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GALLIUM RECOVERY FROM ORES AND SECONDARY RESOURCES (2020–2025): A CRITICAL REVIEW OF PROCESS CHEMISTRY, SELECTIVITY CHALLENGES, AND INDUSTRIAL READINESS

RECUPERAÇÃO DE GÁLIO A PARTIR DE MINÉRIOS E RECURSOS SECUNDÁRIOS (2020–2025): UMA REVISÃO CRÍTICA DA QUÍMICA DE PROCESSOS, DESAFIOS DE SELETIVIDADE E PRONTIDÃO INDUSTRIAL

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ABSTRACT
Gallium recovery from primary and secondary resources has attracted increasing attention between 2020 and 2025 due to its relevance for advanced electronic and energy applications; however, this critical review demonstrates that gallium recovery is rarely constrained by dissolution efficiency and is instead governed by downstream separation and purification challenges. In real industrial liquors, Ga(III) exhibits highly adaptable speciation, leading to strong chemical competition with aluminum, iron, and zinc across acidic, neutral, and alkaline environments. This behavior fundamentally controls selectivity, reagent consumption, and process stability, and explains the frequent discrepancy between laboratory-scale studies using synthetic solutions and performance in multicomponent process liquors. This review critically examines alkaline Bayer-type systems, acidic leaching of red mud, fly ash, and metallurgical residues, halide-based pathways, and recycling-oriented flowsheets for electronic waste, with emphasis on solvent extraction, ion exchange and adsorption, membrane-assisted separations, selective precipitation, and electrochemical polishing as core purification stages. Comparative analysis of flowsheet architectures reveals a systematic shift in process complexity from dissolution to purification, reagent recycling, and residue management, which ultimately determines environmental and economic viability. From a separation and purification perspective, speciation-aware process design, realistic testing under representative liquor conditions, and integrated multistage flowsheets emerge as essential requirements, with selectivity under matrix competition, operational stability over repeated cycles, and closed-loop operation identified as the dominant performance metrics for translating gallium recovery concepts from laboratory studies to industrial implementation.

KEYWORDS. Gallium recovery. Hydrometallurgy. Critical metals. Solvent extraction. Secondary resources.

RESUMO
A recuperação de gálio a partir de recursos primários e secundários tem atraído crescente atenção entre 2020 e 2025 devido à sua relevância para aplicações avançadas em eletrônica e energia. No entanto, esta revisão crítica demonstra que a recuperação de gálio raramente é limitada pela eficiência de dissolução, sendo, em vez disso, governada por desafios nas etapas subsequentes de separação e purificação. Em licores industriais reais, o Ga(III) apresenta especiação altamente

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adaptável, resultando em forte competição química com alumínio, ferro e zinco em ambientes ácidos, neutros e alcalinos. Esse comportamento controla fundamentalmente a seletividade, o consumo de reagentes e a estabilidade do processo, explicando a frequente discrepância entre estudos em escala laboratorial realizados com soluções sintéticas e o desempenho observado em licores de processo multicomponentes. Esta revisão examina criticamente sistemas alcalinos do tipo Bayer, a lixiviação ácida de lama vermelha, cinzas volantes e resíduos metalúrgicos, rotas baseadas em haletos e fluxogramas orientados à reciclagem de resíduos eletrônicos, com ênfase em extração por solventes, troca iônica e adsorção, separações assistidas por membranas, precipitação seletiva e polimento eletroquímico como etapas centrais de purificação. A análise comparativa das arquiteturas de fluxogramas revela uma mudança sistemática na complexidade do processo, que se desloca da dissolução para a purificação, reciclagem de reagentes e gestão de resíduos, fatores que, em última instância, determinam a viabilidade ambiental e econômica. Sob a perspectiva de separação e purificação, o desenvolvimento de processos orientados pela especiação, a realização de testes realistas em condições representativas de licor de processo e a integração de fluxogramas multietapas emergem como requisitos essenciais. Nesse contexto, a seletividade sob competição de matriz, a estabilidade operacional ao longo de ciclos repetidos e a operação em circuito fechado são identificadas como métricas de desempenho dominantes para a transposição de conceitos de recuperação de gálio de estudos laboratoriais para a implementação industrial.

