to burn off polymers. After burning away the encapsulant, the exposed cell materials can be separated and recovered. Alternatively, organic or inorganic solvents can dissolve the EVA layer to delaminate the module without high temperature. Once the cells are freed from encapsulant, chemical methods leach out valuable metals (like Ag) from the cell fragments. Currently, most PV module dismantling techniques remain at the R&D stage, and a combination of methods is often used to improve efficiency and environmental performance. In practice, mechanical, thermal, and chemical approaches are complementary - for instance, mechanical shredding + thermal EVA removal might be followed by chemical leaching of metals.

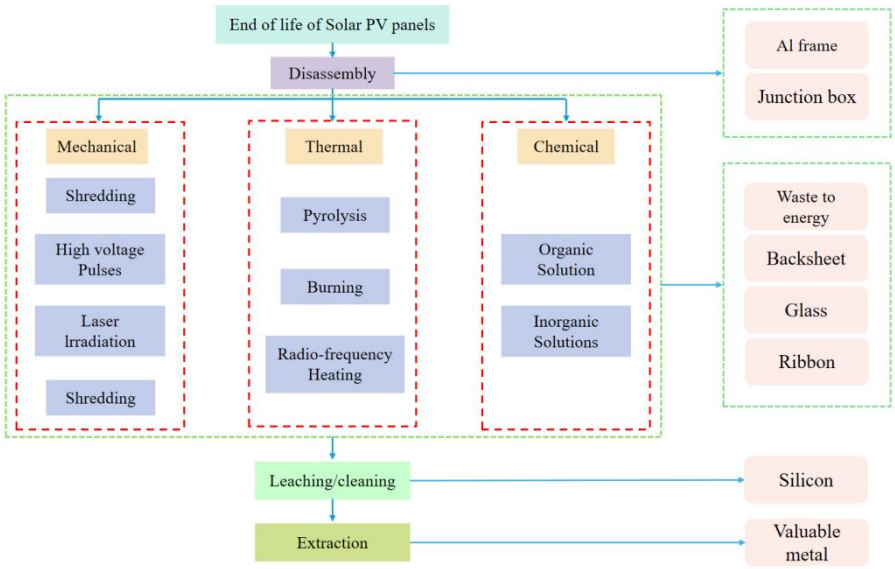


Fig. 4. Recycling process for silicon-based PV panel e-waste

Modern PV recycling systems that integrate physical separation with chemical leaching have shown considerable potential for recovering high-value materials such as silicon wafers and silver contacts. However, the reported reductions in energy consumption and carbon footprint are highly dependent on the selected reference process, system boundary and functional unit. In this review, such comparisons are interpreted using 1 ton of end-of-life crystalline silicon photovoltaic modules as the functional unit. The system boundary should include module dismantling, crushing or separation, thermal or chemical delamination, metal leaching and recovery, reagent make-up or regeneration, wastewater neutralization and off-gas treatment, where data are available. Compared with routes dominated by high-temperature treatment or primary production of equivalent materials, integrated physical–chemical recycling routes generally show lower energy demand and environmental burden. Nevertheless, the values reported in the literature should not be directly generalized unless the same functional unit, recovery-rate definition and environmental boundary are used. Therefore, claims such as “energy consumption reduced by more than 60%” or “carbon footprint reduced to approximately 12% of virgin-material production” should be regarded as case-specific results rather than universal conclusions.

At present, PV recycling technologies and equipment are still under development globally. To scale up sustainably, further innovations are needed in four areas: (i) Green environmental performance-minimizing emissions and ensuring proper waste treatment to avoid secondary pollution; (ii) Economic efficiency - optimizing layered separation techniques to reduce costs and improve recovery rates; (iii) High compatibility - adapting processes to diverse module designs and different end-of-life conditions (intact vs. shattered modules); (iv) Digital & smart operation - leveraging digitalization and intelligent manufacturing for automated processing, real-time monitoring, and full traceability in module recycling. Progress in these areas will drive the PV recycling industry towards large-scale, smart, and sustainable development.

In summary, three primary methods are employed (often in combination) to dismantle waste PV modules: Mechanical methods use physical means (cutting, crushing, screening, and electrostatic separation) to separate aluminum frames, glass, silicon, and metals. This is well-suited for c-Si modules and avoids chemical waste, but it cannot by itself fully delaminate the laminated layers. Thermal

methods heat the module (typically 400-600 °C) [35] to decompose the EVA encapsulant, facilitating separation of glass, cells, and backsheet. Thermal delamination is effective for encapsulant removal, but it requires energy input and appropriate off-gas treatment, especially when fluorinated backsheets Chemical methods use acids, alkalis, or organic solvents to selectively dissolve the EVA and/or metal coatings [36]. Chemi burning off organics cal delamination can yield high-purity outputs (recovering clean silicon wafers and silver), but may generate hazardous waste liquids. Some pilot and demonstration lines have reported high material recovery rates; however, independently verified mass balances, product-quality data and environmental-control information remain limited. [3-7].

4. RECOVERY OF VALUABLE METALS

Recycling PV modules involves recovering metals via two major metallurgical routes: pyrometallurgy and hydrometallurgy. These approaches target efficient extraction of valuable metals like silver, aluminum, copper, silicon, etc., from end-of-life modules. Pyrometallurgical processes use high temperatures to separate metals. A typical pyro-route is to shred the module (removing glass and backsheet) and then melt the remaining material in a furnace >1000 °C. Due to density differences, metals stratify: aluminum frames and copper wires can separate out, while silicon and silver concentrate in the slag. Subsequent oxidative refining or electrorefining can then purify specific metals. Pyrometallurgy can handle large throughput and has a short process flow, but it is energy-intensive and can produce hazardous fumes (e.g., fluorinated gases), necessitating emission control equipment. Hydrometallurgical processes, by contrast, use chemical solvents to selectively dissolve target metals and are particularly suitable for recovering metals like silver and lead. In a typical hydro-process, the module is crushed and then leached with acids (e.g., HNO_3 to dissolve Ag gridlines, or an organic acid to leach Pb). Target metals are recovered from the leachate via replacement reactions, precipitation, or electrodeposition. For example, silver can be leached with nitric acid, precipitated as AgCl by adding NaCl, and then reduced to metallic silver. Hydrometallurgy often achieves high metal recovery yields (Ag recovery can exceed 95%) with lower energy input than pyro-methods, but generates waste solutions that require treatment. In practice, combined processes are frequently used - e.g., a thermal pretreatment (to remove bulk materials) followed by hydrometallurgical refining of critical metals. Looking ahead, researchers are developing greener alternatives such as low-temperature pyrolysis and bioleaching to reduce energy use and pollution, while improving the economic feasibility of recovering precious metals.

4.1 Silicon recovery

Silicon is a primary material in c-Si PV modules, and various pathways exist to reuse or repurpose recovered silicon. Currently, recovered silicon can be processed into new solar cells and wafers, used as anode material for Li-ion batteries, or refined into high-purity silicon and silica particles. As shown in Figure 5, For solar-grade reuse, Lee et al. [37] shredded waste cells and soaked them in a HNO_3 :HF mixture to strip off the metal electrodes, antireflection coating and emitter diffusion layer, yielding regenerated monocrystalline silicon of 6N8 purity (99.99998%). They then mixed 30% of this reclaimed silicon with 70% virgin polysilicon (3:7 ratio) and pulled a 6-inch 7N7 monocrystalline ingot via the Czochralski process. Solar cells made from this mixed-feed ingot reached 20.05% efficiency-only 0.97 percentage points below cells made entirely from virgin silicon. The HNO_3 and KOH were used to dissolved the silver electrodes and aluminum back-surface field of silicon wafers firstly, then etching away the SiN_x AR coating and p-n emitter using a phosphoric-acid paste. A final gradient heat treatment

at 320-400 °C cleansed the wafers further, yielding regenerated wafers over 180 μm thick with resistivity of 0.5-4 Ω/cm on par with commercial virgin wafers [38].

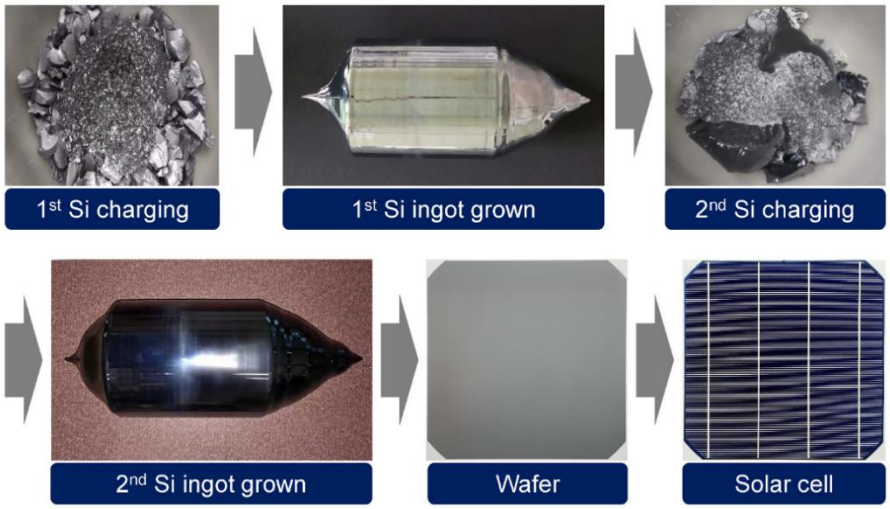


Fig. 5. Overall process flow for preparing c-Si solar cells from recovered silicon waste [37]

In Figure 6 ,Silicon for battery materials: Eshraghi et al. [39]treated solar-cell scrap with 8 M KOH at 60 °C (5 min) and 8 M HNO_3 at 80 °C (15 min) to remove ~98.4% Al and ~99.87% Ag/Pb, yielding 99.99%-pure Si. Used as a Li-ion anode, it delivered 1,400 mAh/g. In Figure 7 [40], the EVA was removed with an organic solvent, leached for high-purity wafers, then ball-milled Si with graphite to form a Si-graphite composite (W-Si-rM@G). After 200 cycles at 500 mA/g, it still achieved ~913 mAh/g with excellent stability. In Figure 8 [41], a two-step 90 °C leach (2×30 min) was used to strip Al, Ag and AR coating in one go. Their upgraded Si anode retained 1,086.6 mAh/g initial capacity, 62.3% after 500 cycles, with >99% coulombic efficiency.

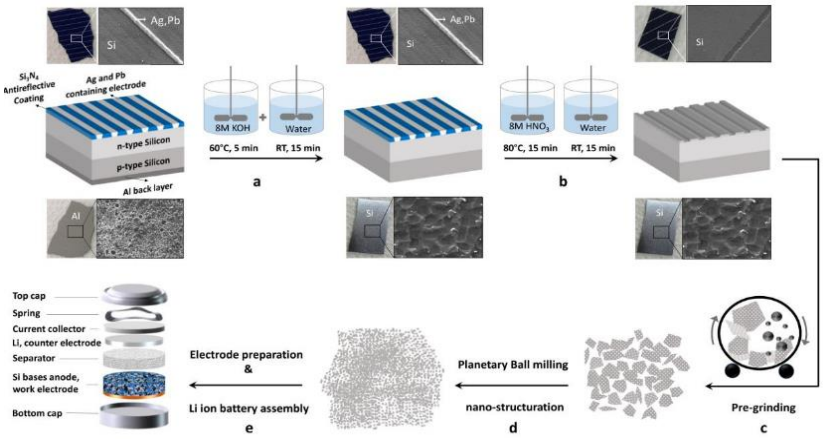


Fig. 6. A schematic diagram of sustainable recovery of silicon from photovoltaic panels for lithium-ion batteries [39]

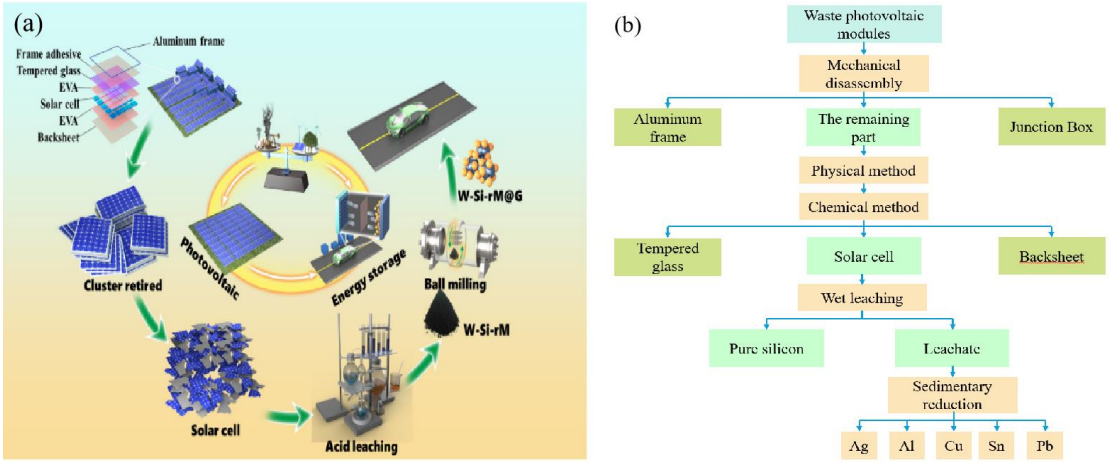


Fig. 7. (a) Flow chart of recovering high-purity silicon wafers from waste photovoltaic modules and preparing high-performance lithium-ion battery anode materials (b) Silicon recovery from photovoltaic cells by single reagent method (Adapted from Adapted from Ref. [40] with permission. and comply with copyright requirements)[40]

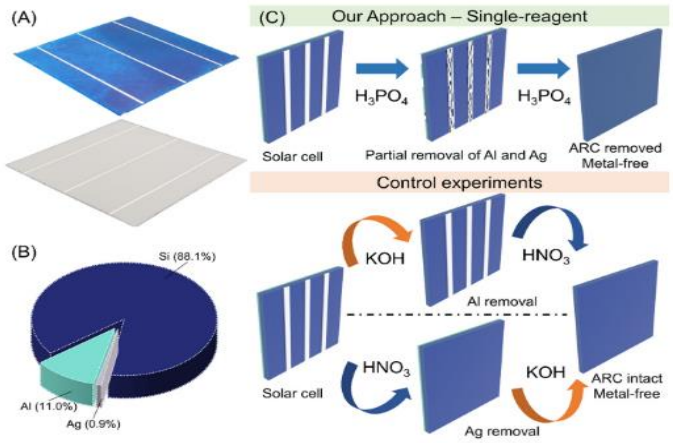


Fig. 8. Recovery of silicon from photovoltaic cells by single reagent method [41]

Kang et al. [42] (Figure 9) developed a three-step flow: EVA swelling to detach glass, thermal decomposition to remove residue, and a 20-min surfactant-assisted chemical etch-achieving 86% Si recovery at 99.999% purity while reclaiming tempered glass. As shown in Figure 10, the waste cells[43] was sequentially dipped in 30% KOH (2-3 min, 60-80 °C) then HNO_3-HF-CH_3COOH-Br_2 (9 s, 40 °C) to remove Al contacts, Ag grids, AR coating and junctions, yielding 99.8%-pure Si. As shown in Figure 11 [44], the modules were mechanically crushed and used 15 kV electrostatic separation to concentrate 0.30-0.45 mm Si particles (91.0% purity, 48.9% recovery). Lee et al. [45] achieved 100% high-purity Si recovery by leaching crushed cells in 5 mol/L HNO_3 at 70 °C for 2 h. Sapra et al. [46] swelled EVA with organic solvents to peel off glass, then applied a two-stage 5 mol/L HNO_3 etch (3 h + 5 h, RT) to produce >99.9%-pure SiO_2 nanoparticles.

