

Mechanistic Pathways of Resource Recovery from Waste PCBs: A Critical Review of Bioleaching, Hydrometallurgical, and Hydrothermal Processing Routes

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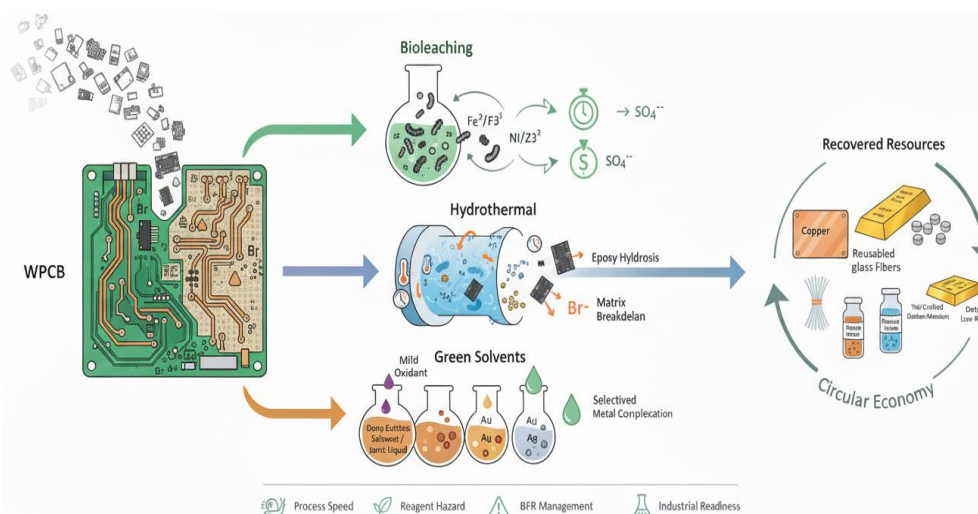
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ABSTRACT

Waste printed circuit boards (WPCBs) constitute the most metal and hazard-intensive fraction of global electronic waste (e-waste), embedding copper, precious metals, and critical elements within a cross-linked brominated epoxy matrix that resists conventional recycling. Global e-waste generation reached 62 million tons (Mt) in 2022 and is projected to reach 82 Mt by 2030, yet only 22.3% is formally collected and recycled, squandering an estimated US\$91 billion in recoverable material value annually. This review critically synthesizes the mechanistic chemistry, performance, and limitations of the principal WPCB resource-recovery technology families: pyrometallurgical and acid/cyanide hydrometallurgical processing; biohydrometallurgy (bioleaching), encompassing contact, non-contact, thiosulfate, and polysulfide mechanisms mediated by acidophilic chemolithotrophs. Hydrothermal processing (HTP) using subcritical and supercritical water (SbCW/SCW), which exploits water's temperature-dependent dielectric constant, ionic product, and density to drive simultaneous epoxy hydrolysis, tetrabromobisphenol-A (TBBPA) debromination, and metal liberation without external reagents; and emerging green-solvent (deep eutectic solvent and ionic liquid) leaching systems. Reaction mechanisms are presented for each pathway with supporting stoichiometry, and a comparative synthesis of metal-specific leaching behavior, process variables, and recovery efficiencies is constructed from recent peer-reviewed literature spanning for the last decade. Life-cycle, circular-economy, and technology-readiness considerations are evaluated alongside future research directions including hybrid bio-HTP and machine-learning-assisted process optimization to guide the industrial deployment of sustainable WPCB recovery technologies.



Keywords- Waste printed circuit boards; Electronic waste; Bioleaching; Hydrothermal processing; Subcritical water.

I. INTRODUCTION

Global electronic waste (e-waste) generation reached 62 million tons (Mt) in 2022, an 82% increase from 34 Mt in 2010 and is projected to rise by a further 32% to 82 Mt by 2030, with annual generation now outpacing documented formal recycling by a factor of nearly five [1]. Despite this growth, only 22.3% of the 2022 total was documented as having been collected and treated through environmentally sound formal channels, leaving an estimated US\$91 billion in recoverable raw-material value, including roughly US\$19 billion in copper and US\$15 billion in gold alone, which were largely unrecovered, dumped, or processed informally [1] (**Figure 1**). This recycling deficit is compounded by the simultaneous release of brominated flame retardants (BFRs), heavy metals, and polybrominated dibenzo-p-dioxins and furans (PBDD/Fs) into terrestrial and aquatic environments wherever e-waste is informally incinerated or landfilled [2], [3].

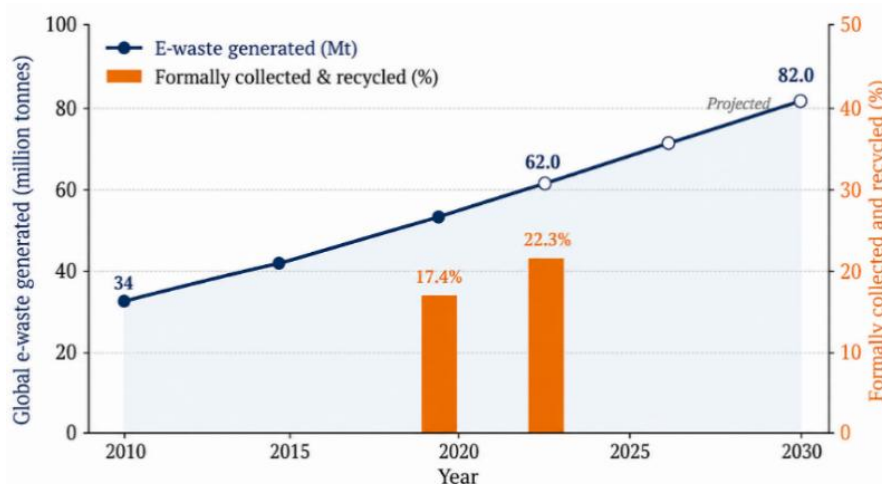


Figure 1. Global e-waste generation versus formally collected and recycled fraction, 2010–2030 (historical and projected), synthesized from Global E-waste Monitor data [1]

Waste printed circuit boards (WPCBs) are the most economically and environmentally significant component of e-waste. Their heterogeneous composition which make up approximately 40 wt% metals, 30 wt% ceramics, and 30 wt% plastics, contains copper at concentrations of 10–30 wt% and precious metals (Au, Ag, Pd) at concentrations 10–100 times higher than natural ore grades [4]. These metals are intimately embedded within FR-4 (fiber glass-reinforced) epoxy resin incorporating 5–15 wt% tetrabromobisphenol A (TBBPA) as a chemically bonded BFR, a combination that renders both conventional thermal and hydrometallurgical treatment routes inadequate on their own [5]. The persistence of this cross-linked thermoset matrix which cannot be remelted or dissolved by simple mechanical or thermal means, is the central technical obstacle motivating the diversity of recovery technologies discussed in this review. Three broad technology families currently compete, and increasingly complement one another, for WPCB resource recovery: (i) pyrometallurgical and conventional acid/cyanide hydrometallurgical processing, which achieve high metal yields but cannot manage BFRs without hazardous emissions or reagents; (ii) biohydrometallurgy (bioleaching), which uses acidophilic, sulfur- and iron-oxidizing microorganisms to mobilize metals through contact, non-contact, thiosulfate, and polysulfide mechanisms; and (iii) HTP using subcritical or supercritical water (SbCW/SCW), which exploits water's temperature-dependent dielectric constant, ionic product, and viscosity to simultaneously hydrolyze the epoxy matrix, debrominate TBBPA, and liberate metals without external reagents [6], [7]. A fourth, more recent family, green solvometallurgy based on deep eutectic solvents (DES) and ionic liquids, has emerged as a complementary low-toxicity alternative and is treated within the comparative synthesis developed in this review. [11]–[13].