PALAVRAS-CHAVE: Recuperação de gálio. Hidrometalurgia. Metais críticos. Extração por solventes. Recursos secundários.

RESUMEN

La recuperación de galio a partir de recursos primarios y secundarios ha atraído una creciente atención entre 2020 y 2025 debido a su relevancia para aplicaciones avanzadas en electrónica y energía. Sin embargo, esta revisión crítica demuestra que la recuperación de galio rara vez está limitada por la eficiencia de disolución, sino que está gobernada principalmente por los desafíos asociados con las etapas posteriores de separación y purificación. En licores industriales reales, el Ga(III) presenta una especiación altamente adaptable, lo que conduce a una fuerte competencia química con aluminio, hierro y zinc en medios ácidos, neutros y alcalinos. Este comportamiento controla de manera fundamental la selectividad, el consumo de reactivos y la estabilidad del proceso, y explica la frecuente discrepancia entre los estudios a escala de laboratorio realizados con soluciones sintéticas y el desempeño observado en licores de proceso multicomponentes. Esta revisión examina críticamente los sistemas alcalinos tipo Bayer, la lixiviación ácida de lodos rojos, cenizas volantes y residuos metalúrgicos, las rutas basadas en haluros y los diagramas de flujo orientados al reciclaje de residuos electrónicos, con énfasis en la extracción por solventes, el intercambio iónico y la adsorción, las separaciones asistidas por membranas, la precipitación selectiva y el pulido electroquímico como etapas centrales de purificación. El análisis comparativo de las arquitecturas de los diagramas de flujo revela un cambio sistemático en la complejidad del proceso, que se desplaza desde la disolución hacia la purificación, el reciclaje de reactivos y la gestión de residuos, factores que finalmente determinan la viabilidad ambiental y económica. Desde la perspectiva de separación y purificación, el diseño de procesos basado en la especiación, la realización de ensayos realistas bajo condiciones representativas de licor de proceso y la integración de diagramas de flujo multietapa emergen como requisitos esenciales. En este contexto, la selectividad bajo competencia de matriz, la estabilidad operativa a lo largo de ciclos repetidos y la operación en circuito cerrado se identifican como métricas de desempeño dominantes para trasladar los conceptos de recuperación de galio desde estudios de laboratorio hacia su implementación industrial.

PALABRAS CLAVE: Recuperación de galio. Hidrometalurgia. Metales críticos. Extracción por solventes. Recursos secundarios.

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1. INTRODUCTION

Gallium (Ga) is vital for advanced tech like optoelectronics and photovoltaics, but its supply depends on recovery from alumina refining and zinc processing. This supply is decoupled from demand and tied to aluminum production, creating vulnerabilities due to geopolitical issues and low recycling. Studies show that secondary sourcing and better recovery are crucial to mitigate long-term risks.

Between 2020 and 2025, research on gallium recovery expanded beyond the Bayer liquor route, examining a variety of feedstocks such as bauxite ores, red mud, fly ash, gangue, zinc residues, and slags. Urban and industrial wastes like LED scrap, GaAs waste, and CIGS PV materials were also studied (Agrawal; Dhawan, 2022; Pan *et al.,* 2023; Hu *et al.,* 2022; Illés; Kékési, 2023). Reviews confirm the technical feasibility of recovering gallium from many matrices but highlight inconsistencies in performance, feedstock realism, and process validation (Huang *et al.,* 2024b; Kluczka, 2024).

A recurring and critical observation across these studies is that gallium dissolution is rarely the limiting step. Both alkaline and acidic leaching routes can effectively transfer Ga into solution under relatively mild conditions. The decisive challenge is selective separation and purification. This challenge is particularly acute in solutions dominated by aluminum, iron, and zinc, where concentrations are several orders of magnitude higher than that of gallium. This issue is intrinsic to Bayer liquor systems, where Ga must be recovered under highly alkaline conditions and extreme aluminum loading (Qu *et al.,* 2024). It becomes even more severe in acidic leachates of red mud, fly ash, and metallurgical residues. In these systems, extensive co-dissolution of Fe and Al severely compromises downstream selectivity (Zhao *et al.,* 2021; Zhu *et al.,* 2024).