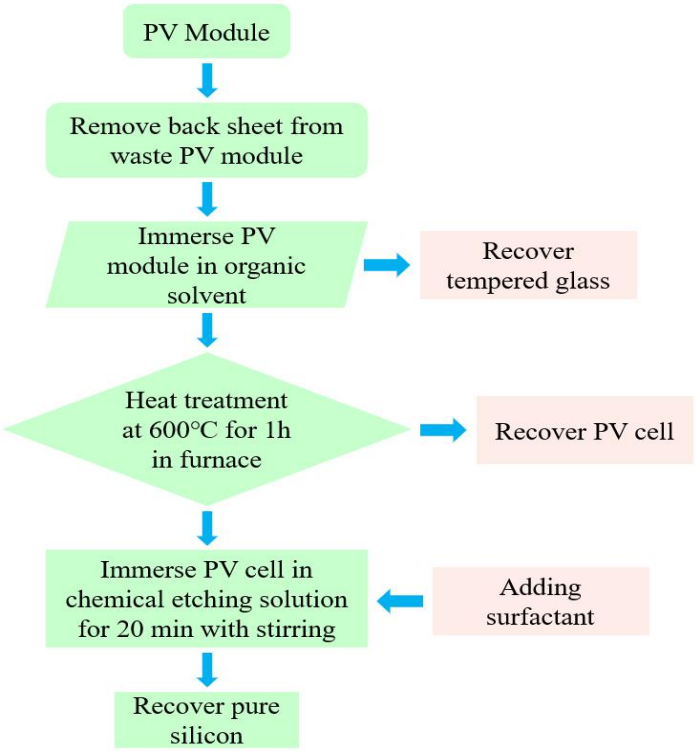


Fig. 9. The process diagram of recovering tempered glass and silicon from waste photovoltaic modules (Adapted from Adapted from Ref. [42] with permission. and comply with copyright requirements)[42]

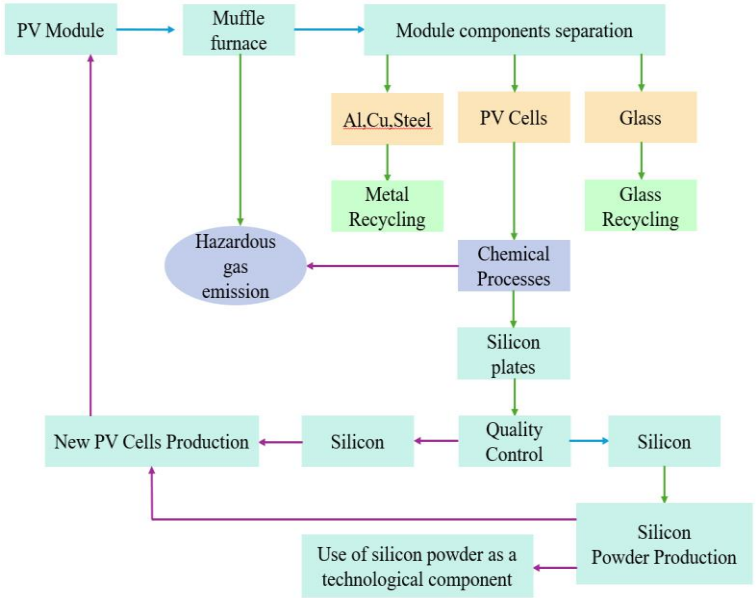


Fig. 10. Thermal and chemical processes in the recovery of photovoltaic crystal cells and photovoltaic modules (Adapted from Adapted from Ref. [43] with permission. and comply with copyright requirements)[43]

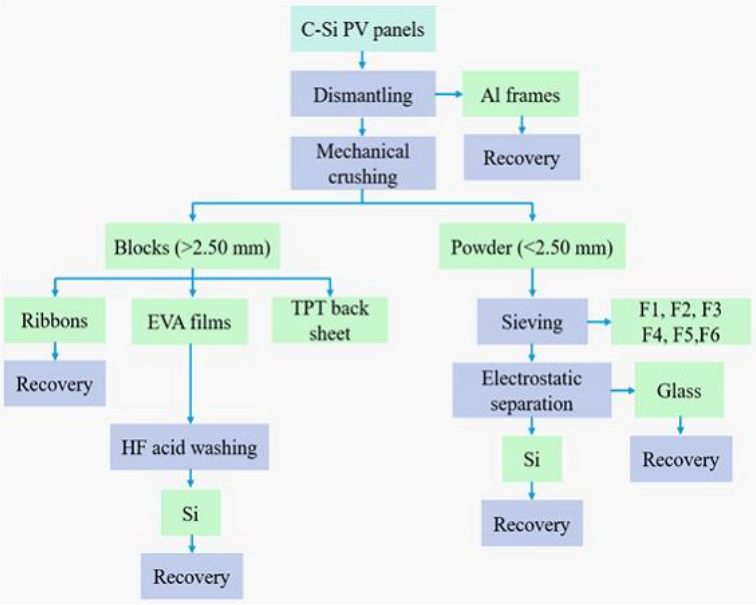


Fig. 11. Flow chart of Si recovery from waste c-Si photovoltaic panels (Adapted from Adapted from Ref. [44] with permission. and comply with copyright requirements)[44]

The silicon recovery process offers high economic and environmental value. By combining mild thermal and chemical etching steps, researchers can effectively remove metallic contacts (Al, Ag), AR coatings (e.g., TiO_2, Si_3N_4), and the junction from silicon cells, yielding PV-grade silicon material that can be directly used to make new cells or other high-value products. Modular sequences (e.g., KOH/NaOH to remove Al, HNO_3 to dissolve Ag, HF/HNO_3 to etch dielectric layers) can achieve >90% overall material recovery from silicon modules, at a processing cost comparable to traditional disposal. However, this approach requires tight control of parameters and must be tailored to cell type (mono vs. multi-Si) to avoid over-etching the silicon wafer (>20 μm thickness loss) or leaving impurities. Moreover, the use of strong acids like HF and HNO_3 introduces safety hazards and waste treatment challenges; incorporating a silver electro-recovery stage is necessary to make the process economically viable by capturing valuable Ag. In short, recovered silicon can be of sufficiently high purity for PV or battery applications, but process optimization and safety measures are essential.

Critical interpretation of silicon recovery: High-purity Si recovery is technically feasible, but different product targets impose different requirements. Reuse as PV-grade feedstock requires strict control of wafer integrity, dopant profiles, surface damage and metallic impurities, whereas use as Li-ion battery anodes tolerates particle breakage but requires additional milling, carbon coating and electrochemical-quality validation. Consequently, Si recovery routes should be evaluated by product specification, reagent consumption, wafer loss and downstream value, not only by purity.

Table 6 shows that high-purity regenerated Si can be obtained by chemical etching, thermal-assisted cleaning or electrostatic concentration. However, direct reuse in new PV cells requires strict control of wafer integrity, dopant profiles, surface damage and impurity levels. By contrast, conversion into Si-based anode materials tolerates more particle breakage but introduces additional milling, carbon coating and battery-grade quality-control requirements. Therefore, the most suitable route depends on whether the target product is a wafer, purified Si feedstock, SiO_2 nanoparticles or battery material.

Table 6. Recovery of silicon from waste photovoltaic modules

Leaching system	Processes	Purity	Refs
HNO_3 + HF	HNO_3 + HF: chemical etching of waste PV modules to remove electrodes, anti-reflection coating (AR), and emitter layer;KOH + IPA solution: texturization of wafer surface	Si: 6N8	[37]
HNO_3 + KOH	HNO_3 (60%, 25 °C, 5 min): dissolve Ag electrode;KOH (45%, 80 °C, 8 min): dissolve Al electrode;H_3PO_4 (320-400 °C stepwise): remove ARC and emitter	Si: 99.99%	[38]
KOH + HNO_3	8 mol/L KOH: Al removal rate 98.403%;8 mol/L HNO_3: Ag and Pb removal rate 99.87%	Si: 99.99%	[39]
HCl + HNO_3 + HF	Toluene (soak 24 h): dissolve EVA encapsulant, separate glass and backsheet;HNO_3 (1 mol/L): remove Ag and other metal impurities;HCl (4 mol/L) + HF (40%) (40 min, 50 °C): remove residual metal impurities and oxide layer	Si: 99.91%	[40]
HNO_3 + H_3PO_4 + KOH	H_3PO_4 (85 wt%, 90 °C): remove ARC, strip Ag and Al;HNO_3 (70%): dissolve Ag and part of Al;KOH (45%): dissolve remaining Al	Si: 99.2%	[41]
HF + HNO_3 + H_2SO_4 + CH_3COOH + CMP-MO-2	Toluene: dissolve and swell EVA resin, separate tempered glass and PV cells;HF (48%) + HNO_3 (70%) + H_2SO_4 (97%) + CH_3COOH (99%) + CMP-MO-2 (20 min): remove metallic impurities	Si: 99.999%	[42]
KOH + HNO_3 + HF + CH_3COOH + Br_2	KOH (30%, 60-80 °C, 2-3 min): remove Al metallization layer;HNO_3 (65%) + HF (40%) + CH_3COOH (99.5%) + Br_2 (3 mL) (40 °C, 9 s): remove Ag coating, ARC, and n-p junction	Si: 99.8%	[43]
HF	HF (20%, S/L = 1:10, 25 °C): soak until EVA and wafer fully separate	Si: 91%	[44]
HNO_3	Toluene: dissolve and swell EVA resin;HNO_3 (5 mol/L, 3 h, 600 rpm): dissolve metal electrodes	SiO_2: 99.9%	[46]

4.2 Silver recovery

Silver is a precious metal used in PV cell metallization as front grid lines. Efficient recovery of Ag from end-of-life cells is crucial. Acid leaching is the preferred first step to dissolve silver electrodes. Not all acids are effective: H_2SO_4, though common industrially, is not effective for leaching Ag from c-Si solar cells, and dilute H_2SO_4 or HCl generally do not dissolve Ag because silver forms insoluble precipitates (Ag_2SO_4, AgCl). Nitric acid (HNO_3) is well known for its ability to leach silver and other metals; researchers have extensively studied HNO_3 leaching for various ores and wastes [47-49]. During HNO_3 leaching of crushed PV cells, metals like Al, Ag, and Cu dissolve into the solution. A key challenge, however, is the selective recovery of each metal from the mixed leachate [50]. Typically, sequential extraction techniques are used: for example, adding specific extractants to pull out heavy metals one by one from the acid leachate [51]. Below we review several chemical extraction methods for silver, followed by reduction and electrorefining methods to produce silver powder.

4.2.1 Chemical extraction of silver

(1) Nitric Acid Leaching

Cell fragments were immersed in 5 mol/L HNO_3 at 200 rpm, achieving ~90 % Ag dissolution [52]. Abdo et al. [53]stirred 10 g crushed PV in 200 mL 5 mol/L HNO_3 (400 rpm, RT, 1 h), yielding ~97 % Ag recovery. The 4 mol/L HNO_3 [54] was used (100 mL/g) at 85 °C for 4 h to leach 99.7 % Ag, then removed 96 % Al with α-Cyanex 272, boosting Ag recovery to 98 %. Shredded cells were leached in 2 mol/L HNO_3 at 100-140 °C (L/S = 1 : 10, 2 h), achieving 100 % Ag dissolution[55].

(2) Hydrochloric Acid Route

The H_2O_2-HCl system was [56] employed to leach metals oxidatively while precipitating Ag as AgCl. Sequential solvent extraction (TBP then LIX984) separates Sn and Cu (TBP is used for the separation and recovery of various other metals. LIX984 can selectively bond with copper ions to form a complex and transfer from the aqueous phase (leach solution) to the organic phase.) Pb is later recovered as $Pb(OH)_2$-yielding efficient multi-metal recovery without lead-contaminated effluent (Figure 12).

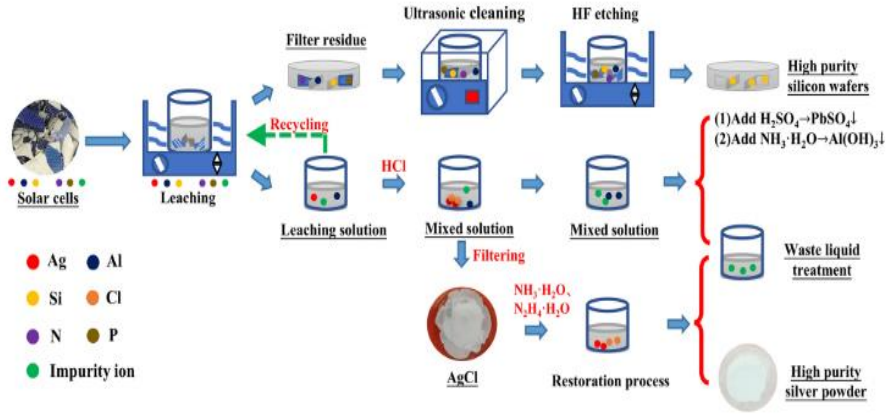


Fig. 12. Flow chart of the wet recovery process of valuable elements from waste solar cells [56]

(3) Sulfuric Acid Leaching

The H_2O_2-H_2SO_4 mix [57] was applied (80 g/L H_2SO_4, 25 g/L H_2O_2) at 75 °C, 120 min, L/S = 8 : 1, 300 rpm, to dissolve Al and Ag. Under these conditions, Ag leaching reached 99.01%, offering a streamlined route for PV-module metal recovery.

Each leaching method has pros and cons. Nitric acid offers high leaching efficiency (often >90% or even complete Ag recovery), and can be coupled with other steps for selective separation of elements. Its drawbacks are the strong corrosivity and oxidizing nature of HNO_3, posing safety risks and potential NO_x gas emissions. Organic acids (like MSA, citric) are milder and more environmentally benign; experiments can optimize conditions to obtain high Ag recovery. Hydrochloric acid leaching has the advantage of etching away the silicon nitride layer on cells (producing clean silicon) and capturing heavy metals (like Pb) as insoluble salts, thus preventing pollution. Its disadvantage is a relatively complex process with multiple steps. Sulfuric acid leaching can efficiently dissolve both aluminum and silver, significantly boosting overall recovery; but H_2SO_4 is highly corrosive, and careful control of conditions is required for safe, effective operation.