Although each of these pathways has been reviewed individually, bioleaching most recently by Hu et al. [9] and Ming et al. [10], hydrothermal and supercritical water (SCW) treatment by Chen et al. [8], and green-solvent leaching by recent DES-focused reviews [12], a unified mechanistic comparison that integrates reaction chemistry, metal-specific reactivity, and leaching behavior across all major technology families within a single critical synthesis remains largely absent from the literature. Most existing reviews are confined to a single technology family and rarely connect the underlying organic-reaction-mechanism chemistry of polymer-matrix decomposition to the metal-leaching outcomes it enables. This review addresses that gap by (i) synthesizing the mechanistic chemistry of polymer decomposition and metal mobilization across all major recovery pathways at a comparable level of mechanistic detail, (ii) critically evaluating recent peer-reviewed advances in each pathway, including emerging green-solvent and hybrid approaches, (iii) constructing a comparative, evidence-based synthesis of process performance, environmental burden, and technology readiness across pathways, and (iv) identifying concrete research gaps and future directions to guide both academic inquiry and industrial technology selection.

II. WPCB COMPOSITION AND THE RESOURCE RECOVERY CHALLENGE

2.1 Material and Metal Composition

WPCBs are heterogeneous composites of approximately 40 wt% metals, 30 wt% ceramics, and 30 wt% plastics (Figure 2a). Copper dominates the metallic fraction, accounting for 10.0 to 26.8 wt%, while precious metals occur at concentrations that are 10 to 100 times higher than those found in natural ores, with gold ranging from 80 to 1,000 ppm, silver from 110 to 3,301 ppm, and palladium from 4.6 to 30 ppm. (Figure 2b) [4], [14], [15]. This concentration profile is what makes WPCBs an attractive secondary resource, but device-to-device variability is substantial: reported copper content across end-of-life electronics ranges from roughly 74,200 mg/kg in calculators to over 313,000 mg/kg in flat-screen televisions, meaning recovery technologies optimized on a single feedstock composition may transfer poorly to mixed industrial WPCB streams, a consideration revisited in the comparative discussion of Section 7 [14], [15].

The plastic fraction which is dominated by thermoset FR-4 epoxy resin, represents the central processing obstacle: its cross-linked molecular network prevents remelting, and its chemically bonded brominated flame retardant (BFR) content, typically 5–15 wt% of the plastic fraction as TBBPA, cannot be removed by mechanical means. Conventional thermal treatment above 400 °C risks formation of polybrominated dibenzo-p-dioxins and furans (PBDD/Fs), while the ceramic fraction (SiO_2 - and Al_2O_3 -dominant, ~30 wt%) is largely inert and does not itself impede metal recovery but reduces overall processing throughput [16].

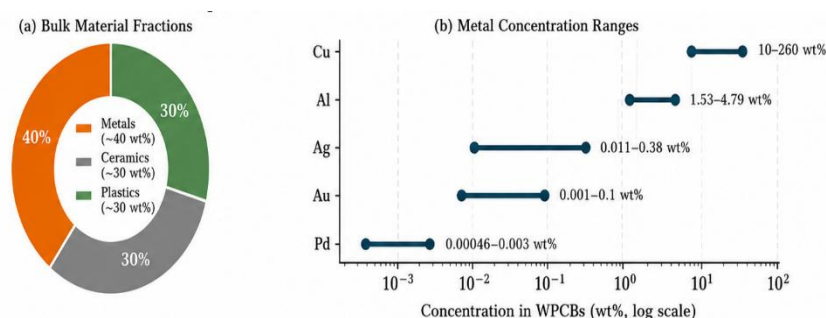


Figure 2. Compositional profile of WPCBs: (a) bulk material fractions and (b) metal concentration ranges, [4], [14]–[16]

2.2 Metal Speciation and Strategic Significance

Metals within WPCBs occur in multiple physical and chemical forms as pure metallic phases (copper traces, gold contacts), alloys (tin–lead and lead-free solders), intermetallic compounds, oxides and sulfides formed during use or environmental exposure, and surface platings (Ni, Cr, precious-metal finishes) [17]. This diversity of speciation, combined with intimate physical and chemical association with the polymer matrix, means that no single recovery mechanism is equally effective for all metals, a theme developed mechanistically in Sections 4–6. Beyond base and precious metals, WPCBs are increasingly recognized as a secondary source of strategic and critical metals, including rare-earth elements (REEs) used in microwave dielectric and magnetic components. Xia et al. [18] demonstrate that, although rare-earth dilution has historically limited REE recovery from PCBs relative to dedicated secondary sources such as permanent magnets, targeted dismantle-and-sort strategies, physically isolating REE-bearing components prior to leaching, can render REE recovery economically viable, exemplified by a demonstrated neodymium recovery route based on selective acid leaching and oxalate precipitation. This broadens the resource-recovery rationale for WPCB processing beyond copper and precious metals and reinforces the need for recovery technologies capable of accommodating compositional heterogeneity across both common and critical elements.

III. CONVENTIONAL RESOURCE RECOVERY METHODS AND THEIR LIMITATIONS

3.1 Pyrometallurgical and Hydrometallurgical Processing

Pyrometallurgical smelting at integrated copper smelters (e.g., Umicore, Boliden Rönnskär; $>1,000$ °C) recovers more than 95% of gold and platinum-group metals through copper-matte collection followed by electrorefining, with the polymer fraction serving as fuel and reductant [19]. However, combustion of BFRs above 400 °C generates PBDD/Fs, requiring expensive flue-gas treatment, and no value is recovered from the non-metallic fraction. Recent integrated life-cycle and techno-economic analyses confirm that, while pyrometallurgical routes retain a cost and yield advantage at present, their environmental burden is dominated by energy-intensive smelting and flue-gas abatement, with waste-heat recovery and grid decarbonization identified as the most impactful levers for burden reduction; comparative thermal-treatment studies further

indicate that steam gasification generates substantially lower dioxin and furan emissions than direct incineration or pyrolysis, making thermal pre-treatment atmosphere itself a meaningful design variable [24], [65]. Hydrometallurgical processing, by contrast, employs aqueous leaching, solvent extraction, precipitation, ion exchange, and electrowinning to selectively dissolve and recover metals: the H₂SO₄/H₂O₂ system achieves approximately 95% copper recovery within 12 hours at 25 °C [20], while cyanide-based systems achieve 78–99% gold recovery [21]. Both routes require extensive mechanical preprocessing to expose encapsulated metals, generate large volumes of hazardous leachate, and in the case of cyanide, face increasing regulatory restriction; neither addresses the polymer or BFR fraction of the WPCB.

Biohydrometallurgical processing using acidophilic, chemolithotrophic bacteria such as *Acidithiobacillus ferrooxidans* and *A. thiooxidans* offers markedly lower reagent and energy input but proceeds over 10–30 days for equivalent metal yields and, in its conventional form, does not address BFR content [22]. Bioleaching mechanisms are treated in full mechanistic detail in *Section 4*. **Table 1** summarizes the principal limitations of these conventional routes that motivate the mechanistic and experimental investigation of hydrothermal, biological, and green-solvent alternatives developed in *Sections 4–6*.