In this context, separation and purification technologies—rather than extraction efficiency—ultimately determine the technical and economic viability of gallium recovery flowsheets. As a result, solvent extraction, ion exchange and adsorption, membrane-based separations, and electrochemical polishing have emerged as core unit operations for gallium concentration and purification. Numerous studies report promising selectivity using tailored extractants, functionalized sorbents, or hybrid separation schemes (Asadian; Ahmadi, 2020; Guo *et al.,* 2020; Zhang *et al.,* 2021). Nevertheless, when evaluated under industrially relevant conditions, many of these approaches exhibit critical weaknesses. These include poor tolerance to matrix impurities, phase disengagement problems, limited regenerability, and high reagent consumption. Collectively, these limitations constrain technology readiness levels (Dhiman *et al.,* 2024; Losev *et al.,* 2024).

Secondary-resource routes add complexity. Although often seen in circular-economy narratives, gallium recovery from red mud, coal ash, and urban wastes faces challenges from unfavorable mass balances. Aggressive chemical needs limit sustainability. Reagent recycling and residue management are often inadequately integrated (Archambo; Kawatra, 2021; Pavón *et al.,*

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2025). In coal and ash systems, gallium presence depends on mineralogy, affecting leaching and separation (Wen et al., 2021; Rudnik, 2024). Urban mining streams are richer in gallium but pose challenges, needing selective, robust separation strategies for complex, hazardous mixtures (Valero *et al.,* 2021; Hu *et al.,* 2022; Karali; Shah, 2022; Liu *et al.,* 2024a).

This article reviews gallium recovery from 2020-2025, focusing on separation and purification. It covers sources, leaching, and downstream selectivity challenges. Techniques like solvent extraction, ion exchange, membranes, and electrochemical methods are compared on Ga/Al–Fe–Zn selectivity, impurity tolerance, reagent use, and application. The review highlights advances and bottlenecks to guide industrial gallium separation tech (Pan *et al.,* 2024).

Accordingly, the next section analyzes gallium-bearing feedstocks and modes of occurrence. These parameters fundamentally govern impurity co-dissolution and define the separation-selectivity challenges that dominate downstream purification performance.

2. METHODOLOGY

This review followed PRISMA 2020 guidelines, tailored to engineering, focusing on separation and purification tech rather than quantitative meta-analysis (Page *et al.,* 2021).

The survey reviewed peer-reviewed articles, review papers, theses, conference proceedings, and authoritative reports from 2020-2025 on gallium recovery from ores and secondary sources. Searches in Scopus, Web of Science, ScienceDirect, and Google Scholar used keywords like gallium recovery, hydrometallurgy, solvent extraction, ion exchange, membrane separation, electrochemical processes, Bayer liquor, red mud, zinc residues, coal wastes, and urban mining streams.

Records were initially screened based on title and abstract. This step ensured relevance to gallium separation and purification. Studies focusing exclusively on geological characterization, analytical detection, or unrelated material applications were excluded. Full-text assessment then prioritized works reporting separation performance. Particular attention was given to selectivity in aluminum-, iron-, and zinc-rich matrices. Process robustness and evidence of applicability to real process liquors or integrated flowsheets were also considered.

Ninety-eight references met inclusion criteria. Instead of merely aggregating extraction efficiencies, studies were critically evaluated on separation-relevant criteria like selectivity, impurity tolerance, reagent use, recyclability, and technology readiness. The PRISMA framework ensured transparency, reproducibility, and systematic review, facilitating critical, comparative process analysis (Page *et al.,* 2021).

To further ensure transparency and reproducibility in the literature selection process, this review followed a structured methodology based on the PRISMA 2020 framework.

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Figure 1 summarizes the identification, screening, eligibility, and inclusion steps. These steps were applied to literature published between 2020 and 2025 on gallium recovery from primary and secondary sources, with a specific emphasis on separation and purification technologies.