4.2.2 Reduction methods for silver powder

Once silver is leached into solution as Ag^+, chemical or electrochemical reduction is used to produce solid silver powder or crystals. Chemical reduction methods can recover Ag with high purity and allow control over particle morphology, and they often achieve high yields for precious metals. Jung et al. [52] (Figure 13) used a four-step sequence-Ag^+ precipitation as AgCl by chlorination, AgCl dissolution in KOH, hydrazine reduction to Ag powder, and electrolytic refining-to obtain 99.99%-pure silver and remove ~93% of Pb as insoluble compounds. Klugmann et al. [43] combined HNO_3 leaching with direct electrolysis for Ag recovery, but flagged the electro-deposition stage as too energy-intensive for industrial scale.

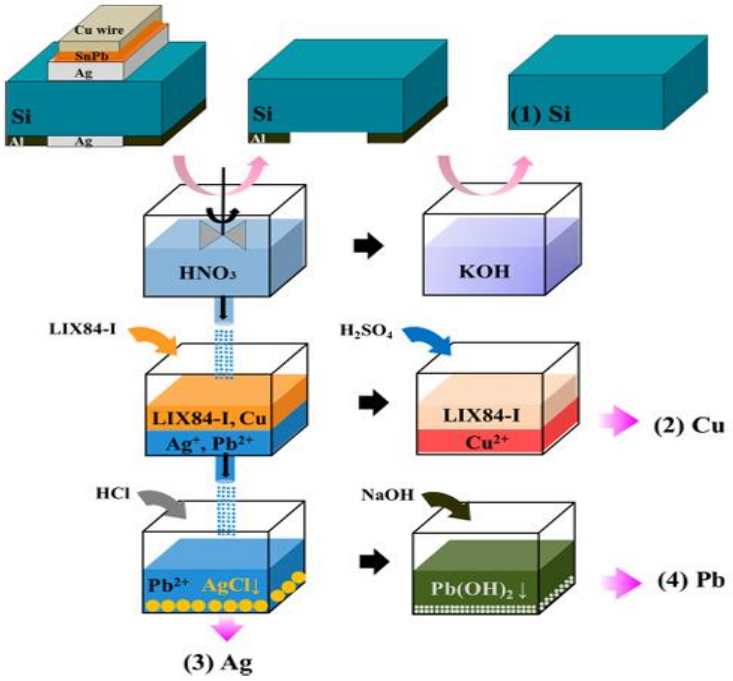


Fig. 13. Process flow of recovering raw metal from solar cells[52]

Dias et al. [58] (Figure 14) manually removed module frames, crushed the glass and cells to <0.5 mm powder, leached in HNO_3, then precipitated AgCl with NaCl-achieving ~94% Ag recovery-and evaluated how a prior pyrolysis step impacted yields. Wongnaree et al. [59] similarly leached scraps in 2-4 mol/L HNO_3 for 24 h, precipitated AgCl with NaCl, reduced it with sucrose under alkaline conditions, and heat-treated the residue in an acetylene flame to yield 99.98%-pure silver-but noted the long, costly process limits scalability(Figure 15).

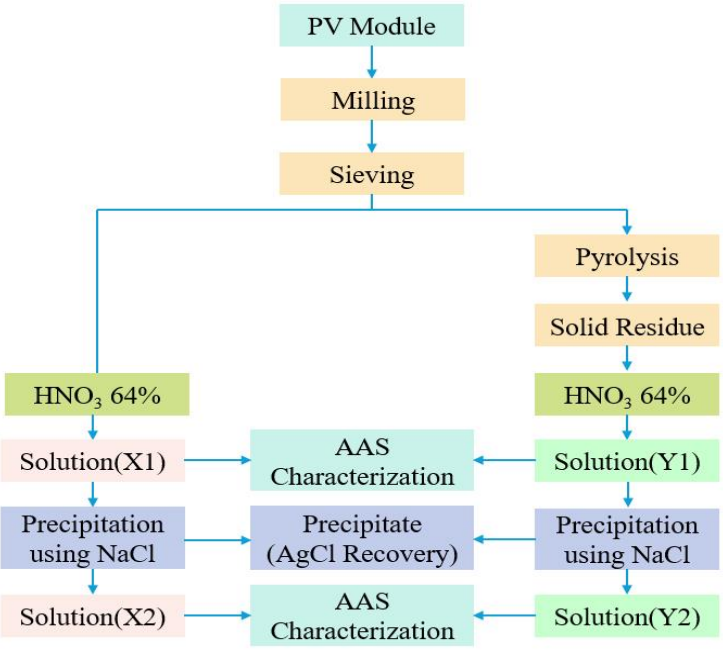


Fig. 14. Flow chart of Ag extraction and concentration steps (Adapted from Adapted from Ref. [58] with permission. and comply with copyright requirements)[58]

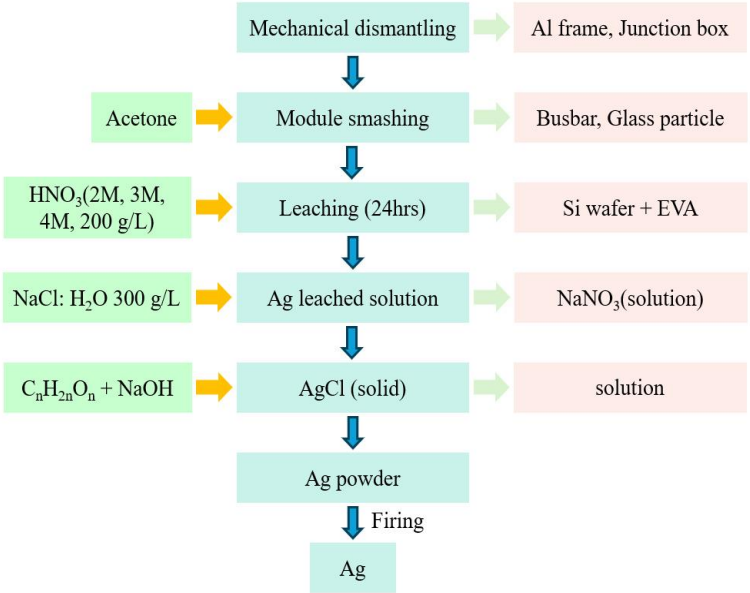


Fig. 15. Recovery process of silver from photovoltaic waste (Adapted from Adapted from Ref. [59] with permission and comply with copyright requirements)[59]

Beyond traditional reagents, novel lixiviants have been explored. Chung et al. [60](Figure 16) pioneered an iodide-based leachant-an I_2/KI solution-that matches nitric acid's Ag-leaching performance, demonstrating a non-acid alternative. Yue et al. [61] developed a kinetic model and used CFD-DEM simulations to optimize Ag leaching on fragmented cells. The sequential acid and alkali etch

[62] was used to recover ~1.6 kg Ag per ton of PV waste, highlighting economic viability. As shown in Figure 17, the choline chloride-urea deep eutectic solvent with CuCl as oxidant was introduced [63]. Ag is oxidized to AgCl and then precipitated by water addition; after vacuum-drying, the non-toxic, non-corrosive DES (Deep Eutectic Solvent) and Cu^{2+} are fully reusable, offering a greener silver recovery route.

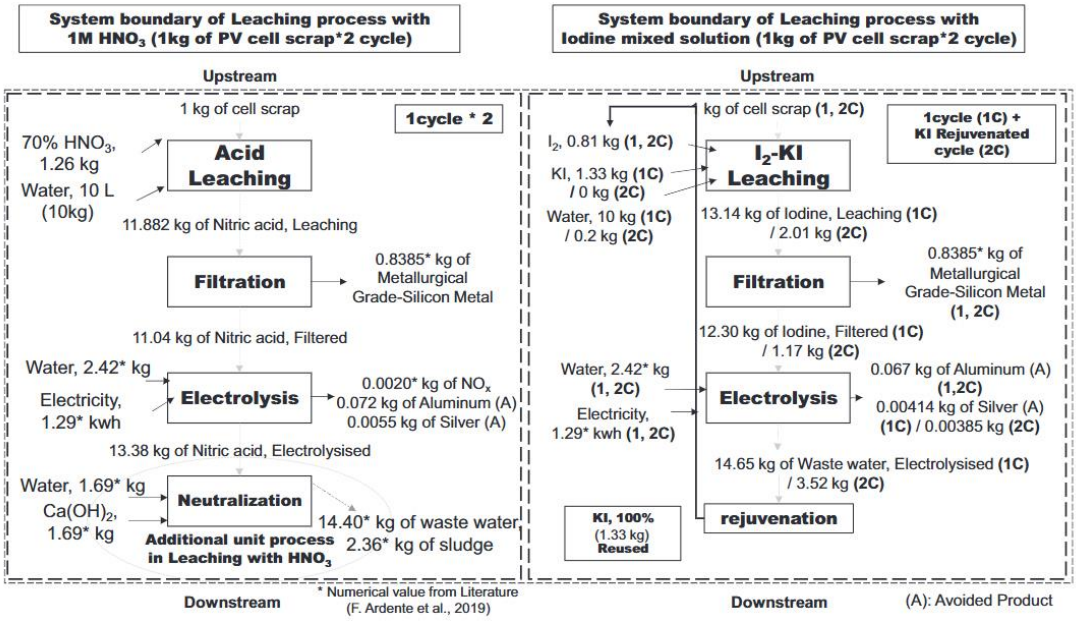


Fig. 16. The system boundary of leaching process is 1M HNO3 and 0.35M I2-0.7M KI solution. [60]

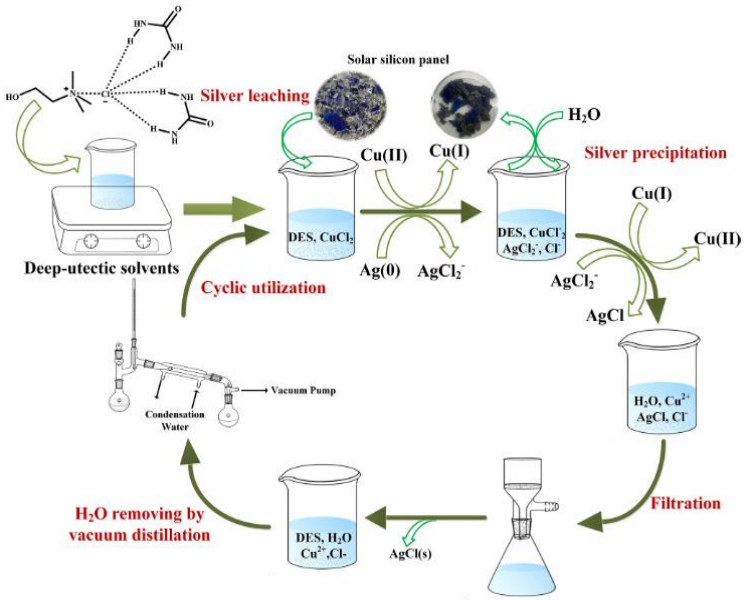


Fig. 17. Silver extraction process based on choline chloride-urea cocrystal solvent (DES) [63]

Chemical reduction of Ag is simple and low-cost, yielding >99.9% pure silver powders whose morphology (plate-like vs. spherical) can be tuned by choice of reductant and pH. Green reductants (e.g. ascorbic acid) or DES avoid strong-acid hazards, but toxic chemicals like hydrazine still pose risks. Impurities (chlorides, organics) and nanoparticle agglomeration require extra washes, heat treatment, or dispersants. Hence, chemical reduction is ideal for small-scale, high-purity silver production, while large-scale work favors greener but slightly more complex routes.

4.2.3 Electrolytic refining of silver

Electrolysis can be used either to directly recover Ag from leach solutions or to purify chemically recovered silver to ultra-high purity. Yang et al. [51] applied the same 9:1 MSA:H_2O_2 leach to c-Si cell scrap, with HCl precipitation, NaOH/H_2O_2 reduction, and electrorefining, also achieving 99.995% Ag. Although this "green" MSA system yields very pure silver and easy-to-treat effluent, it remains lengthy and complex. Theocharis et al. [64] (Figure 18) crushed and sieved PV modules, directly leached the powder in HNO_3, then precipitated Ag with HCl or NaCl and electrolyzed to obtain Ag powder. Raffaele et al. [65] (Figure 19) optimized an EDRR (electrodeposition-redox replacement) on an alkaline persulfate-ammonia leachate via DoE: deposition at E_1 = -0.17 V and replacement at E_2 = +0.2 V vs Ag/AgCl for t_1 = 10 s, yielding 98.7 ± 1.4% Ag. SEM-EDX confirmed pure Ag on reticulated vitreous carbon with no detectable Cu, demonstrating selective precious-metal recovery.

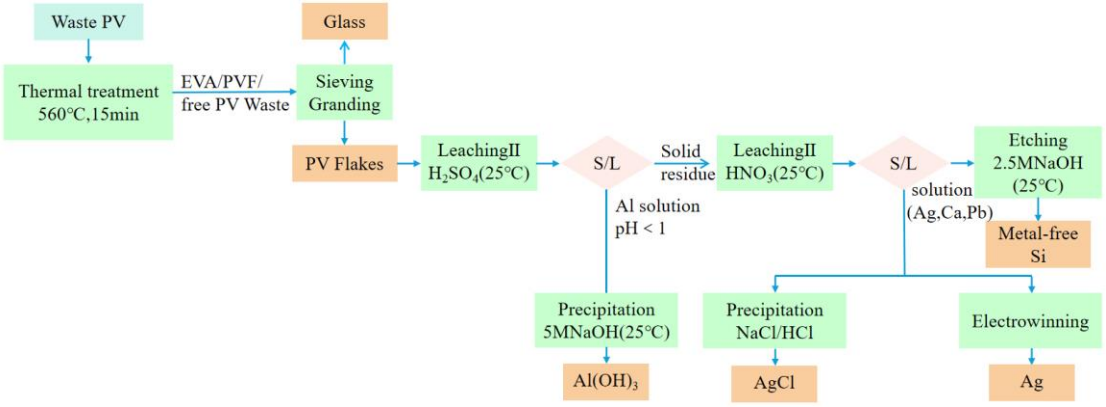


Fig. 18. The process flow chart of silver powder preparation. (Adapted from Adapted from Ref. [64] with permission. and comply with copyright requirements)[64]

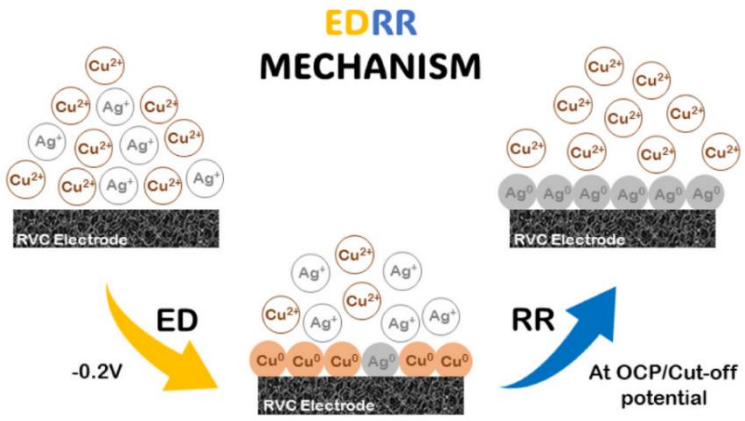


Fig. 19. Mechanism of electrodeposition-redox replacement. [65]

Electrolytic silver recovery offers distinct advantages: ultra-high purity (up to 99.93%), tolerance of low-grade feedstocks, scalability for industrial production, and lower unit costs once established. However, it demands complex equipment, long runs (2-24 h), significant energy input, and for nano-silver-extra steps plus precise electroplating control to ensure uniform particle size and prevent aggregation. In summary, electrolytic methods excel at producing ultra-pure Ag at scale but must be carefully optimized for efficiency.