Table 1. Principal limitations of conventional WPCB resource-recovery technologies [19]–[22]

Method	Metal Recovery	BFR / Polymer Management	Key Limitation
Pyrometallurgy	>95% Au, PGMs	Combusted — PBDD/F risk	Expensive gas treatment; no polymer value recovery
Acid hydrometallurgy	~95% Cu	None	Requires preprocessing; large hazardous leachate volume
Cyanide leaching	78–99% Au	None	Extremely toxic CN ⁻ ; regulatory restriction
Bioleaching (conventional)	60–80% Cu (typical)	None	Slow kinetics (10–30 days); sensitive to complex matrices

IV. BIOLEACHING MECHANISMS OF WPCBS

Bioleaching mobilizes metals from WPCBs through microbial activity operating via three general mechanisms: (i) production of organic or inorganic acids (protons), (ii) oxidation–reduction reactions, and (iii) excretion of complexing agents [23]. The specific pathway followed depends on whether the responsible microorganisms act through direct physical contact with the solid substrate (contact mechanism) or remotely via dissolved oxidizing agents (non-contact mechanism). For sulfur and iron-oxidizing bacteria such as *Acidithiobacillus ferrooxidans* and *A. thiooxidans*, three named sub-mechanisms are recognized: the indirect ferric–ferrous cycle, the thiosulfate mechanism, and the polysulfide mechanism, summarized schematically in **Figure 3**.

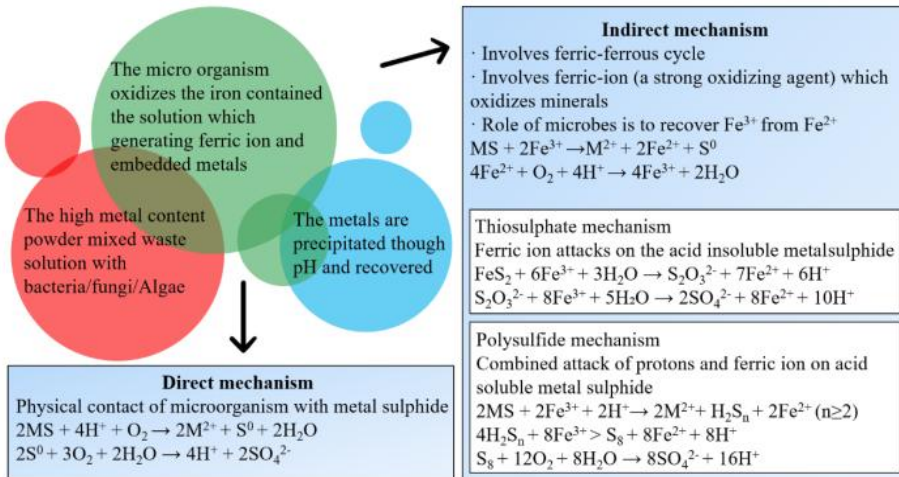


Figure 3. Schematic comparison of contact and non-contact bioleaching mechanisms for metal sulfide dissolution in WPCB bioleaching, adapted from [22], [23]

4.1 Contact Bioleaching Mechanism

In contact bioleaching, microorganisms physically attach to the metal sulfide surface (e.g., pyrite, FeS₂). Metal solubilization occurs as *A. ferrooxidans* oxidizes the metal sulfide directly, obtaining electrons from the reduced material.

Ferric ion (Fe_3^+) held within the extracellular polymeric substance (EPS) layer surrounding the cell accepts an electron and is reduced to Fe_2^+ , which diffuses to the outer membrane where it may be re-oxidized to Fe_3^+ . The reaction sequence is given by Equations (1)–(5).



Equations (1)–(2) describe stepwise oxidation of elemental sulfur to sulfuric acid. Equation (3) is the general metal-solubilization reaction via ferric-ion attack under acidic, oxygenated conditions. Equations (4)–(5) describe oxidative dissolution of pyrite to ferrous sulfate and sulfuric acid, followed by oxidation of ferrous to ferric sulfate, regenerating the Fe_3^+ oxidant that sustains the cycle.

Silva et al. [25] demonstrated the importance of the contact mechanism using a partition system that physically separated bacteria from the WPCB substrate: disabling contact reduced copper extraction by 25%, with bacterial attachment measured at 4.3×10^7 cells/g. Feng et al. [26] showed via micromorphological analysis that intensive adsorption sites (rills, micropores) on the mineral surface with pore size consistent with *A. caldus* cell dimensions promote strong contact-mechanism dependence in sulfur-oxidizing bacteria.

4.2 Non-Contact (Indirect) Bioleaching Mechanism

In non-contact bioleaching, planktonic (free-living) bacteria oxidize Fe_2^+ to Fe_3^+ and sulfur species to sulfuric acid in bulk solution; the resulting Fe_3^+ then acts as a strong oxidant, accepting electrons from metal sulfides at a distance and being reduced back to Fe_2^+ . The role of the microorganisms is essentially regenerative, continuously recycling Fe_3^+ to sustain oxidative attack on the mineral (Equations (6)–(8)).



Gu et al. [27] demonstrated copper bioleaching from WPCBs using a nitrogen-doped carbon-nanotube-modified electrode with *A. ferrooxidans*, in which Fe_2^+ served as a bacterial nutrient and was oxidized to Fe_3^+ , which then oxidized metallic copper (Equations (9)–(11)). The modified electrode's high conductivity and surface area increased copper-leaching rate to 99%, that is approximately 20% higher than the unmodified control.



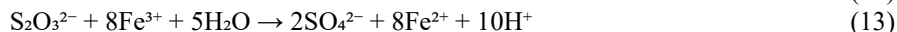
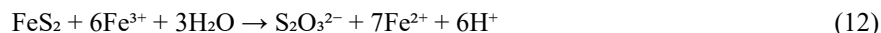
Dong et al. [28] isolated a purely non-contact configuration for vanadium recovery from low-grade stone coal using *Bacillus mucilaginosus*, in which only molecular organic acids present in bacterial metabolites, rather than physical contact, interacted with the mineral. Macromolecular metabolite compounds were unable to complex with mineral metals, thereby limiting bacterial access to nutrients and highlighting a key constraint of purely non-contact systems.

4.3 Thiosulfate and Polysulfide Mechanisms

Beyond the broad contact/non-contact classification, indirect ferric-ion attack on metal sulfides proceeds via two named sub-pathways distinguished by the acid solubility of the target mineral.

4.3.1 Thiosulfate Mechanism (Acid-Insoluble Sulfides)

The thiosulfate mechanism applies to acid-insoluble metal sulfides such as pyrite (FeS_2) and molybdenite. Ferric ion attacks the sulfide directly, generating thiosulfate as the key intermediate, subsequently oxidized to sulfate (Equations (12)–(13)).



This pathway is characteristic of acid-insoluble sulfides, for which Fe_3^+ is the sole oxidant capable of breaking down the mineral structure; protons alone are insufficient.

4.3.2 Polysulfide Mechanism (Acid-Soluble Sulfides)

The polysulfide mechanism applies to acid-soluble metal sulfides (sphalerite, galena, chalcopyrite), attacked by the combined action of protons and ferric ion, producing polysulfide and elemental-sulfur intermediates (Equations (14)–(16)).



Unlike the thiosulfate pathway, this route requires combined proton attack and ferric-ion oxidation, reflecting the greater acid solubility of these minerals. The final sulfate product forms via oxidation of an elemental sulfur intermediate, typically catalyzed in WPCB bioleaching systems by *A. thiooxidans*.

4.4 Recent Advances: Novel Strains, Electro-Bioleaching, and Biosorption

Recent literature has substantially expanded the bioleaching toolkit beyond the classical *Acidithiobacillus* consortia reviewed above. Hu et al. [9] note that downstream biosorption of dilute leachates using biochar, algal biomass, and engineered biosorbents, which is increasingly studied as a complementary concentration step following primary bioleaching, given that the global value of metals recoverable from e-waste reached an estimated US\$91 billion in 2022. Adetunji et al. [29] highlight that heterotrophic fungi such as *Aspergillus niger* mobilize metals predominantly through organic-acid excretion (citric, oxalic, gluconic) rather than the ferric-ion redox cycle characteristic of autotrophic *Acidithiobacillus* species, offering a mechanistically distinct and often faster-acting alternative for base-metal recovery, albeit one less effective for sulfide-hosted precious metals. Isolation of novel metal-tolerant heterotrophs directly from e-waste-contaminated environments. For example, *Enterobacter quasihormaechei* strains achieving 87.5% silver and 60.5% aluminum recovery within five days, illustrates the continuing expansion of the microbial toolkit, with such isolates frequently showing faster kinetics and broader multi-metal recovery profiles than classical autotrophic consortia [9].

Electrochemically assisted bioleaching, exemplified by the nitrogen-doped carbon-nanotube electrode system of Gu et al. [27] (Section 4.2), accelerates the $\text{Fe}^{2+}/\text{Fe}^{3+}$ regeneration cycle that otherwise rate-limits non-contact leaching, shortening total processing time toward the lower end of the conventional 10–30-day range while improving copper-recovery yield. Ming et al. [10] further synthesize bioleaching alongside biosorption-based purification as components of an integrated “biorecovery” framework for precious-metal extraction, concluding that integration with efficient downstream purification can substantially improve the overall economic viability of biohydrometallurgical WPCB processing relative to treating bioleaching in isolation.

4.5 Synthesis: Comparative Reactivity and Dominant Mechanism

Sections 4.1–4.3 have shown that contact and non-contact bioleaching proceed through distinct physical and electron-transfer pathways, mediated by different organisms and supported by different experimental evidence. Table 2 synthesizes this comparison directly, contrasting the two mechanisms across physical contact requirements, electron-transfer pathway, key organisms, and supporting experimental findings, drawing together the contact-pathway evidence of Silva et al. [25] and Feng et al. [26] with the non-contact-pathway evidence of Gu et al. [27] and Dong et al. [28].

Table 2. Comparative summary of contact and non-contact bioleaching mechanisms [23]–[29]

Feature	Contact Mechanism	Non-Contact Mechanism
Physical contact required	Yes — direct bacterial attachment to FeS_2 surface	No — planktonic cells act via dissolved $\text{Fe}^{3+}/\text{Fe}^{2+}$ cycle
Electron transfer pathway	Direct from sulfide to Fe^{3+} within the EPS layer	Fe^{3+} generated extracellularly, oxidizes mineral at a distance
Key organisms	<i>A. ferrooxidans</i> , <i>A. thiooxidans</i> , <i>A. caldus</i>	<i>A. ferrooxidans</i> , <i>Bacillus mucilaginosus</i> , heterotrophic fungi
Experimental evidence	Disabling contact cut Cu extraction by 25% [25]	Vanadium leaching via organic acids only, no contact [28]

Contact bioleaching frequently dominates over the non-contact mechanism, yielding greater overall metal recovery because direct physical contact appears to accelerate electron transfer relative to the diffusion-limited non-contact pathway [23]. The two mechanisms are, however, not mutually exclusive: practical bioleaching systems typically involve simultaneous contact-mediated attack at colonized surface sites and non-contact ferric-ion attack via planktonic cells, with the relative contribution of each governed by bacterial attachment efficiency, mineral surface topology, and whether the target sulfide is acid-soluble (favoring the polysulfide pathway) or acid-insoluble (favoring the thiosulfate pathway). The continuing expansion of strain diversity, electro-assisted intensification, and integrated biosorption purification (Section 4.4) suggests that the principal future gains in bioleaching performance will arise less from new mechanistic discovery than from process integration built upon the established mechanistic foundation reviewed here, a theme revisited in Section 8.

V. HYDROTHERMAL PROCESSING: PHYSICOCHEMICAL FOUNDATIONS AND REACTION MECHANISMS

HTP exploits the dramatically altered physicochemical properties of pressurized water between 100 °C and the critical point (374 °C, 22.1 MPa) to drive chemical transformations difficult to achieve in ambient aqueous systems [30], [31]. As temperature rises toward the critical point, the dielectric constant (ϵ_r) falls from 78.5 to below 10, the ionic product (pK_w) rises to a maximum near 250–300 °C before declining, density decreases from ~1.0 to 0.2–0.5 g/cm³, and diffusivity increases sharply [32], as illustrated in Figure 4 and summarized in Table 3.

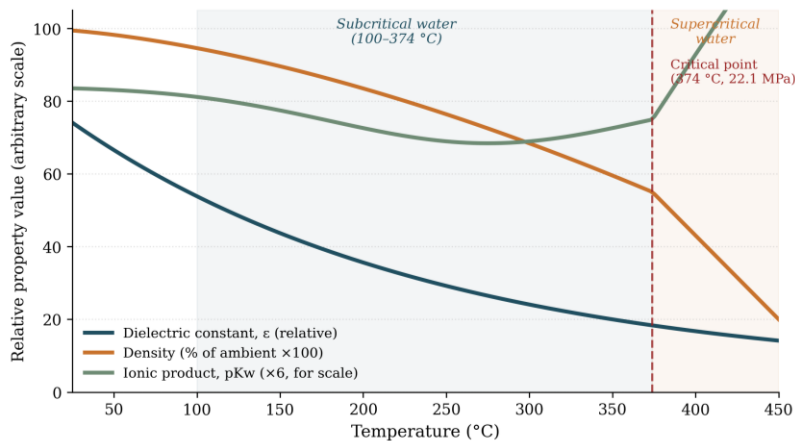


Figure 4. Schematic variation of key water properties — dielectric constant, density, and ionic product — from ambient to supercritical conditions, constructed from reported trends in [30]–[33]

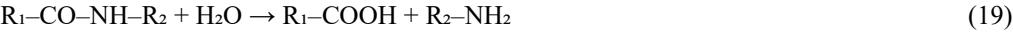
Table 3. Key physicochemical properties of water under ambient, subcritical, and supercritical conditions [32], [33]

Property	Ambient (25 °C, 0.1 MPa)	Subcritical (175–350 °C, 2–22 MPa)	Supercritical (>374 °C, >22.1 MPa)
Density (g/cm ³)	0.997	0.6–0.9	0.2–0.5
Dielectric constant (ε)	78.5	20–35	< 10
Ionic product (pKw)	14.0	11.2–12	> 19
Dynamic viscosity (mPa·s)	0.89	0.07–0.12	< 0.03
Hydrogen bonding	Strong	Moderate	Weak / absent
Solubility behavior	Polar solutes only	Enhanced organic solubility	Gas-like / nonpolar

Hydrolysis reaction rates under subcritical conditions are 10³–10⁶ times faster than under ambient conditions, driven by elevated H⁺/OH[−] concentrations, reduced activation energies, and improved mass transfer [34], [35]. Three hydrothermal variants are conventionally distinguished by severity: hydrothermal carbonization (HTC, 180–280 °C), liquefaction (HTL, 280–380 °C), and gasification (HTG, >380 °C); for WPCB treatment, HTC operates within practical reactor parameters while achieving effective epoxy hydrolysis and TBBPA debromination, retaining metals in a concentrated solid/liquid stream amenable to downstream recovery [36]. Chen et al. [8], in a recent dedicated review of supercritical water treatment of e-waste, similarly conclude that subcritical and near-critical operating windows are generally preferred over fully supercritical operation for WPCB treatment specifically, since the marginal gains in organic-matrix decomposition above the critical point are offset by sharply increased reactor cost, corrosion severity, and energy demand.