Critical interpretation of silver recovery: Ag recovery efficiencies above 95% are frequently reported at laboratory scale, but this does not by itself prove industrial feasibility. HNO_3 systems are efficient but may generate NO_x and nitrate-rich effluents; chloride systems require corrosion and AgCl management; DES routes reduce some strong-acid risks but need evidence of solvent stability and recyclability; and electrochemical routes can improve purity while increasing equipment and electricity demands.

Table 7 indicates that Ag recovery efficiencies above 95% are common in laboratory studies, especially for HNO_3-based, chloride-assisted, DES-based and electrochemical routes. Nevertheless, the environmental and economic ranking is not determined by recovery percentage alone. Nitric acid routes are efficient but may release NO_x and co-dissolve base metals; chloride systems need corrosion and AgCl management; DES routes are promising but still require viscosity, solvent aging and regeneration studies; electrochemical routes improve purity but add energy and equipment costs.

Table 7. Silver recovery from waste PV modules

Leaching system	Processes	Recovery rate	Refs
MSA + H_2O_2	MSA: 30 wt% : H_2O_2 = 1:1, 25 °C, 6 h; Precipitation (35 wt% NaCl); Reduction (2 wt% NaOH + 30 wt% H_2O_2); Electrodeposition (10 wt% $AgNO_3$), 86.96 A/m², 25 °C	Ag: 100%	[51]
H_2SO_4 + H_2O_2	80 g/L H_2SO_4, 25 g/L H_2O_2, 120 min, 75 °C, 300 rpm; liquid-solid ratio 8:1	Ag: 99.2%	[57]
MI_2 + 1 M KI	0.35 mol/L I_2 + 1 mol/L KI, 1 g:15 mL, pH = 9.6, 5 min	Ag: >95%	[60]
Base-activated persulfate + NH_3 solution	*EDRR:* E_1 = -0.17 V, E_2 = +0.2 V vs. Ag/AgCl, t_1 = 10 s	Ag: 98.7 ± 1.4%	[65]
HNO_3	First extraction (30% TBP) and stripping (1 mol/L HNO_3); Second extraction (5% LIX984N) and stripping (3 mol/L H_2SO_4).Ag: 5 mol/L HNO_3; Precipitation (NaCl); Reduction (NaOH + glucose)	Ag: 99.7%	[66]
HNO_3	5 mol/L HNO_3, 20 °C, 1 h, 200 rpm	Ag: 80%	[67]
$ChCl{\cdot}4H_2O$ + $FeCl_3$ (DES)	0.5 mol/L $FeCl_3$, $ChCl{\cdot}4H_2O$, 65 °C	Ag: 95%	[68]
HNO_3	18% HNO_3, 32 min, 60 °C; solid-liquid ratio 1:30	Ag: 98%	[69]

4.3 Aluminum recovery

Aluminum in PV modules comes mainly from the frame and minor amounts in cell metallization. Recycling Al is important for resource recovery, though technically it is one of the easier materials. In metallurgical processing of PV waste, aluminum can be recovered either by solvent extraction from leach solutions or by direct physical separation. Al^{3+} extraction from acidic solutions can be enhanced

by adding organic ligands such as tributyl phosphate (TBP) [69], di-(2-ethylhexyl) phosphoric acid (P204) [70] or N1923 (a mono-alkyl phosphoric acid) [71]. Generally, strong acids are used to dissolve aluminum from PV waste, but this poses challenges: when the acid leachate is later evaporated or crystallized to recover Al, the presence of excess acid can hinder efficient recovery and reuse of both aluminum and acid. As an alternative, Aluminum was precipitated by adjusting the pH of the leachate. However, the precipitated Al formed a hydroxyl-rich colloidal gel, causing other metals to be lost from solution in the process [72]. Hydrothermal techniques have also been applied to separate Al from acid leachates. It was demonstrated that approximately 94% of aluminum could be precipitated as boehmite (AlOOH) particles from a simulated PV module leachate under hydrothermal conditions (270 °C for 20 hours). Although this method proved effective for aluminum impurity removal, the high temperature and prolonged duration were deemed impractical for industrial applications. Consequently, research efforts are being directed toward developing milder yet effective aluminum separation methods from leach solutions [73].

One recent approach by Li et al. [57] achieved ~99.2% Al leaching from PV waste under mild conditions: 80 g/L H_2SO_4 + 25 g/L H_2O_2, 75 °C, 120 min, L/S = 8:1, 300 rpm-greatly improving metal recovery and offering a new PV-waste utilization route. PV scrap was pre-treated by removing the fluoropolymer backsheet and thermally degrading EVA, then studied hydrothermal leaching (L/S, HNO_3 concentration, time, temperature) [74]. They found Al formed stable Al-Si compounds, yielding only ~56.6-61% leaching. Nonetheless, hydrothermal leaching was more efficient and eco-friendly than conventional methods, and "urban mining" of PV waste shows significant economic potential.

In terms of physical recovery, Rodrigo de Souza et al. [75] observed 49.22% of crushed/sieved PV module waste mass in the fine fraction (<0.5 mm), enriched in Ag, Al, and Si. Using an electrostatic separator (75 rpm, 38 kV, 25 cm gap, 55° angle), they recovered 35.21% of the Al in that fraction. This showing electrostatic methods can reclaim cell/interconnection Al, while most frame Al is recovered by disassembly.

An innovative method for delaminating modules and recovering aluminum was developed [76] a green, biodegradable, low-cost deep eutectic solvent (DES) for EVA removal in end-of-life modules, achieving 100% EVA separation and 98.4% Al removal by etching cell metallization under optimized conditions. As shown in Figure 20, heating above 175 °C induces differential thermal expansion between EVA and the TPT backsheet-promoting delamination-while the DES's hydrogen-bond donors convert EVA ester groups to hydroxyls, dissolving the polymer; compared to toluene, this DES more effectively dissolves EVA, preserves silicon wafer integrity, and can be reused at least 10 times with no loss of performance. Table 8 provides an overview of various aluminum recovery processes and their outcomes.

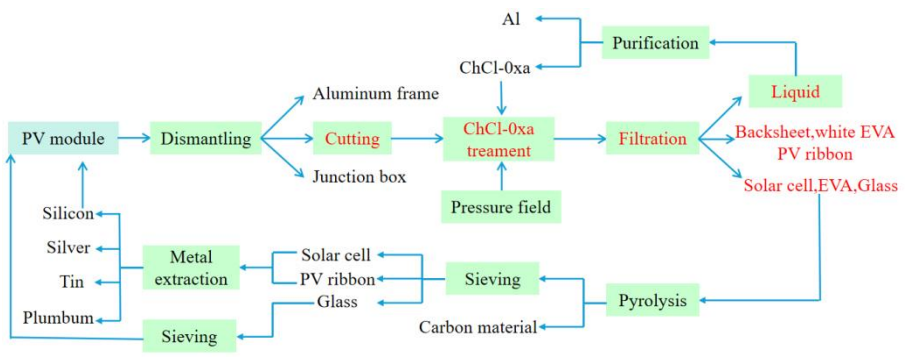


Fig. 20. The schematic diagram of recycling waste photovoltaic modules. (Adapted from Adapted from Ref. [76] with permission. and comply with copyright requirements)[76]

Critical interpretation of aluminum recovery: Al frame removal is already close to commercial practice, whereas chemical Al removal from cell fragments mainly serves as a pretreatment for Ag or Si recovery. The benefit of Al recovery should therefore be assessed together with glass quality, Si loss, acid consumption and the treatment of Al-rich leachates.

Table 8 suggests that Al can be recovered either mechanically from frames or chemically from cell back contacts. Frame recovery is technologically mature and economically attractive, whereas chemical Al leaching from cell fragments is mainly a pretreatment step that improves subsequent Ag or Si recovery. The value of Al recovery should therefore be assessed together with the quality of separated glass and Si fractions, because excessive crushing or acid consumption may offset the benefit of high leaching efficiency.

Table 8. Recovery of aluminum from waste photovoltaic modules

Leaching system	Processes	Recovery rate	Refs
HNO_3	HNO_3 (1-2 mol/L, 100-140 °C, L/S = 20:1, 30-90 min)	Al: 97%-99%	[74]
$H_2SO_4 + H_2O_2$	H_2SO_4 (80 g/L) + H_2O_2 (25 g/L) (75 °C, S/L = 8:1, 120 min, 300 rpm)	Al: 99.20%	[57]
Mechanical processing + electrostatic sep.	Mechanical processing: F1 (<0.5 mm), F2 (0.5-1.0 mm), F3 (>1.0 mm);Electrostatic separation (38 kV)	Al: F1 (0.759%), F2 (0.19%), F3 (0.18%)	[75]
DES	DES (ChCl:oxalic acid = 1:1) (175 °C, 12.5 h)	Al: 98.4%	[76]

4.4 Copper recovery

Hydrometallurgical and hybrid methods are commonly used for Cu. For instance, the sequential solvent extraction and precipitation was applied to recover Pb, Sn, and Cu oxides from PV ribbon scrap [66]. After HCl leaching, TBP/LIX984N extraction, Sn stripping with HNO_3 ($Sn(NO_3)_2$), Cu/Pb conversion to $CuSO_4$ and $Pb(ClO_4)_2$, then ammonia precipitation of $Sn(OH)_4$, $Cu(OH)_2$, and $Pb(OH)_2$ for high-purity separation. Layer-by-layer delamination of CIGS (Copper Indium Gallium Selenide) panels (thermal Se removal) was performed, followed by HNO_3 leaching and pH-tuned solvent extraction: Indium was extracted with P204 into the organic phase, then Ga/Cu separation was achieved. This process attained >90% recovery of In, Ga, and Cu, converting them to >99% pure oxides via hydroxide precipitation and calcination [16]**.**Approximately 79% Cu was recovered and Pb was left as insoluble compounds from PV ribbon leachate through HNO_3 dissolution, extraction of Cu^{2+} with 20% LIX84-I, stripping with H_2SO_4 to $CuSO_4$, electrowinning to pure Cu, while Pb remained as $PbSO_4/PbO_2$ [52].A closed-loop Cu/Pb/Sn process was developed, which involved the following steps (Figure 21): toluene encapsulant dissolution, 800 °C heat treatment to separate Cu strips and Pb-Sn alloy, followed by HNO_3 leaching, NaOH treatment, CuO formation, 170 °C calcination, H_2SO_4 dissolution, and Zn cementation to yield pure Cu powder and safely isolate Pb/Sn [77]. Jin-Seok Lee et al. [78] (Figure 22) combined oxidation (300-900 °C) of PV ribbon to peel off a Pb-Sn-rich oxide layer (~69 wt% Pb, 31 wt% Sn), leaving Cu tape at 99.5 wt% purity, then zone-melting to 4N-grade Cu (>99.99% purity). The leaching behavior of PVP residues in an HCl-NaCl-H_2O_2 mixture was studied [79]. Microwave experiments were conducted at 80 °C, revealing that the copper leaching was markedly influenced by H_2O_2 concentration. Under optimized conditions (0.5 mol/L HCl, 200 g/L NaCl, 7.5 wt% H_2O_2, 60 min), a maximum copper leaching rate of 81.2% was achieved.

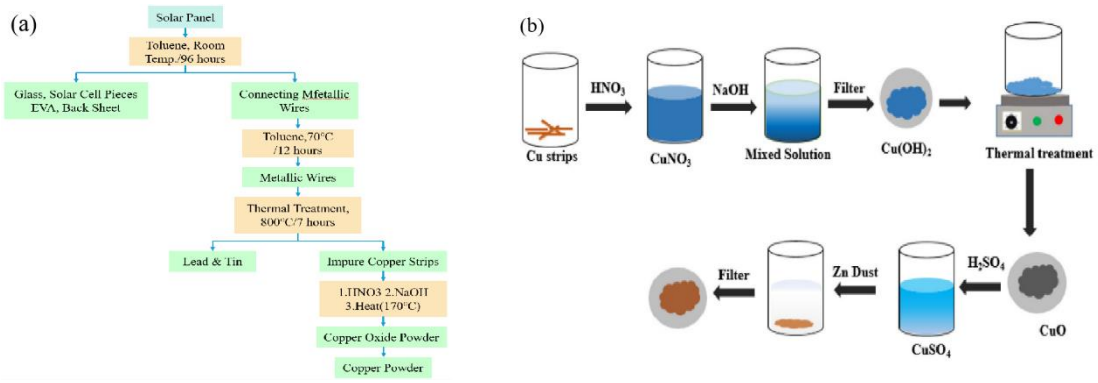


Fig. 21. (a) Process flow diagram of copper powder extraction from waste silicon solar panels (b)The schematic diagram of the conversion of impure copper strip into copper powder. (Adapted from Recovery of 4N-grade copper from photovoltaic ribbon in spent solar module. and comply with copyright requirements)[77]

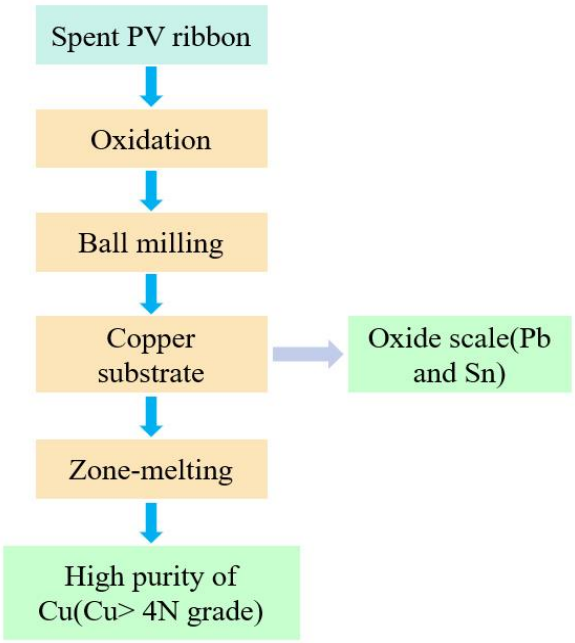


Fig. 22. Preparation of 4N grade pure copper by overall recovery process. (Adapted from Adapted from Ref. [78] with permission. and comply with copyright requirements)[78]

In summary, copper from PV modules can be recovered efficiently by various methods. Hydrometallurgical acid leaching with solvent extraction separates Cu from Sn, Pb, In, etc., yielding solutions for electrowinning. Pyro/thermochemical treatments volatilize or segregate other metals, leaving Cu-rich phases for easier purification. Emerging methods (e.g., sealed-tube thermal reduction, DES leaching) offer more controlled, eco-friendly recovery. Method choice depends on whether copper is needed as metal, oxide, or alloy feed.