5.1 Organic Reaction Classes in Sub- and Supercritical Water

Water in the hydrothermal regime functions not only as solvent but as reactant and catalyst, enabling four principal classes of organic transformation without external catalysts: hydrolysis, dehydration, decarboxylation/decarbonylation, and condensation [34]. Because the FR-4 epoxy/TBBPA matrix of WPCBs is itself an organic polymer network, these reaction classes govern the polymer-degradation chemistry that liberates embedded metals. The general hydrolysis mechanism involves addition of H⁺ and OH[−] from water across a cleaved bond (Equation (17)), a generic scheme that governs glycosidic-bond cleavage in polysaccharides (Equation (18)), peptide-bond hydrolysis (Equation (19)), triglyceride hydrolysis (Equation (20)), and most relevantly for WPCBs, ether-bond hydrolysis in lignin and epoxy-resin networks (Equation (21)) [37]–[40].



Equation (21) is the direct mechanistic analogue of DGEBA (diglycidyl ether of bisphenol A) ether-linkage hydrolysis in FR-4 epoxy resin: water cleaves Ar–O–Ar ether bonds, physically liberating encapsulated metal particles and generating carboxylic-acid and phenolic by-products that subsequently act as metal-complexing ligands. This reaction proceeds with first-order kinetics (activation energy 100–130 kJ/mol), achieving 60–80% conversion at 250–300 °C within 30–60 minutes [41].

Three further reaction classes accompany hydrolysis. Dehydration removes water from organic compounds to form unsaturated or cyclic structures (Equation (22)) exemplified by carbohydrate dehydration to furanic platform chemicals

(glucose/fructose to 5-hydroxymethylfurfural, xylose to furfural) and proceeds efficiently in SbCW/SCW due to favorable thermodynamics and enhanced acid catalysis at elevated temperature [42], [43]. Carboxylic acids generated by hydrolysis may subsequently undergo decarboxylation, releasing CO₂ (Equation (23)): in pure SCW (>374 °C), free-radical pathways dominate via homolytic C–C bond cleavage adjacent to the carboxyl group, whereas under subcritical conditions or in the presence of metal ions, ionic mechanisms dominate, in which the metal coordinates to the carboxyl group and facilitates concerted decarboxylation, a pathway of direct relevance to organic-acid-mediated metal complexation in WPCB leachates (Section 5.3) [44]–[46]. Condensation reactions combine molecules with elimination of water (Equation (24)), encompassing Friedel–Crafts alkylation, aldol condensation (Equation (25)), and Cannizzaro disproportionation (Equation (26)) [47], [48]; above 300 °C, secondary condensation between phenolic intermediates released by epoxy hydrolysis reduces monomer yield, defining a practical optimal window of 250–300 °C for both polymer-fragment recovery and metal liberation.



Underlying both wet oxidation (with O₂) and oxidant-free thermal hydrolysis is free-radical chain chemistry proceeding through initiation, propagation, and termination. Thermolytic bond homolysis generates alkyl and hydrogen radicals (Equation (27)), while oxygen attack on weak C–H bonds provides an additional initiation pathway in wet oxidation (Equation (28)) [49]. Propagation proceeds via hydroxyl-radical abstraction and peroxy-radical chemistry, while termination yields stable low-molecular-weight species — alcohols, ketones, and especially volatile fatty acids. Acetic acid is the most persistent terminal product, with an activation energy of only 167.7 kJ/mol, making it a practical marker of HTP extent and a refractory bottleneck in complete organic mineralization [49].



5.2 TBBPA Debromination Mechanisms

TBBPA, chemically bonded at the 3,3',5,5' positions of the bisphenol-A unit within the epoxy backbone, is debrominated via two parallel pathways. Hydrolytic debromination involves nucleophilic substitution of aryl–bromine bonds by OH[−], converting organic bromine to water-soluble Br[−] and preventing PBDD/F formation; reductive debromination is facilitated by in-situ H₂ generated via water–gas-shift-type reactions, abstracting aromatic bromine through homolytic C–Br cleavage [50]. The hydrolytic pathway predominates below 250 °C, while reductive contributions become significant above 280 °C; near-complete debromination (>95%) is achievable above 300 °C, with solid-phase bromine declining from ~22,000 mg/kg to below 300 mg/kg [51]. Gandon-Ros et al. [52] provide direct experimental confirmation at a practical, sub-laboratory scale relevant to industrial pre-treatment: using potassium carbonate as a debromination additive in subcritical water at a comparatively mild 225 °C, they achieved 50 wt% debromination of large (up to 80 mm × 33 mm) WPCB pieces within 360 minutes while simultaneously recovering reusable FR-4 reinforcement from the treated boards, demonstrating that hydrothermal debromination and material-fraction recovery can proceed concurrently even without size-reduction pre-processing.

5.3 Metal Leaching Mechanisms in Hydrothermal Media

Metal leaching in hydrothermal media operates through four synergistic mechanisms. Direct hydrolysis of metal–oxygen bonds in oxides and intermetallic compounds (Equation (29)) becomes thermodynamically favorable as temperature rises, with rates significantly enhanced in the 200–350 °C range [53]. Above 200 °C, water can act as both oxidant and reductant, driving oxidative dissolution of elemental metal accompanied by hydrogen evolution (Equation (30)), which in turn creates locally reducing conditions affecting co-present redox-sensitive species such as Cr(VI) [54]. The enhanced ionic product of water up to ~250–300 °C also provides elevated H⁺/OH[−] concentrations that drive self-generated, proton-mediated dissolution without external acid addition (Equation (31)), particularly effective for zinc, iron, and aluminum [54]. Finally, carboxylic acids and phenolic compounds released by the hydrolysis chemistry of Section 5.1 act as ligands, stabilizing dissolved metal ions in solution (Equation (32)), exemplified for copper and substantially enhancing apparent leaching efficiency relative to systems containing water alone [55].



The coupling between these four mechanisms and the concurrent organic-reaction chemistry of Section 5.1 is the defining mechanistic feature of hydrothermal WPCB treatment: polymer-matrix decomposition simultaneously liberates encapsulated metal particles, expands reactive surface area, generates chelating ligands in situ, and modifies local pH, collectively producing higher leaching efficiencies than equivalent hydrometallurgical treatment of pre-shredded, polymer-depleted WPCB fractions [56]. Chen et al. [8] reach a consistent conclusion, noting that metal-dissolution behavior in pure

water alone is consistently outperformed once organic acids and complexing intermediates are allowed to accumulate in situ, reinforcing this mechanistic coupling as a target for deliberate process design rather than an incidental side effect.

5.4 Process Variables Governing Hydrothermal Leaching Efficiency

Table 4 summarizes literature-reported optimal temperature windows for hydrothermal leaching of the principal WPCB metals, reflecting the competing influence of dissolution kinetics, redox transformation, and reprecipitation phenomena.

Table 4. Optimal temperature ranges for hydrothermal leaching of metals from WPCBs [57]–[60]

Metal	Optimal Range (°C)	Key Observations
Copper (Cu)	280–320	Rapid increase above 250 °C; reprecipitation risk above 320 °C
Aluminum (Al)	250–300	Dissolution begins ~200 °C; oxide reprecipitation at high T
Iron (Fe)	280–350	Higher T favors complete dissolution; reducing conditions assist
Zinc (Zn)	250–320	Efficient across broad range; sulfate precipitation possible
Nickel (Ni)	270–330	Moderate sensitivity; organic-ligand complexation important
Lead (Pb)	225–260	Sharp decline above 275 °C from PbSO ₄ /Pb ₃ (PO ₄) ₂ reprecipitation
Chromium (Cr)	150–250	Lower T preserves Cr speciation control
Au, Ag, Pd	>300	Require high T and/or oxidizing conditions for mobilization

Pressure primarily maintains water in the liquid phase but also influences density and ionic product: increasing pressure from 8 to 15 MPa at 280 °C improved copper recovery from 76% to 89%, with diminishing returns above 15 MPa [36]. Residence time effects are metal-dependent, base metals approach maximum extraction within 30–60 minutes, while precious metals typically require 60–120 minutes due to nobility and encapsulation depth [61]. The solid-to-liquid (S/L) ratio inversely affects extraction efficiency, with copper recovery decreasing from 94% at 1:20 (g/mL) to 78% at 1:5; an optimal range of 1:10–1:20 balances extraction efficiency against energy and reactor-volume requirements [62]. Preetam et al. [63] extend this analysis to subcritical-to-supercritical methanol as a non-aqueous hydrothermal analogue, reporting that solvent selection materially alters the depolymerization pathway: methanol-mediated treatment over 150–300 °C achieved effective separation of the non-metallic fraction from concentrated metals while generating a liquid product enriched in low-molecular-weight aromatics, indicating that the reaction-class framework developed in Section 5.1 for water extends, with quantitative modification, to other hydrothermal solvent media.

VI. EMERGING GREEN-SOLVENT AND HYBRID RECOVERY TECHNOLOGIES

6.1 Deep Eutectic Solvents and Ionic Liquids: Mechanism and Performance

Beyond the classical technology families reviewed in Sections 3–5, deep DES and ionic liquids (ILs) have emerged over the past decade as a fourth, low-toxicity leaching medium for WPCB metal recovery. DESs are formed by combining a hydrogen-bond donor (typically a carboxylic acid, polyol, or amide) with a hydrogen-bond acceptor (commonly a quaternary ammonium salt such as choline chloride) in a defined molar ratio; the resulting hydrogen-bond network depresses the mixture's melting point well below that of either constituent, yielding a stable, tunable liquid at near-ambient temperature without a true chemical reaction between components [12]. Metal dissolution in DES media proceeds primarily through coordination of the metal center by the hydrogen-bond-donor ligand (most often a carboxylate or chloride species) rather than the strong mineral-acid protonation that dominates conventional hydrometallurgy, which is the mechanistic basis for the markedly lower corrosivity and toxicity profile of DES leaching relative to H₂SO₄ or cyanide systems [12].

Reported extraction efficiencies for DES- and IL-based WPCB leaching span a wide range, reflecting strong sensitivity to solvent composition and target metal. Lukomska et al. [13] evaluated two DESs and four ILs for copper, silver, aluminum, iron, and zinc recovery from pre-treated WPCBs, finding that a choline chloride–malonic acid DES achieved only 15.7 wt% copper and 17.6 wt% silver extraction after two extraction and two stripping stages, indicating that early-generation DES chemistries can substantially underperform optimized acidic systems. By contrast, oxidant-augmented formulations achieve markedly higher yields: a choline chloride–acetic acid–iodine DES has been reported to achieve 99% copper, 92% nickel, and 90% gold extraction from PCB powder, demonstrating that adding a mild oxidant to an otherwise weakly acidic DES can close much of the performance gap with conventional acid leaching while retaining DES media's lower-toxicity profile [12]. Oke and Potgieter [11] further report that acidic DES formulations are particularly effective for the hazardous base metals lead, chromium, zinc, and nickel, contrasting with earlier ionic-liquid systems that achieved less than 10% lead extraction and conclude that solvent acidity and oxidant co-formulation, rather than the DES/IL distinction itself, are the primary determinants of leaching performance.

6.2 Comparative Position and Hybrid Process Concepts

Table 5 situates DES/IL leaching alongside the conventional and hydrothermal pathways reviewed in Sections 3–5. DES/IL systems share with bioleaching the advantage of comparatively benign reagents and avoid the high-pressure reactor infrastructure required for HTP, but neither classical DES leaching nor bioleaching alone fully replicates the

combined metal-liberation and BFR-management capability of HTP; current DES literature addresses metal leaching from WPCBs but does not report comparable debromination performance to the hydrothermal pathway of *Section 5.2*, identifying this as a specific direction for hybrid process development discussed further in *Section 8*.

Table 5. Comparative positioning of deep eutectic solvent / ionic liquid leaching relative to other WPCB recovery pathways [11]–[13]

Attribute	DES / Ionic Liquid Leaching	HTP (Sec. 5)	Bioleaching (Sec. 4)
Typical reagent toxicity	Low — biodegradable components common	None — water as sole reagent	Low — biological metabolites
Reported metal yields	16–99% (highly formulation-dependent)	76–99% for base metals; >300 °C needed for Au/Ag/Pd	60–99% Cu (system-dependent)
BFR / polymer management	Not addressed in reviewed literature	Concurrent debromination (>95% achievable)	Not addressed
Typical processing time	Hours	30–120 minutes	Days to weeks
Infrastructure demand	Low: ambient pressure	High: pressurized reactor	Moderate: bioreactor, long residence

Several recent studies combine elements of the pathways reviewed above into hybrid process trains. SCW pre-treatment followed by conventional acid leaching (*Section 5*) substantially reduces the acid demand and residence time of the subsequent hydrometallurgical step relative to acid leaching of untreated WPCBs, and SCW oxidation coupled with an electrokinetic recovery step has similarly been shown to improve copper yield beyond either technique alone. These hybrid concepts point to a broader pattern: rather than a single “winning” technology, the WPCB recovery field is converging on combinations of a polymer-matrix-disrupting pre-treatment (hydrothermal or strong-acid) with a selective, lower-impact metal-separation step (DES, bioleaching, or electrowinning), and a synthesis developed further in *Section 7*.