Critical interpretation of copper recovery: Cu is mainly present in interconnect ribbons and wiring in c-Si modules, so early mechanical separation can reduce the load on subsequent leaching. For mixed or crushed feeds, selective Cu separation is necessary because co-dissolved Cu may contaminate Ag products and complicate downstream purification.

Table 9 shows that Cu recovery is feasible by leaching, solvent extraction, precipitation, electrowinning and physical concentration. For c-Si modules, Cu is mainly present in ribbons and interconnects, so early mechanical separation can reduce the chemical load. For mixed feeds, selective Cu separation is important because Cu co-dissolution can contaminate Ag products and complicate downstream purification.

Table 9. Copper recovery from waste PV modules

Leaching system	Processes	Recovery rate	Refs
HNO_3 + NH_4OH	HNO_3: acid leach to dissolve CIGS oxides; $NH_3 \cdot H_2O$: chemical precipitation of metal hydroxides (Cu, In, Ga); D2EHPA: solvent extractant to separate In and Ga	Cu: >90%	[16]
H_2SO_4 + LIX84-I	HNO_3 (5 mol/L dissolve metals (Ag, Al, Cu, Pb); H_3PO_4 (90%, 160 °C, 60 min): remove SiN_x (ARC); KOH (45%, 80 °C, 10 min): remove Al electrode; LIX84-I (20%): extract Cu; HCl (5 mol/L): precipitate AgCl; NaOH (5 mol/L): form Ag_2O and $Pb(OH)_2$; Na_2S (5 mol/L): precipitate PbS; H_2SO_4 (150 g/L, 0.5 A/dm², 24 h): Cu electrowinning	Cu: 90%	[52]
HNO_3 + KOH + HCl	HNO_3 (5 mol/L, 80 °C, L/S: 25 mL/g, 1 h): remove Ag and Al; KOH (1 mol/L): remove Al-Si compounds; HCl (3 mol/L) + H_2O_2 (6%): separate Ag, Cu, Pb, Sn; TBP (30%): extract Sn; LIX984N (5%): extract Cu; NH_4OH: precipitate metal hydroxides ($Cu(OH)_2$, $Sn(OH)_4$, $Pb(OH)_2$)	Cu: 98.5%	[66]
HNO_3 + H_2SO_4 + NaOH	Toluene (70 °C, 12 h): separate panel components (glass, EVA, cells, wires); HNO_3 (5 mol/L): dissolve Cu wiring to form $Cu(NO_3)_2$; NaOH (2 mol/L): precipitate $Cu(OH)_2$; H_2SO_4: dissolve CuO to form $CuSO_4$; Zn dust (1.5 g): cementation reducing Cu^{2+} to copper powder	Cu: 90%	[77]
O_2 (oxidation)	800 °C, 30 min, air	(-)	[78]
HCl + H_2O_2	HCl (0.5 mol/L) + H_2O_2 (7.5 wt%) (80 °C, L/S: 10 mL/g, 60 min): dissolve metals	Cu: 81.2%	[79]

(Note: "(-)" indicates data not provided.)

4.5 Lead recovery

Lead in crystalline silicon PV modules is mainly present in solder (Pb-Sn) on ribbons, while in perovskite solar modules lead is in the perovskite absorber. Removing and reclaiming lead is vital due to its toxicity. A recent study developed an innovative lead-free copper ribbon process to recover interconnect metals while eliminating lead. In a H_2O_2-HCl selective leach [66], Ag was first precipitated as AgCl by oxidative leaching with H_2O_2 in HCl. TBP and LIX984 were then added stepwise to extract Sn and Cu, respectively; Pb remained in solution and was finally recovered as $Pb(OH)_2$ with NH_4OH, leaving a lead-free copper product. The leaching of "P(Pb)-Sn" solder residues in HCl-NaCl-H_2O_2 under microwave heating at 80 °C was investigate [79]. Pb leaching was strongly affected by NaCl concentration. Under optimized conditions (0.5 mol/L HCl, 200 g/L NaCl, 7.5 wt% H_2O_2, 60 min), a Pb

leaching rate of 77.6% was achieved. Copper was subsequently recovered through iron-powder cementation, and Pb/Zn separation was accomplished by CTAB ion flotation. As shown in Figure 23, A two-step leach was employed on crushed c-Si panels. First, ~76.1% of Pb was dissolved through a 5-minute leach in 1.5 mol/L HNO_3 at 60 °C. The Pb was then precipitated as $Pb(OH)_2$ using 1.5 mol/L NaOH. After drying, the precipitate was fully converted to PbO by calcination at 500 °C for 2 hours[80]. Acetic-acid leaching followed by electrowinning was demonstrated. Rapid Pb leaching was enabled by key factors including maximized H_2O_2 diffusion, excess acetic acid and H_2O_2 (≥2:1 H_2O_2:Pb ratio), and a low solution-to-Pb ratio (~0.005 L/g). Through 24 hours of electrowinning at -0.8 to -1.0 V vs Ag/AgCl, >99% Pb was deposited on the cathode while PbO_2 was formed on the anode, along with some basic lead acetates [81].

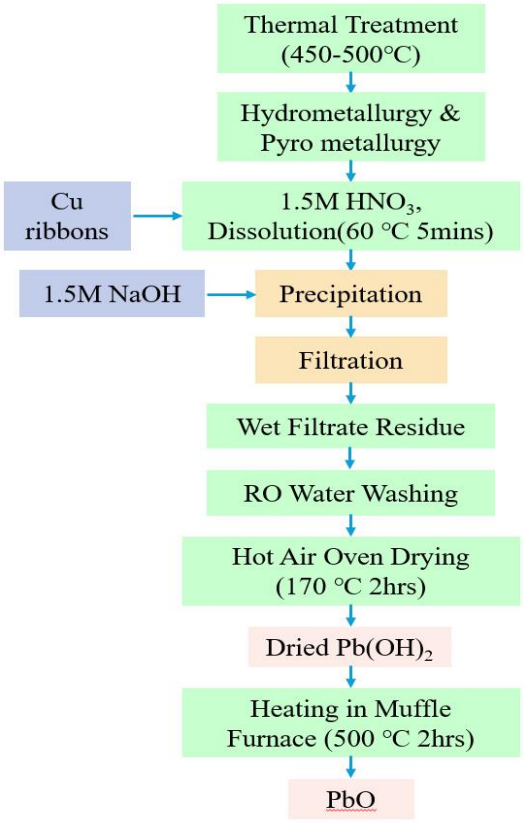


Fig. 23. Process flow diagram for recovery of lead from waste silicon solar panels. (Adapted from Adapted from Ref. [80] with permission. and comply with copyright requirements)[80]

Finally, an emerging concern is lead in perovskite solar modules. As shown in Figure 24, Chen et al. [82] developed a recycling method for encapsulated perovskite PV modules. After thermal delamination to separate the glass layers, a carboxylate-type cation-exchange resin captures Pb^{2+} from the DMF perovskite solution; the resin is then regenerated with HNO_3 to release Pb^{2+}, which precipitates as PbI_2 upon NaI addition. The process preserves intact front ITO/glass and back glass substrates, and the reclaimed PbI_2 and glass are used to remanufacture perovskite cells matching the performance of those made from virgin materials. This approach combines effective lead-pollution control with high-value material recycling for perovskite PV technology.Table 10 compiles various lead recovery results from PV waste.

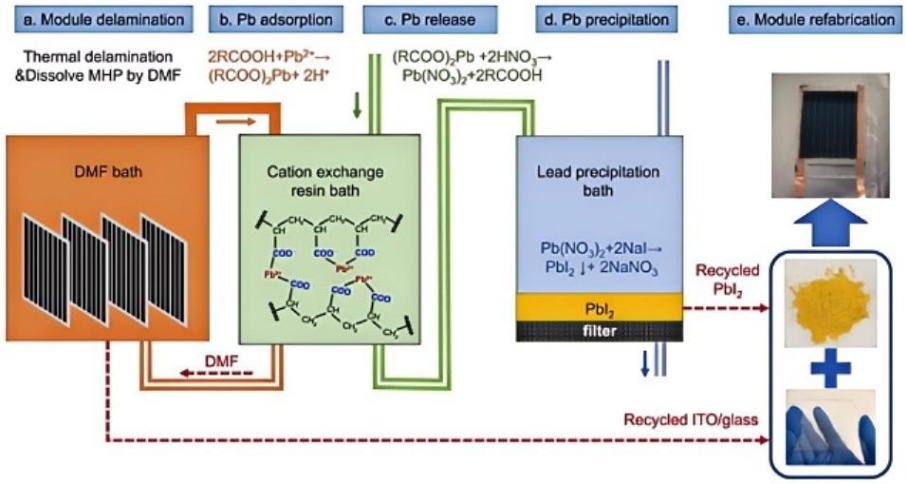


Fig. 24. Recovery of perovskite solar modules. (a) The encapsulated perovskite solar module is layered, and the MHP is dissolved in DMF; (b) Removal of lead ions from DMF by carboxylic acid cation exchange resin. (c) Release of lead ions adsorbed by the resin into aqueous solution through HNO3 regeneration process.(d) Injection of NaI into a solution containing Pb(NO3)2 to precipitate PbI2.(e) Remanufacturing of components based on recycled materials [82].

Critical interpretation of lead recovery: Pb recovery should be considered both a resource-recovery step and a pollution-control requirement. Mild organic acids and electrochemical routes may reduce some hazards, but Pb-bearing solutions and residues must be recovered, stabilized or treated to avoid secondary contamination.

Table 10 highlights that Pb recovery is closely linked to solder removal and hazardous-waste control. Acetic acid and electrochemical routes may reduce the use of strong inorganic acids, but Pb-containing leachates and residues must be stabilized or recovered to prevent secondary contamination. Pb recovery should thus be discussed as both a resource-recovery step and a pollution-control requirement.

Table 10. Lead recovery from waste PV modules

Leaching system	**Processes**	**Recovery rate**	**Refs**
HNO_3 + KOH + HCl	HNO_3 (5 mol/L, 80 °C, L/S: 25 mL/g, 1 h): remove Ag and Al; KOH (1 mol/L): remove Al-Si compounds; HCl (3 mol/L) + H_2O_2 (6%): separate Ag, Cu, Pb, Sn; NH_4OH: precipitate metal hydroxides ($Cu(OH)_2$, $Sn(OH)_4$, $Pb(OH)_2$)	Pb: 98.3%	[66]
HCl + H_2O_2	HCl (0.5 mol/L) + H_2O_2 (7.5 wt%) + NaCl (200 g/L) (80 °C, L/S: 10 mL/g, 60 min): dissolve metals	Pb: 77.6%	[79]
HNO_3 + NaOH	HNO_3 (1.5 mol/L) (60 °C, 5 min, S/L: 1:15): selectively leach lead solder from Cu ribbon; NaOH (1.5 mol/L): adjust leachate to alkaline pH, precipitating Pb^{2+} as $Pb(OH)_2$	Pb: 76.7%	[80]
CH_3COOH + H_2O_2	CH_3COOH (20%) + H_2O_2 (1.5 mL); reduction potential: -0.8 V or -1.0 V vs. Ag/AgCl	Pb: 99%	[81]

Leaching system	Processes	Recovery rate	Refs
DMF + HNO_3 + NaI	DMF: dissolve perovskite layer lead; HNO_3 (0.16-2 mol/L): resin regeneration to release adsorbed Pb^{2+}; NaI: convert $Pb(NO_3)_2$ into PbI_2 precipitate	Pb: 99.2%	[82]

4.6 Gallium and indium recovery

Gallium and indium are critical metals found in CIGS (Cu-In-Ga-Se) thin-film PV modules (and Ga in GaAs cells). Both pyrometallurgical and hydrometallurgical techniques have been developed to recover Ga and In (along with Cu and Se) from CIGS waste.

4.6.1 Pyrometallurgical recovery

High-temperature processes can volatilize and separate volatile elements like Se, and convert Ga/In into extractable forms. Huang et al. [83]combined microwave pyrolysis, thermal oxidation, and chlorination to recover Se, Ga, and In from CIGS cells (Figure 25): Se is fully recovered by air oxidation (800 °C/30 min or 600 °C/40 min); Ga is 56 % recovered at 260 °C and nearly fully at 380 °C under Cl_2; and In requires 580 °C chlorination for complete recovery. It was shown that roasting CIGS at 500 °C prior to leaching in 1 mol/L H_2SO_4 (60 °C, 1 h) resulted in >99.9% recovery of Cu, In, and Ga [84]. However, when roasting was performed at 600 °C, Ga recovery was reduced to approximately 90% due to the formation of insoluble Ga_2O_3.Batchwise NH_4Cl chlorination was used to volatilize Ga and In from CIGS waste, with optimal temperatures of 260 °C and 340 °C being employed for Ga and In, respectively. Recovery rates of 97.2 ± 2.3 wt% Ga and 93.6 ± 2.1 wt% In were achieved within 6 hours, while Cu was also reclaimed during the process[85].

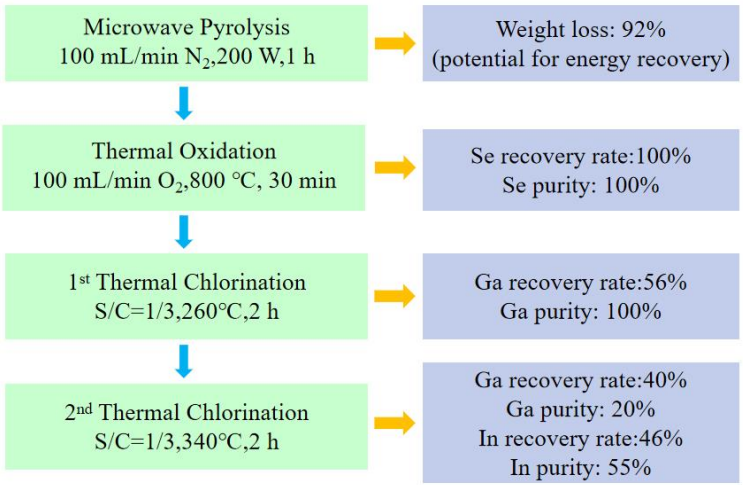


Fig. 25. Metal recovery from CIGS solar cells using microwave pyrolysis, thermal oxidation, and thermal chlorination (Adapted from Adapted from Ref. [83] with permission. and comply with copyright requirements)[83]

4.6.2 Hydrometallurgical recovery

Teknetzi et al. [86] leached indium from shredded CIGS panels with HNO_3 (area:liquid = 1:3 cm^2/mL, 24 h): 2 mol/L HNO_3 at room temperature recovered ~85 % In, whereas 0.5 mol/L yielded only ~30 %, highlighting the strong acid-concentration dependence. The hydrometallurgical-electrochemical route

was developed [12] (Figure 25). HCl/H_2O_2 leaching produces Cu^{2+}, In^{3+}, Ga^{3+}, and SeO_3^{2-}; Se and Cu are electrodeposited on Ti/Pt electrodes; then $SOCl_2$ reflux and distillation exploits $GaCl_3$'s high solubility versus $InCl_3$ to sequentially recover In and Ga, achieving 99.99 % for both. A process involving oxidation roasting followed by HCl leaching and P204 solvent extraction was proposed (Figure 27). During this process, metals were converted to oxides through roasting while Se was volatilized. Leaching in 4 mol/L HCl (80 °C, 3 h, L/S = 10 mL/g) resulted in extraction efficiencies of 99.98% Cu, 93.40% In, and 96.86% Ga. Subsequently, In (99.92%) and Ga (99.34%) were extracted using P204 while Cu remained in solution. Finally, In (99.90%) and Ga (99.93%) were recovered through HCl stripping [87].