VII. DISCUSSION: COMPARATIVE SYNTHESIS ACROSS RECOVERY PATHWAYS

7.1 Mechanistic Comparison

The mechanistic chemistry reviewed in *Sections 3–6* reveals a consistent structural pattern across all WPCB recovery pathways: effective metal recovery requires both (i) disruption of the cross-linked epoxy matrix that physically encapsulates metal particles, and (ii) a chemical driving force: acid, redox, biological, or solvating, capable of mobilizing the liberated metal into solution. Pyrometallurgy and conventional hydrometallurgy satisfy the first requirement through combustion or mechanical comminution and the second through high-temperature collection or strong-acid/cyanide chemistry, but at the cost of either uncontrolled BFR emission or complete neglect of the polymer fraction. Bioleaching satisfies the chemical driving-force requirement elegantly, through biologically regenerated Fe₃⁺ and self-generated acids, but depends on prior mechanical liberation of metal surfaces and proceeds over days to weeks because microbial reaction rates are inherently slower than thermochemical ones. HTP is mechanistically distinctive in that the same medium. Water at elevated temperature and pressure, simultaneously performs both functions: the organic-reaction chemistry of *Section 5.1* disrupts the polymer matrix while the coupled leaching mechanisms of *Section 5.3* mobilize the liberated metals, explaining the comparatively short residence times (30–120 minutes) achievable relative to bioleaching. DES and ionic-liquid leaching, reviewed in *Section 6*, occupy an intermediate position: they provide an effective and tunable chemical driving force at near-ambient temperature and pressure, but, as currently formulated, do not independently disrupt the cross-linked epoxy matrix or manage BFR content, and therefore perform best as a downstream step following mechanical or thermal pre-treatment. **Figure 5** summarizes these trade-offs visually across six performance dimensions: pyrometallurgy scores highest on industrial maturity and precious-metal recovery but lowest on BFR/polymer management and reagent safety; bioleaching scores highest on reagent safety but lowest on process speed. HTP is the only pathway scoring well on both BFR/polymer management and process speed simultaneously, though it remains comparatively weak on industrial maturity; and DES/ionic-liquid leaching occupies a middle position overall, strongest on reagent safety and process speed but structurally limited on BFR/polymer management together confirming that pathway selection is a multi-criteria decision rather than a search for a single dominant technology.

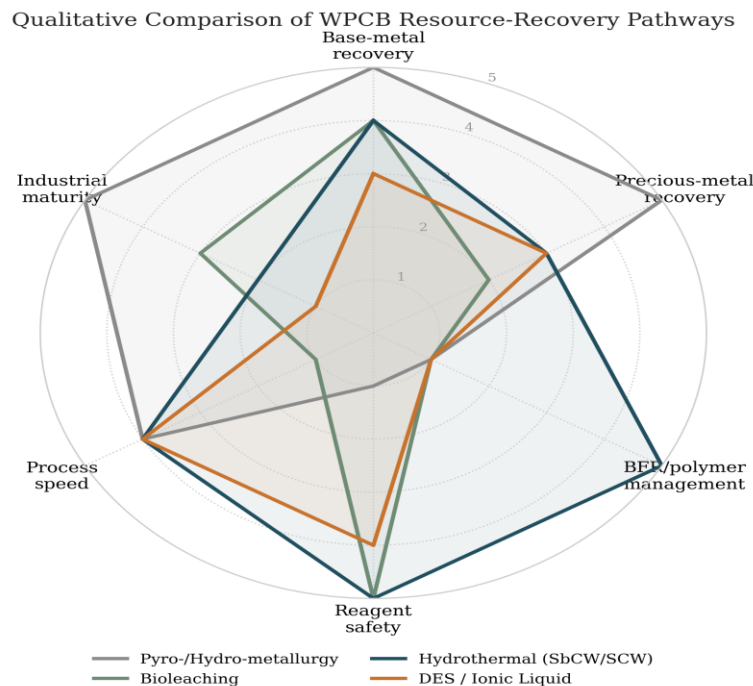


Figure 5. Qualitative comparison of WPCB resource-recovery pathways across six performance dimensions, synthesized from the evidence reviewed in Sections 3–6 and summarized in Table 8

7.2 Performance and Process Synthesis

Table 6 synthesizes representative performance, environmental, and economic indicators across all reviewed pathways. No single technology dominates across all criteria. Pyrometallurgy retains the highest precious-metal recovery and the most mature industrial infrastructure but carries the greatest emissions liability and forgoes all polymer-fraction value. HTP offers the most complete single-step solution, enabling simultaneous metal liberation and BFR destruction; however, it remains comparatively immature at the industrial scale, with most supporting evidence still derived from laboratory batch reactors rather than continuous pilot-scale or industrial systems. Bioleaching offers the lowest reagent and energy burden per unit of metal recovered but the longest processing time, limiting throughput-constrained applications. DES/IL leaching offers low toxicity and ambient operating conditions but, in the absence of an effective matrix-disruption step, depends on hybridization with another pathway to reach industrially relevant overall recovery.

Table 6. Comparative synthesis of WPCB resource-recovery pathways across key performance dimensions [9]–[13], [19]–[22], [36], [52], [57]–[63]

Dimension	Pyro-/Hydro-metallurgy	Bioleaching	Hydrothermal (SbCW/SCW)	DES / Ionic Liquid
Precious-metal recovery	Highest (>95% Au)	Limited; needs long contact	Moderate–high (>300 °C needed)	Formulation-dependent (up to ~90% Au reported)
Base-metal recovery	High (~95% Cu)	Moderate–high (60–99%)	High (76–94% Cu typical)	Variable (16–99% Cu reported)
BFR / polymer management	Combustion only (PBDD/F risk)	Not addressed	Concurrent debromination (>95%)	Not addressed
Reagent hazard	High (acid/cyanide)	Low (biogenic)	None (water only)	Low–moderate
Typical residence time	Hours	10–30 days	30–120 minutes	Hours
Industrial maturity	Mature, commercial scale	Pilot to early commercial	Laboratory to pilot scale	Laboratory scale

Figure 6 illustrates this trade-off concretely for copper, the highest-value base metal common to all four pathways: acid hydrometallurgy delivers a reliable ~95% within hours, HTP reaches a comparable 76–94% within 30–120 minutes,

and bioleaching and DES/IL leaching can each match or exceed both but only under favorable, well-optimized conditions, with substantially wider reported ranges reflecting their greater sensitivity to formulation and feedstock.

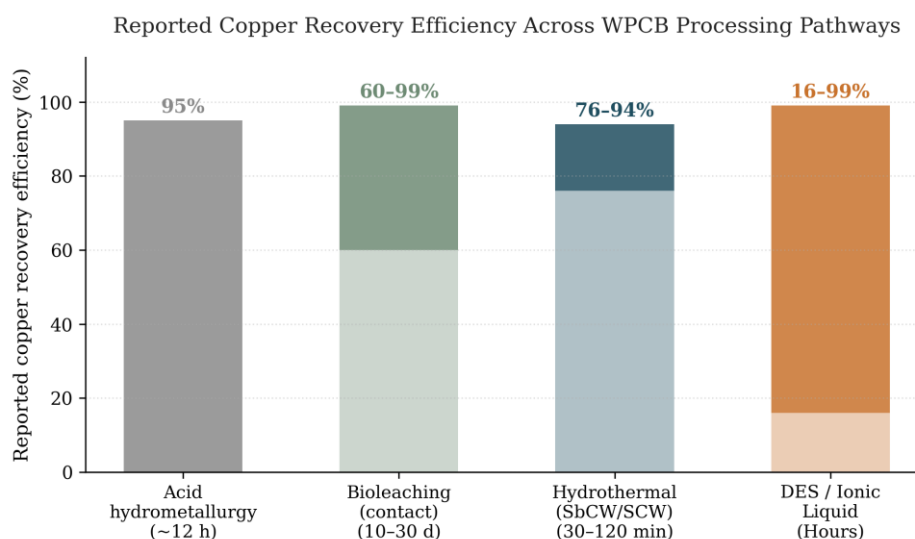


Figure 6. Reported copper recovery efficiency and typical processing time across WPCB resource-recovery pathways, synthesized from [19]–[22], [36], [57]–[63]

7.3 Environmental Performance and Circular-Economy Alignment

Life-cycle assessment (LCA) studies of e-waste recycling pathways consistently identify metal-recovery value as the dominant factor offsetting process-stage environmental burdens, but also confirm that the choice of recovery technology materially affects net environmental performance. A comprehensive review of LCA applications in e-waste recycling concludes that environmental sustainability gains are most pronounced for high-value metal recovery and that biometallurgical pathways remain comparatively under-studied from an LCA perspective despite their generally lower reagent and energy intensity, identifying this as a notable evidence gap rather than a demonstrated environmental disadvantage [64]. More recent integrated LCA and techno-economic analysis of pyrometallurgical WPCB processing demonstrates that targeted interventions, substituting natural gas for diesel, recovering waste heat for power generation, and pursuing grid decarbonization which can reduce environmental burdens by 7–52% without changing the underlying pyrometallurgical technology, indicating that incremental process optimization within an existing technology family can deliver environmental gains comparable to switching technology families altogether [65]. For HTP specifically, dedicated LCA studies at pilot or industrial scale remain scarce in the literature reviewed for this paper, a gap discussed further in *Section 8*.

Within a circular-economy framework, WPCB recovery technologies should be evaluated not only on metal-recovery efficiency but on their capacity to recover value from all three major material fractions, such as metal, ceramic, and polymer. By this broader criterion, HTP is mechanistically best positioned among the pathways reviewed here, since it is the only route demonstrated to simultaneously recover metals, destroy hazardous BFR content, and, as shown by Gandon-Ros et al. [52], recover the glass-fiber reinforcement fraction in reusable form. Realizing this circular-economy advantage at scale, however, depends on closing the techno-economic and life-cycle evidence gaps discussed in *Section 8*.

VIII. FUTURE PERSPECTIVES

The comparative synthesis of *Section 7* points to a field in which no single pathway is yet complete: direct cross-pathway mechanistic comparisons on identical feedstocks remain rare, techno-economic and life-cycle evidence for HTP at scale is sparse relative to the pyrometallurgical and bioleaching literature, and the reaction mechanisms governing precious-metal mobilization in hydrothermal media remain comparatively underdeveloped relative to the well-characterized base-metal chemistry of *Section 5.3*. Four directions appear particularly promising for closing these gaps and advancing WPCB resource-recovery science toward industrial deployment.

8.1 Hybrid Bio-Hydrothermal Process Trains

The mechanistic complementarity established in *Section 7.1*, with HTP excelling at rapid matrix disruption and concurrent BFR destruction and bioleaching excelling at low-impact, highly selective metal mobilization, suggests that a hybrid process could be advantageous. In such a process, mild hydrothermal pre-treatment (e.g., 200–250 °C), sufficient to hydrolyze the epoxy matrix without causing excessive reprecipitation as indicated in **Table 4**, would first be used to liberate

metal particles and reduce particle size. This step would then be followed by bioleaching of the resulting metal-enriched, polymer-depleted solid fraction, thereby combining the short residence time of the thermal stage with the low reagent demand of the biological stage. Realizing this concept requires dedicated experimental work quantifying whether residual hydrothermal-stage organic intermediates (*Section 5.1*) are inhibitory or beneficial to the acidophilic consortia reviewed in *Section 4*, since elevated dissolved organic-acid concentrations could plausibly affect bacterial viability.

8.2 Machine-Learning-Assisted Process Optimization and Standardized Reporting

The multi-variable, often nonlinear and metal-specific optimization landscape evident in **Table 4** and *Section 5.4*, spanning temperature, pressure, residence time, and S/L ratio, with distinct optima for each target metal is well suited to data-driven optimization approaches. Machine-learning surrogate models trained on the heterogeneous experimental datasets reviewed in this paper could, in principle, identify joint operating windows that balance recovery across multiple target metals simultaneously, a multi-objective optimization problem that is difficult to solve through traditional one-variable-at-a-time experimentation. Realizing this direction is presently constrained by inconsistent baseline reporting across the literature. WPCB source and pre-treatment, particle size, S/L ratio, and analytical method for metal quantification are not uniformly reported. Standardized data reporting would be a near-term prerequisite for productive application of machine-learning methods to this field.

8.3 Standardized Environmental and Economic Performance Metrics

Closing the life-cycle evidence gap for HTP will require the WPCB recovery research community to adopt more consistent LCA system boundaries and functional units, enabling direct comparison against the comparatively well-characterized pyrometallurgical [65] and bioleaching [9] LCA literature. Given the demonstrated sensitivity of pyrometallurgical environmental performance to energy-source decisions such as waste-heat recovery and grid decarbonization [65], future hydrothermal LCA studies should explicitly account for reactor heating-energy source, since this factor is likely to be similarly material to HTP's net environmental performance.

8.4 Targeted Mechanistic Studies of Precious-Metal and Critical-Metal Mobilization

Addressing the mechanistic gap around precious-metal behavior will require dedicated spectroscopic and kinetic studies of gold, silver, and palladium speciation and dissolution under hydrothermal conditions, analogous to the established base-metal framework of *Section 5.3*. Given the emerging recognition of WPCBs as a secondary critical-metal resource discussed in *Section 2.2* [18], future mechanistic work should also extend beyond the classical base- and precious-metal focus of the present literature to characterize rare-earth and other critical-element mobilization under hydrothermal and hybrid bio-hydrothermal conditions, supporting the broader resource-recovery rationale established in this review.

IX. CONCLUSION

This review has critically synthesized the mechanistic chemistry, performance, and limitations of the principal technology families used for resource recovery from waste printed circuit boards (WPCBs): pyrometallurgical and acid/cyanide hydrometallurgical processing, biohydrometallurgical bioleaching, Hydrothermal processing (HTP) using subcritical and supercritical water (SbCW/SCW), and emerging green-solvent leaching based on deep eutectic solvents and ionic liquids. Each pathway addresses the central technical obstacle posed by the cross-linked, brominated epoxy matrix of WPCBs through a distinct mechanistic strategy: thermal or strong-chemical disruption in conventional processing, biologically mediated redox and acid generation in bioleaching, coupled organic-reaction and metal-leaching chemistry within a single aqueous medium in HTP, and tunable coordination chemistry in DES/IL systems. The comparative synthesis developed in *Section 7* demonstrates that no single pathway currently dominates across all performance, environmental, and economic dimensions, and that HTP occupies a mechanistically distinctive position as the only reviewed route capable of simultaneously liberating metals, destroying brominated flame retardants, and recovering reusable glass-fiber reinforcement within a single processing step.

With global e-waste generation on track to reach 82 million tons (Mt) by 2030 against a formal recycling rate that remains below one quarter of generated mass [1], the resource-recovery technologies reviewed in this paper represent a substantial and currently underexploited opportunity for both environmental harm reduction and material-value recovery. Realizing this opportunity at industrial scale will depend on the development of unified cross-pathway performance data, robust techno-economic and life-cycle evidence for HTP, and systematic exploration of hybrid bio-hydrothermal and hydrothermal-DES process trains. The future research directions proposed in *Section 8* are intended to provide a concrete agenda for accelerating the translation of the mechanistic understanding synthesized in this review into deployable, circular-economy-aligned WPCB recovery technology.

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CONFLICT OF INTEREST

The author declares no conflict of interest.

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