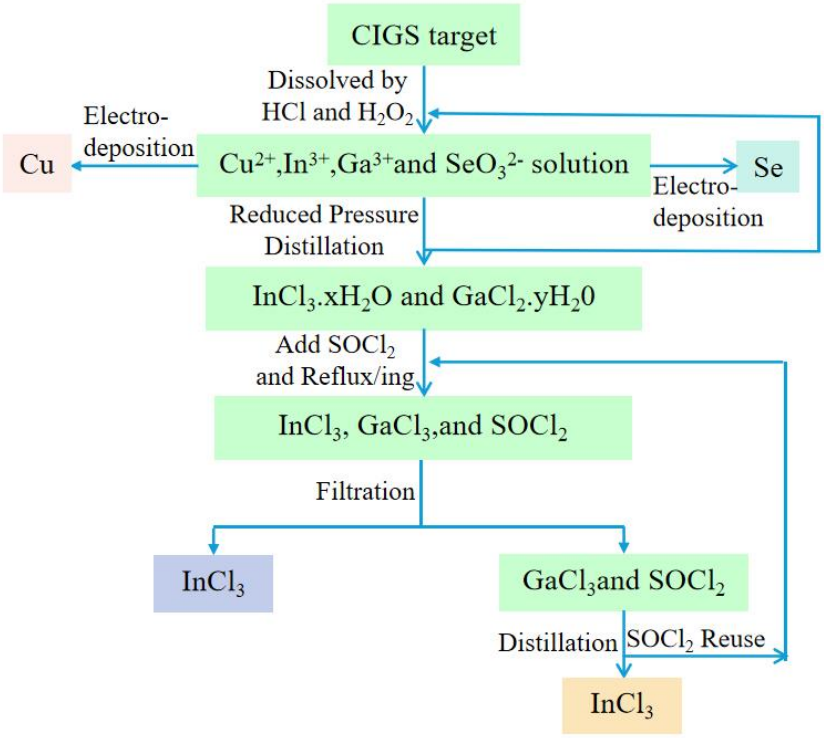


Fig. 26. Schematic of the DEDD method for CIGS target recycling (Adapted from Adapted from Ref. [12] with permission. and comply with copyright requirements)[12]

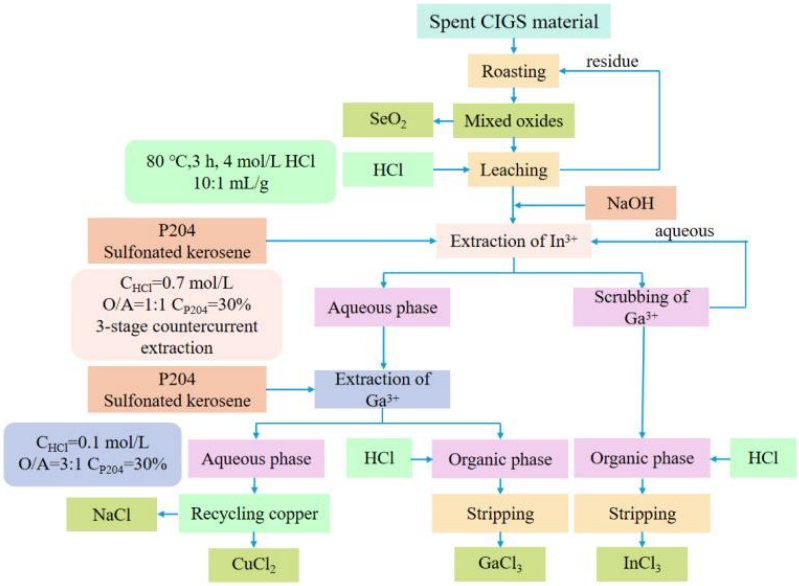


Fig. 27. Separation and recovery flow chart for valuable components in waste CIGS material. (Adapted from Adapted from Ref. [87] with permission. and comply with copyright requirements) [87]

As shown in Figure 28, Valuable metals were efficiently recovered from CIGS waste through nitric acid leaching. During the process, Se was oxidized to selenite (SeO_3^{2-}) while In precipitated as indium selenite, enabling effective separation. The optimal leaching conditions were determined to be 90 °C, 3.5 h, 3.2 mol/L HNO_3, with a liquid-to-solid ratio of 9:1 mL/g. Following leaching, Cu, Ga, and Se were precipitated using MgO, and Se was subsequently separated by maintaining the temperature at 800 °C for 90 min. Final recovery rates of 99.23% Cu, 96.82% In, 98.08% Ga, and 96.38% Se were achieved [88]. Cyanex 923 was utilized as an extractant, with HCl and EDTA serving as stripping agents, to achieve successful separation of Cu, Ga, and In. During the extraction of Ga and In, partial co-extraction of Cu occurred, necessitating its scrubbing from the organic phase using fresh leachate. Subsequently, Ga was stripped from the organic phase using 0.8 mol/L HCl, while the remaining In was efficiently recovered through treatment with 0.1 mol/L EDTA [89]. An efficient hydrometallurgical process was developed to recover Cu, In, and Ga from CIGS solar cells. Stepwise delamination and annealing were first performed to remove Se, followed by HNO_3 leaching of the metals. The D2EHPA solvent extraction conditions were optimized through two stages: initial extraction at pH ≈ 1 with 0.05 mol/L D2EHPA to recover In, followed by a second extraction at pH ≈ 2 with 0.06 mol/L D2EHPA to recover Ga. Finally, In and Ga were stripped from the organic phase using 2 mol/L and 1 mol/L HCl, respectively. Finally, via chemical precipitation and calcination at targeted temperatures (CuO at 873 K, In_2O_3 at 673 K, Ga_2O_3 at 773 K), high-purity oxides were obtained. This process achieved recovery rates of 88.9% for Cu, 98.2% for In, and 97.1% for Ga, with product purities all above 99% [16].

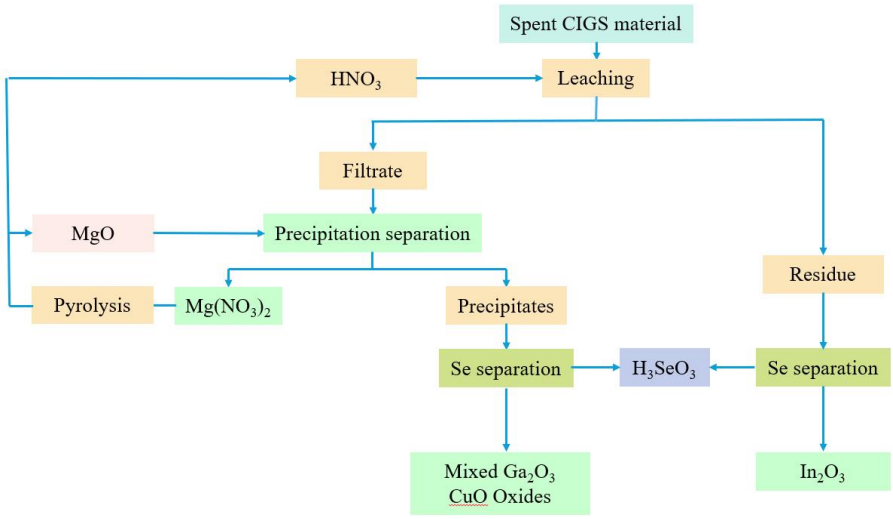


Fig. 28. Flow chart of valuable component separation and recovery from waste CIGS material. (Adapted from Adapted from Ref. [88] with permission. and comply with copyright requirements) [88]

As shown in Figure 29, Wang et al [90]. innovatively developed a P507@MAC composite adsorbent by loading the extractant P507 onto coconut-shell-derived mesoporous activated carbon (MAC), significantly increasing the adsorption capacities for Ga^{3+} (67.0 mg·g^{-1}) and In^{3+} (52.6 mg·g^{-1}). These capacities are 1.23-1.85 times higher than those for the single-component adsorbents, and exhibit excellent metal selectivity. This eco-friendly adsorbent outperforms conventional P507-impregnated resins (Ga^{3+}: 11.8 mg·g^{-1}; In^{3+}: 36.5 mg·g^{-1}), providing a new approach for efficient recovery of these dispersed metal. As shown in Figure 30, Xu et al. [91] proposed tuning amino acid ligands via heteroatom (S, O, N) substitution, discovering that an oxygen-containing hard ligand (denoted AA-O) exhibits excellent selectivity for Ga^{3+}/In^{3+}. Experiments and theoretical calculations confirmed that AA-O can directly and selectively extract Ga^{3+} (increasing purity from 8.73% to 78.31%) and In^{3+} (from 21.39% to 97.05%) from a leachate containing $Al^{3+}/Cu^{2+}/Zn^{2+}$, without the need for additional extractants, providing a highly efficient novel extraction system for recovering dispersed metals.

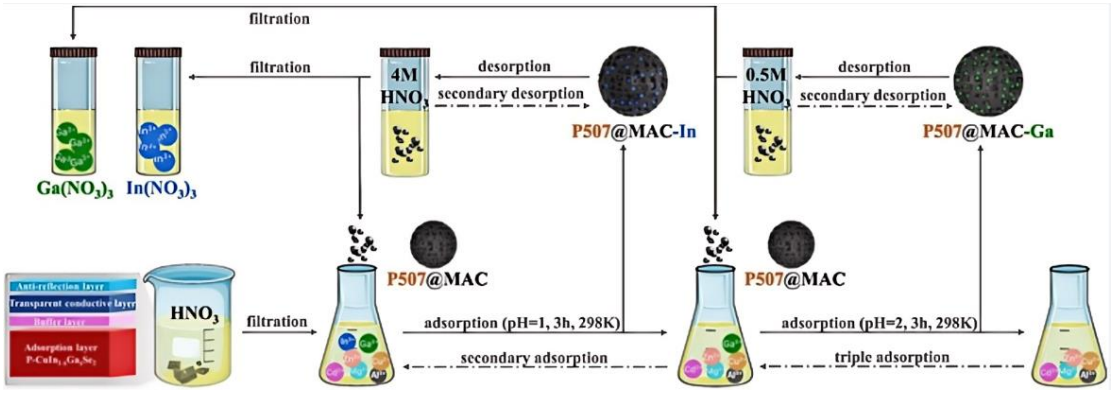


Fig. 29. Selective adsorption-desorption process for extracting Ga^{3+} and In^{3+} from CIGS leachate using P507@MAC [90]

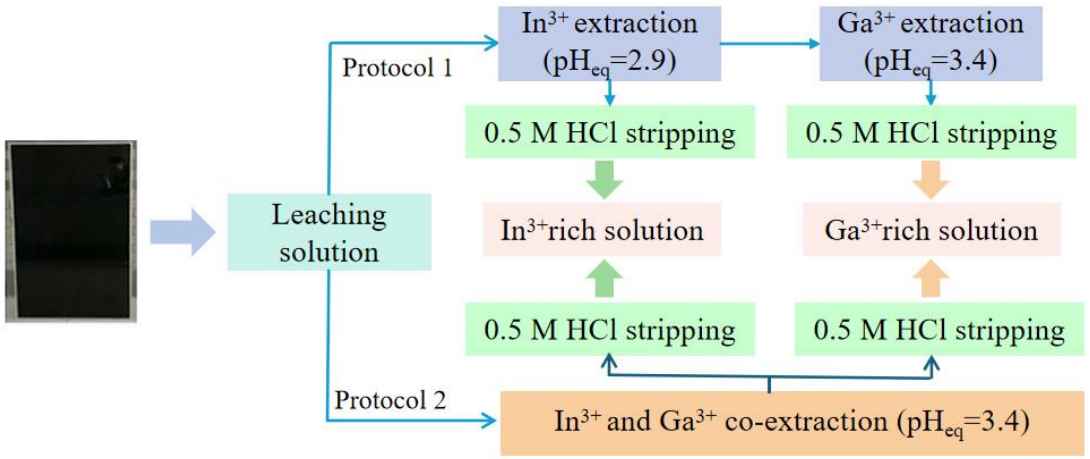


Fig. 30. Two schemes for recovering Ga and In from waste CIGS solar cells (Adapted from Ref. [91] with permission. and comply with copyright requirements) [91]

In summary, recovering Ga and In from PV waste (especially CIGS) uses thermal treatments to volatilize these metals or chemical routes for selective leaching and extraction. Pyrometallurgy provides direct separation (e.g., Se distillation, Ga/In chlorination), hydrometallurgy offers precise solution-based control, and combining both (roast then leach/extract) is particularly effective. As strategic, expensive materials, Ga and In recovery enhances PV recycling's sustainability and economics.Table 11 compiles various results for the recovery of gallium and indium from photovoltaic waste.

Critical interpretation of Ga and In recovery: Many high-recovery studies use spent CIGS targets or chamber waste rather than complete end-of-life modules. Thus, additional validation is needed for real modules, including delamination, glass/polymer separation, Se management, reagent recycling, feed heterogeneity and integrated mass balance.

Table 11 indicates that CIGS-related recycling often achieves selective recovery through oxidation roasting, chlorination, acid leaching, solvent extraction or adsorption. These routes are promising for strategic-metal recovery, but many studies treat spent targets or chamber waste rather than complete modules. Consequently, additional work is needed on feed variability, separation of glass and polymer layers, Se management, reagent recycling and integrated flowsheets for real end-of-life thin-film modules.

Table 11. Gallium and indium recovery from waste PV modules

Leaching system	**Processes**	**Recovery rate**	**Refs**
$HCl + H_2O_2$	$HCl + H_2O_2$: dissolve metals	In: 99.99% Ga: 99.98%	[12]
HNO_3 + D2EHPA + $HCl + H_2SO_4$ + $NH_3 \cdot H_2O$	HNO_3 (4 mol/L, 25 °C, 2 h, S/A = 10:1): leach Ga and In;D2EHPA (0.05 mol/L, O/A = 4:1, 5 min, 25 °C): extract Ga and In;HCl (6 mol/L, 10 min, 25 °C): strip In;H_2SO_4 (1 mol/L, 30 min, 25 °C): strip Ga	In: 98.2% Ga: 97.1%	[16]
H_2SO_4	Pre-roasting: 400-600 °C, 30 min;H_2SO_4 (1 mol/L, 1 h, 60 °C, S/A = 200:1): acid leaching	In: >99.9% Ga: >99.9%	[84]

Leaching system	Processes	Recovery rate	Refs
$NH_4Cl + Ga_2O_3 + HNO_3$:HCl = 1:3 + H_2SO_4	NH_4Cl: chlorinating agent for high-temp chlorination;Ga_2O_3 (260 °C, 4 h): model compound for Ga chlorination;H_2SO_4: dissolve residual Se;HNO_3:HCl = 1:3: dissolve de-selenized CIGS	In: >93% Ga: >97%	[85]
HNO_3	HNO_3 (S/L = 1:3, 24 h, 2 mol/L)	In: 85%	[86]
HCl + P204	HCl (4 mol/L, 80 °C, 3 h): dissolve metals;P204 (30%, 5 min, O/A = 1:1): extract metals from solution	In: 93.4% Ga: 96.86%	[87]
HNO_3	HNO_3 (3.2 mol/L, 90 °C, 3.5 h): leach Ga and In	In: 98.08% Ga: 96.82%	[88]
HCl + H_2O_2	HCl + H_2O_2 (3 mol/L, 75 °C, 120 min, S/A = 100:1): leach Ga and In;Cyanex 923 (5%, 25 °C, 5 min, O/A = 1:1): extract Ga and In from solution	In: >90% Ga: >90%	[89]
P507 + HNO_3 + $NH_3 \cdot H_2O$	P507 + MAC (coconut-shell mesoporous AC) (25 °C, 0.6 mL/g, 24 h): synthesize P507@MAC;HNO_3: adjust solution pH, desorb adsorbed metals;$NH_3 \cdot H_2O$: adjust solution pH	In: 52.6 mg/gGa: 67.0 mg/g	[90]
HNO_3 + HCl	HNO_3 (7 mol/L, 12 h): dissolve waste solar cells;HCl (0.5 mol/L): stripping agent;AA-O ligand: extract Ga^{3+} and In^{3+} from solution	In: 91.17%Ga: 87.34%	[91]

4.7 Other metals

4.7.1 Cadmium and tellurium recovery

Cd and Te are critical in CdTe thin-film modules, and their safe recovery is a priority due to cadmium's toxicity and tellurium's value. Electrochemical extraction has been applied to remove cadmium from waste CdS/solution in the CdTe cell manufacturing process [92]. By applying a constant current of 0.2 A at <5 V for 23 h, they removed ~98% of Cd from the waste solution. Fthenakis et al. [93] leached spent CdTe modules in 1 mol/L H_2SO_4 + H_2O_2 (L/S = 476 mL/kg), extracting 99.99 % of Cd (and Te).For tellurium, high-temperature and adsorption techniques are prominent.

A sulfur-assisted multi-step vacuum distillation process was developed for Te recovery. In this method, sulfur was reacted with CdTe (in the waste) to form volatile Te gas (TeS_x), while Cd was converted to non-volatile CdS. Through a two-stage distillation process—high-temperature vacuum distillation (HTVD) and low-temperature vacuum distillation (LTVD)—Te was efficiently separated.As a result, Te with >99.97% purity and CdS with >99.6% purity were obtained as a byproduct. Both Te and Cd yields exceeded 99%, and the recovered CdS could be directly reused in PV production, enabling full-component, high-value recycling of CdTe waste [94]. Acidic CdTe leachates were treated with sulfonated magnetic PSt-DVB-SNa beads, resulting in the adsorption of >80% of Cd^{2+}/Te^{2+} within 5 minutes. Cd^{2+} concentration was reduced to <5.3 mg/L, while Te remained in solution for further conversion [95]. Zhang et al. [95] combined sulfidation smelting and vacuum distillation (550-800 °C, 15 Pa, 30 min) to yield 99.93 % pure Te (94.14 % recovery) and 99.5 % pure CdS, both reusable in PV manufacturing. Bemfert et al. [96] developed a CVT method using S, air, and CH_4 at ~400 °C to volatilize ~97.8% of Te, followed by 900 °C oxidation and 750 °C reduction to recover Cd, completing a full Cd/Te recovery flowsheet.

Recycling of CdTe modules now achieves near-complete Cd and Te recovery, mitigating environmental risks and reclaiming valuable Te. Integrating electrochemical extraction, chemical leaching/electrodeposition, and thermal processes secures Cd containment and efficient Te recovery. These combined strategies are vital for sustainable thin-film PV technologies.Table 12 compiles the results of the recovery of tellurium and cadmium from photovoltaic waste.

CdTe-module recycling can achieve high Cd and Te recovery when dedicated processes and emission-control systems are available. Nevertheless, cadmium toxicity requires strict separation, leachate treatment, off-gas management and residue stabilization. Therefore, CdTe recycling should be evaluated primarily by closed-loop control of hazardous materials and compliance with environmental regulations, not only by metal recovery percentage.

Table 12. Tellurium and cadmium recovery from waste PV modules

Leaching system	Processes	Recovery rate	Refs
Electrolysis	current 0.2 A, voltage <5 V, time 23 h	Cd: 98%	[92]
$H_2SO_4 + H_2O_2$	H_2SO_4 (1 mol/L) + H_2O_2 (4.8 mL/kg): dissolve metals;Na_2CO_3: neutralize acidic solution;Na_2S: precipitate Te (as Te sulfide)	Te: 99.95% Cd: 99.97%	[93]
S	S (CdTe:S = 1:1.1): form Te and CdS;Te separation: 700 °C, 40 min;CdS enrichment: 750 °C;S removal: 500 °C	Te: >99% Cd: >99%	[94]
$H_2SO_4 + H_2O_2$	Synthesize magnetic resin adsorbent:Fe_3O_4 core: $FeCl_3 \cdot 6H_2O$ (13.5 g in 500 mL ethylene glycol), CH_3COONa (36 g);Silica coating: TEOS (2.4 g), $NH_3 \cdot H_2O$ (28 wt%), 60 °C, 8 h;Surface modification: 3-MPS (12 mL), 60 °C, 8 h;Polymerization: St (40 g), DVB (10 g), BPO (- g), gelatin (2.5 g), 90 °C, 8 h;Sulfonation: H_2SO_4 (1 M) + H_2O_2, 90 °C, 8 h	Te: >80% Cd: >80%	[95]
	S (CdTe:S = 1:1.1, 400 °C, 30 min): produce Te and CdS	Te: 94.14%	[95]
$S + O_2 + CH_4$	S (400 °C): form CdS;O_2 (900 °C): oxidize CdS to CdO;CH_4 (750 °C): reduce CdO to metallic Cd	Te: 97.8%	[96]

4.7.2 Selenium recovery

Gustafsson et al. [13] oxidized CIGS at 800 °C for 1 h to volatilize Se as SeO_2, which was crystallized and then reduced (with organic reductants or SO_2 gas) to yield high-purity Se. Cu-Ga selenite was precipitated using MgO [87], then roasted the residue at 800 °C for 90 min to separate and recover Se with 96.38 % efficiency. CIGS, a chalcopyrite-structure semiconductor [83], retains its primary phase after 400 °C roasting ($In_2O_3 + Cu_{2-x}Se$), shifts to $Cu_2SeO_4 + In_2O_3$ at 500 °C (with minor $In_2O_3 + Cu_{2-x}Se$), and converts fully to Cu_2SeO_4, In_2O_3, and β-Ga_2O_3 at 600 °C, indicating complete selenide removal. A two-step process was developed for selenium recovery, where CIGS material was first oxidized at 800 °C for 1 hour to produce SeO_2, followed by bubbling SO_2 through the SeO_2 at 82 °C for 15 minutes. This method achieved over 99% recovery of selenium [97].Ma et al. [15] applied a two-stage H_2SO_4 roast (acid:CIGS = 2.5 g/g) at 600 °C for 3 h, converting Se to SeO_2 (99.96 % yield); in stage 2, In and Ga sulfates turned to oxides, while $CuSO_4$ remained unchanged. Lv et al. [14] achieved 99.9 % Se recovery by roasting CIGS at 1000 °C for 3 h, effecting the necessary phase transformations.

Critical interpretation of Cd, Te and Se recovery: Thin-film PV recycling requires a different risk profile from c-Si recycling. For CdTe modules, the main challenge is closed-loop control of Cd and Te, while CIGS-related streams require safe handling of Se-bearing gases or solutions. Therefore, these routes should not be evaluated only by recovery yield; emission capture, wastewater treatment and residue stabilization must be reported before scale-up claims are made.

Table 13. Selenium recovery from waste PV modules

Leaching system	**Processes**	**Recovery rate**	**Refs**
H_2SO_4	H_2SO_4 (1 mol/L, 60 °C, 1 h, S/L = 200:1): dissolve metals	(-)	[83]
O_2 + SO_2 / CH_3COOH + $C_2H_5OC_2H_5$	O_2 (800 °C, 1 h): form SeO_2;SO_2 reduction: SO_2 (80 °C, 15 min): form Se;Riley reduction: CH_3COOH + $C_2H_5OC_2H_5$ (126 °C, 3 h): form Se	Se: 96.38%	[13]
O_2 + H_2 / C	O_2 (700 °C, 2 h): form SeO_2;H_2 (400-500 °C, 1-2 h): form Se;C (400-500 °C, 1-2 h): form Se	Se: >99%	[97]
H_2SO_4	H_2SO_4 (600 °C, 3 h): convert Se to SeO_2;Roasting (710 °C, 2 h): $In_2(SO_4)_3$ and $Ga_2(SO_4)_3$ → In_2O_3, Ga_2O_3;Water leach (60 °C, 2 h): separate Cu	Se: >99%	[15]
H_2SO_4 + NH_4OH + LIX984	Roasting (1000 °C): produce SeO_2, In_2O_3, Ga_2O_3, CuO;H_2SO_4: dissolve metals;NH_4OH: adjust pH, precipitate In, Ga;LIX984: extract Cu	Se: 99.9%	[14]

(Note: "(-)" indicates data not provided.)

Tables 12 and 13 show that thin-film PV recycling requires different priorities from crystalline silicon module recycling. For CdTe modules, the key issue is safe and closed-loop control of Cd and Te rather than only recovery yield. For CIGS-related streams, Se volatilization or oxidation can enable recovery, but toxic Se-bearing gases or solutions require capture and treatment. These processes therefore need dedicated environmental-control systems before scale-up.

5. CRITICAL COMPARISON, ENVIRONMENTAL IMPLICATIONS AND SCALE-UP READINESS

A cross-route comparison is necessary because high laboratory recovery efficiencies do not automatically imply industrial feasibility. Table 14 summarizes the main advantages, limitations and environmental/safety issues of major PV recycling routes. The comparison indicates that mature industrial deployment is most likely for hybrid flowsheets that use mechanical separation for bulk materials, controlled thermal or chemical delamination for encapsulant removal, and targeted hydrometallurgical/electrochemical steps for critical metals.

Table 14. Critical comparison of major PV module recycling and metal-recovery routes

Route	Targets and typical conditions	Advantages	Limitations	Environmental and safety issues	Readiness
Mechanical/physical separation	Al frames, glass, junction boxes, Cu wires and Si/metal fractions; dry cutting, crushing, screening, density/electrostatic separation	Low reagent demand; robust pretreatment; suitable for high-throughput handling	Limited delamination and selectivity; mixed fines; product quality depends on sorting	Dust, glass fines, noise and mixed residues require control	High for frame/glass removal; medium for high-purity fractions
Thermal delamination/pyrolysis	EVA removal and cell/glass separation; typically several hundred degrees Celsius; often combined with mechanical and wet routes	Effective encapsulant removal; compatible with integrated flowsheets	Energy demand; possible glass/wafer damage; needs temperature and residence-time optimization	VOC, fluorinated off-gases and Pb-containing residues require capture and treatment	Medium to high
Hydrometallurgy	Ag, Al, Cu, Pb, In, Ga, Cd and Te; acids/oxidants such as HNO3, H2SO4, HCl, HF, iodine/iodide or organic acids	High selectivity and recovery at relatively low temperatures	Reagent consumption, co-dissolution and wastewater treatment; feed pretreatment required	NOx, fluoride, chloride and heavy-metal leachates may cause secondary pollution	Medium; many lab/pilot cases
Pyrometallurgy/high-temperature treatment	Mixed metal-bearing fractions, solder and thin-film materials; high-temperature smelting/roasting/chlorination	High throughput; tolerant of complex feeds; short flowsheet	High energy input; loss/dilution of minor metals; refining required	Off-gas cleaning, slag management and volatilized toxic elements must be controlled	Medium; scalable but PV-specific optimization needed
Electrochemical recovery	Ag, Cu, Pb and selected critical metals; electrodeposition, electrorefining, electrodeposition-redox replacement (EDRR)	High product purity; potential reagent regeneration and selectivity	Longer operation; electrolyte control; equipment and electricity cost	Electrolyte aging, impurity build-up and energy consumption must be reported	Low to medium
DES/organic-solvent routes	EVA delamination and Ag/Al/Cu leaching; choline chloride-urea or other DES/solvent systems	Milder media and possible solvent reuse; lower NOx risk than nitric acid routes	High viscosity, mass-transfer limits, solvent aging and impurity accumulation	Solvent toxicity, loss, regeneration and final disposal need quantification	Low to medium; mostly laboratory scale

Route	Targets and typical conditions	Advantages	Limitations	Environmental and safety issues	Readiness
Bioleaching/biochemical routes	Low-grade metals or selected thin-film elements; microbial or bio-organic leaching	Low temperature and potentially low chemical input	Slow kinetics, feed sensitivity and difficult process control	Metal-bearing bio-solutions and biological stability require management	Low; exploratory

Environmental and safety evaluation should be explicit for any process described as "green". HF-containing etchants can dissolve anti-reflective coatings but introduce fluoride hazards; HNO_3 is effective for Ag dissolution but may generate NO_x and nitrate-rich effluents; HCl and chloride systems cause corrosion and chloride-bearing wastewater; H_2SO_4 and oxidants increase acid load; DMF, hydrazine and some organic solvents have toxicity concerns; and thermal processes must address energy demand and off-gas treatment. A process should therefore be considered environmentally preferable only when reagent recovery, effluent treatment, off-gas capture, residue stabilization and worker safety are demonstrated within a defined system boundary.

Scale-up readiness differs strongly by material and route. Al-frame removal, junction-box removal and glass separation are closest to commercial practice. High-purity Ag and Si recovery are technically successful but require reliable feedstock sorting, low-loss delamination, reagent recycling, product-quality assurance and stable markets. Ga, In, Cd, Te and Se recovery from thin-film modules is strategically important but often limited by feed availability, module heterogeneity and hazardous-material control. Future studies should report not only recovery efficiency, but also complete mass balance, reagent recycling rate, energy use, waste generation, product specifications, process cost, validation scale and LCA/TEA assumptions.

For LCA and TEA reporting, the comparison basis should be standardized. Recommended minimum information includes module type and age, functional unit (e.g., per kg module or per kW module), recovery-rate definition, product-purity definition, reagent make-up and recycling, electricity/thermal energy use, wastewater and off-gas treatment, residue handling, labor and equipment assumptions, and allocation between recovered glass, Al, Si, Ag and other metals. Without these parameters, numerical claims such as energy reduction or carbon-footprint reduction are not directly comparable across studies.

6. REVIEW METHODOLOGY AND SCOPE

This article is designed as a critical, structured narrative review rather than a formal PRISMA-based evidence synthesis. Its objective is to identify representative studies and industrial cases on the dismantling, separation and recovery of metals from end-of-life PV modules, and to compare them using engineering, environmental and scale-up criteria rather than only reporting recovery percentages.

Literature was collected from Web of Science, Scopus, ScienceDirect, SpringerLink and Google Scholar, supplemented by official reports from organizations such as IEA PVPS and IRENA and by industrial or demonstration-line information where available. The search terms combined "end-of-life photovoltaic module", "PV module recycling", "crystalline silicon solar panel", "silver recovery", "silicon recovery", "hydrometallurgy", "pyrometallurgy", "electrochemical recovery", "deep eutectic solvent", "bioleaching", "CIGS", "CdTe", "indium", "gallium", "tellurium" and "cadmium". The search mainly covered publications from 2010 to 2025, while earlier sources were retained when they provided foundational process data, waste projections or industrial context.

Studies were included when they reported material composition, dismantling or delamination strategies, metal-recovery efficiency, product purity, process conditions, environmental implications, life-cycle or techno-economic information, or industrial implementation. Studies were excluded when they focused only on PV power-generation performance, device physics without recycling relevance, module degradation without end-of-life treatment, unrelated electronic waste or recovery routes without sufficient process information. The final synthesis was based on the references cited in this manuscript and emphasizes comparability rather than a quantitative meta-analysis.

The scope was clarified as follows: crystalline silicon (c-Si) modules are the primary focus because they represent the dominant share of installed PV capacity and current recycling streams, while thin-film technologies such as copper indium gallium selenide (CIGS), cadmium telluride (CdTe) and perovskites are discussed selectively because they contain critical or hazardous elements requiring dedicated recovery and safety strategies.

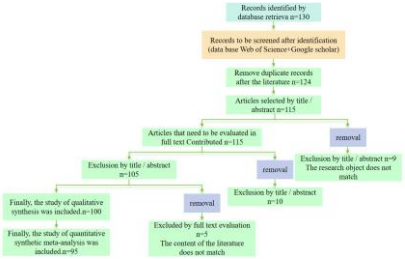
To strengthen comparability, the article evaluates each route according to recovery efficiency, product purity, selectivity, reagent and energy consumption, wastewater and off-gas generation, worker safety, secondary-waste formation, technology readiness and scalability. A comparative table and additional critical discussion distinguish laboratory-scale proof-of-concept results from pilot- and commercial-scale practices.

Table 15. Preferred Reporting Items for Systematic reviews and Meta-Analyses extension for Scoping Reviews (PRISMA-ScR) Checklist

SECTION	ITEM	PRISMA-ScR CHECKLIST ITEM	REPORTED ON PAGE #
TITLE			
Title	1	Identify the report as a scoping review.	page1.: a systematic review
ABSTRACT			
Structured summary	2	Provide a structured summary that includes (as applicable): background, objectives, eligibility criteria, sources of evidence, charting methods, results, and conclusions that relate to the review questions and objectives.	page1.:background:**PV growth creates hazardous waste** **objectives:Evaluate solar recycling technologies' effectiveness** sources of evidence:a synthesis of recent studies in the field of PV recycling technology. **Charting Methods:**module dismantling techniques (mechanical, thermal, chemical) and 2) metal recovery processes (hydrometallurgical, pyrometallurgical, electrochemical). Conclusions:While current methods are capable of high recovery rates for valuable and hazardous materials, they require further optimization to address persistent challenges related to energy intensity and waste management.

SECTION	ITEM	PRISMA-ScR CHECKLIST ITEM	REPORTED ON PAGE #
INTRODUCTION			
Rationale	3	Describe the rationale for the review in the context of what is already known. Explain why the review questions/objectives lend themselves to a scoping review approach.	page1.:The rapid development of the global photovoltaic industry has led to severe waste disposal challenges, urgently necessitating efficient recycling technologies to achieve both resource circulation and environmental protection goals.
Objectives	4	Provide an explicit statement of the questions and objectives being addressed with reference to their key elements (e.g., population or participants, concepts, and context) or other relevant key elements used to conceptualize the review questions and/or objectives.	page1:This review focuses on the recycling processes and technologies for mainstream photovoltaic modules, such as crystalline silicon and thin-film. The scope encompasses recycling methods (e.g., physical, chemical, and pyrolysis), material regeneration pathways, technological maturity, and environmental impact.
METHODS			
Protocol and registration	5	Indicate whether a review protocol exists; state if and where it can be accessed (e.g., a Web address); and if available, provide registration information, including the registration number.	This scoping review followed an internally developed and unregistered protocol. However, the research process strictly adhered to the PRISMA-ScR guidelines.
Eligibility criteria	6	Specify characteristics of the sources of evidence used as eligibility criteria (e.g., years considered, language, and publication status), and provide a rationale.	**Original research (e.g., experimental studies, case studies), reviews, conference papers, reports, and theses/dissertations were included** Limited to Chinese and English literature.The literature search covered the period from January 2000 to December 2024. The included publications focus on the recycling technologies, processes, economics, or environmental assessments of photovoltaic modules (e.g., crystalline silicon, thin-film). This timeframe was selected because the large-scale application of crystalline silicon photovoltaics began at the turn of the 21st century.

SECTION	ITEM	PRISMA-ScR CHECKLIST ITEM	REPORTED ON PAGE #
Information sources*	7	Describe all information sources in the search (e.g., databases with dates of coverage and contact with authors to identify additional sources), as well as the date the most recent search was executed.	We systematically searched the following electronic databases: Web of Science, CNKI, and Google Scholar. Key reports, such as those from the International Renewable Energy Agency (IRENA), were also reviewed. Additionally, we manually screened the reference lists of included studies to identify additional relevant publications.
Search	8	Present the full electronic search strategy for at least 1 database, including any limits used, such that it could be repeated.	The search query was constructed based on the PICOS framework (Population, Concept, Context), utilizing Boolean operators to connect core concepts with "AND" and to expand synonyms with "OR". The resulting query,(, was directly entered into the Google Scholar search bar. Subsequently, the date range was limited by selecting "Custom range" in the sidebar or dropdown menu on the search results page and setting it from 2000 to 2024."photovoltaic module*"OR "solar panel*"OR"cdTe"OR "thin film")AND(recycly* OR recover*OR "circular economy"OR "resource recovery")AND("cadmium" OR "tellurium" OR "critical metal")
Selection of sources of evidence†	9	State the process for selecting sources of evidence (i.e., screening and eligibility) included in the scoping review.	**Initial Screening:** The relevance of each record was initially evaluated by reviewing its title and abstract, leading to the exclusion of clearly ineligible studies. **Full-text Review:** For studies that appeared eligible, the complete articles were reviewed. A final decision on inclusion was made by applying the pre-defined eligibility criteria to the full text. All screening was performed using EndNote and Rayyan software to organize and track decisions.
Data charting process‡	10	Describe the methods of charting data from the included sources of evidence (e.g., calibrated forms or forms that have been tested by the team before their use, and whether data charting was done independently or in duplicate) and any processes for obtaining and confirming data from investigators.	Data were charted using a standardized, piloted extraction form. This process was carried out in duplicate by two independent researchers, who then compared their results. Disagreements were resolved through consensus or, when required, by adjudication from a third researcher to guarantee accuracy.

SECTION	ITEM	PRISMA-ScR CHECKLIST ITEM	REPORTED ON PAGE #
Data items	11	List and define all variables for which data were sought and any assumptions and simplifications made.	Basic Information: Author, publication year, document type, country. Study Characteristics: PV module type under investigation (e.g., crystalline silicon, CdTe, CIGS); target materials for recovery (e.g., silicon, silver, cadmium, tellurium). Intervention/Technology: Specific description of the recycling technology/process (e.g., pyrolysis, chemical leaching, physical separation). Key Findings: Recycling efficiency, economic evaluation, environmental impact (e.g., LCA results), and identified research gaps or future directions.
Critical appraisal of individual sources of evidence§	12	If done, provide a rationale for conducting a critical appraisal of included sources of evidence; describe the methods used and how this information was used in any data synthesis (if appropriate).	Consistent with scoping review methodology, the included studies did not undergo a quality assessment, as the objective was to map the extent and range of evidence, not to evaluate the robustness of individual study findings
Synthesis of results	13	Describe the methods of handling and summarizing the data that were charted.	A descriptive summary, presented in the form of tables, was used to outline the metal leaching methods.
RESULTS			
Selection of sources of evidence	14	Give numbers of sources of evidence screened, assessed for eligibility, and included in the review, with reasons for exclusions at each stage, ideally using a flow diagram.	 Figure1.PRISMA Flowchart The literature screening process is summarized in Figure 1 (PRISMA flow diagram). Initial searches yielded 130 citations. Following the removal of duplicates, 124 records underwent title/abstract screening, resulting in the exclusion of 115. The remaining 100 full-text articles were retrieved and assessed, with ultimately included. The predominant reason for exclusion at the full-text stage was irrelevant content.

SECTION	ITEM	PRISMA-ScR CHECKLIST ITEM	REPORTED ON PAGE #
Characteristics of sources of evidence	15	For each source of evidence, present characteristics for which data were charted and provide the citations.	The manuscript summarizes the types of photovoltaic modules and the primary recycling technologies assessed.
Critical appraisal within sources of evidence	16	If done, present data on critical appraisal of included sources of evidence (see item 12).	As described in the methods section (Item 12), a critical appraisal (quality assessment) of the included studies was not performed, as the purpose of this scoping review is to map the available evidence rather than to synthesize the findings.
Results of individual sources of evidence	17	For each included source of evidence, present the relevant data that were charted that relate to the review questions and objectives.	Tables 7 to 13 detail the specific process conditions (e.g., leaching agent, concentration, temperature) and the corresponding metal recovery efficiencies for the chemical leaching methods employed in the different studies.
Synthesis of results	18	Summarize and/or present the charting results as they relate to the review questions and objectives.	**Crystalline Silicon Recycling:** The combination of physical separation and pyrolysis was the most commonly reported pre-treatment method. **Precious Metal Recovery:** Nitric acid leaching emerged as the predominant chemical technique for reclaiming valuable metals. **Research Gaps in Thin-Film Modules:** Investigations into recycling methods for emerging thin-film modules (e.g., CIGS) are still limited, with the majority of efforts confined to the laboratory scale.
DISCUSSION			
Summary of evidence	19	Summarize the main results (including an overview of concepts, themes, and types of evidence available), link to the review questions and objectives, and consider the relevance to key groups.	The analysis identified three central research themes: Improving recovery efficiency and product purity. Minimizing the environmental footprint of recycling process. Assessing the economic viability of the technologies.
Limitations	20	Discuss the limitations of the scoping review process.	By its nature, the methodological objective of a scoping review did not include a quality appraisal of the evidence. Consequently, it is beyond the scope of this review to comment on the relative robustness or reliability of the findings from different studies.

SECTION	ITEM	PRISMA-ScR CHECKLIST ITEM	REPORTED ON PAGE #
Conclusions	21	Provide a general interpretation of the results with respect to the review questions and objectives, as well as potential implications and/or next steps.	For the recovery of precious metals, nitric acid leaching was identified as the most well-established chemical method. Several core themes emerged from the evidence: 1) enhancing recovery efficiency and purity, 2) reducing environmental impact, and 3) evaluating the economic feasibility of the technologies. However, the distribution of evidence is highly skewed, with research on recycling emerging thin-film modules, such as CIGS, remaining very limited and largely confined to the laboratory scale.
FUNDING			
Funding	22	Describe sources of funding for the included sources of evidence, as well as sources of funding for the scoping review. Describe the role of the funders of the scoping review.	This work was supported by the [Open Fund of National Nickel and Cobalt New Materials Engineering Technology Research Center #1] under Grant [number GCZX2025JSKF002]; [Key Project of Natural Science Foundation of Gansu Province #2] under Grant [number 25JRRA063]; [Lanzhou Youth Science and Technology Talent Innovation Project #3] under Grant [number 2023-QN-94] and [National Science Foundation of China #4] under Grant [number 51904140].

JBI = Joanna Briggs Institute; PRISMA-ScR = Preferred Reporting Items for Systematic reviews and Meta-Analyses extension for Scoping Reviews.

* Where *sources of evidence* (see second footnote) are compiled from, such as bibliographic databases, social media platforms, and Web sites.

† A more inclusive/heterogeneous term used to account for the different types of evidence or data sources (e.g., quantitative and/or qualitative research, expert opinion, and policy documents) that may be eligible in a scoping review as opposed to only studies. This is not to be confused with *information sources* (see first footnote).

‡ The frameworks by Arksey and O'Malley (6) and Levac and colleagues (7) and the JBI guidance (4, 5) refer to the process of data extraction in a scoping review as data charting.

§ The process of systematically examining research evidence to assess its validity, results, and relevance before using it to inform a decision. This term is used for items 12 and 19 instead of "risk of bias" (which is more applicable to systematic reviews of interventions) to include and acknowledge the various sources of evidence that may be used in a scoping review (e.g., quantitative and/or qualitative research, expert opinion, and policy document).

From: Tricco AC, Lillie E, Zarin W, O'Brien KK, Colquhoun H, Levac D, et al. PRISMA Extension for Scoping Reviews (PRISMAScR): Checklist and Explanation. Ann Intern Med. 2018;169:467–473. doi: 10.7326/M18-0850.

7. CONCLUSION AND OUTLOOK

Mechanical separation, thermal delamination, hydrometallurgy, pyrometallurgy, electrochemical recovery, DES-based routes and bioleaching each have specific advantages and limitations. Mature

industrial practice is most likely to rely on integrated flowsheets: physical separation for bulk materials, controlled delamination for layer separation, and targeted hydrometallurgical or electrochemical steps for high-value or hazardous metals.

High laboratory recovery efficiencies should be interpreted cautiously. Many routes that recover >95% Ag, high-purity Si or high percentages of Cu/Pb/In/Ga/Cd/Te still rely on hazardous acids, organic solvents, high temperatures, long reaction times or incomplete waste-treatment data. Therefore, future publications should distinguish laboratory proof-of-concept, pilot demonstration and commercial operation, and should report recovery efficiency together with selectivity, mass balance, reagent recycling, energy use, emissions, residue treatment and product quality.

The main research gaps are: (i) scalable, low-loss delamination methods for aged and broken modules; (ii) closed-loop hydrometallurgical and electrochemical systems with quantified wastewater and off-gas control; (iii) standardized reporting of recovery rate, purity and system boundary; (iv) integrated recovery of Ag, Si, Cu and Pb from c-Si modules without excessive reagent consumption; (v) safe treatment of Cd, Te, In, Ga and Se in thin-film modules; and (vi) combined LCA and TEA to identify routes that are not only technically effective but also environmentally and economically viable.

Overall, PV recycling should move from efficiency-centered laboratory studies toward engineering-centered evaluation. A route can be considered sustainable only when high recovery, safe chemical management, stable product quality, economic feasibility and verified pilot- or commercial-scale performance are demonstrated together.

DECLARATION OF COMPETING 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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DATA AVAILABILITY

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

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