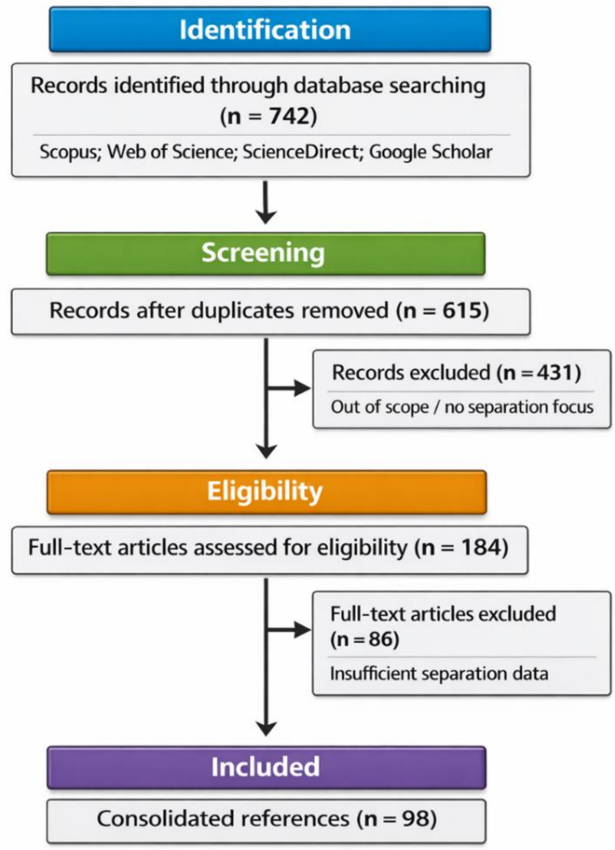

Figure 1. PRISMA 2020 flow diagram illustrating the literature identification, screening, eligibility assessment, and inclusion process adopted in this review. Adapted from Page et al. (2021).

As shown in Figure 1, the initial database search yielded 742 records, which were reduced to 615 after duplicate removal. Title and abstract screening excluded 431 records that were outside the scope of this review or lacked a clear focus on separation and purification processes. Full-text assessment of the remaining 184 articles excluded 86 studies for insufficient separation-related data, resulting in a final dataset of 98 references included in the qualitative synthesis.

3. SEPARATION AND PURIFICATION TECHNOLOGIES

3.1. General considerations: selectivity as the governing criterion

From 2020 to 2025, separation and purification—rather than dissolution—are the main process constraints for gallium feedstocks. Gallium occurs at trace to minor levels, while solutions mainly contain aluminum, iron, zinc, or alkali metals, creating unfavorable concentration ratios that hinder separation (Qu *et al.,* 2024; Rudnik, 2024). Separation must be evaluated by selectivity, impurity tolerance, and robustness, not just extraction yield.

This selectivity challenge is particularly evident in Bayer liquor systems. In these systems, gallium must be recovered under strongly alkaline conditions and in the presence of extremely high aluminum concentrations (Bagdaulet *et al.,* 2024; Qu *et al.,* 2024). Similar limitations occur in acidic leachates derived from red mud, fly ash, zinc residues, and electronic waste. In these cases, extensive co-dissolution of iron and zinc significantly hampers selective gallium recovery (Zhao *et al.,* 2021; Zhu *et al.,* 2024). These pronounced matrix effects help explain why many laboratory-scale studies fail to translate into integrated or industrially relevant flowsheets, despite reporting high apparent gallium recoveries.

3.2. Solvent extraction

Solvent extraction (SX) remains the most extensively studied separation technology for gallium recovery. This prominence stems largely from its scalability and compatibility with established hydrometallurgical circuits. Organophosphorus extractants, tertiary amines, hydroxamic acids, and ionic-liquid-based systems have been widely explored and applied for gallium separation from both alkaline and acidic solutions (Song *et al.,* 2020; Zhang *et al.,* 2021; Guo *et al.,* 2024).

In Bayer liquor applications, SX must operate under highly alkaline conditions while handling extreme Al/Ga concentration ratios. Studies using selective extractants or multi-stage extraction–stripping schemes show that gallium can be effectively concentrated. However, this often entails high reagent consumption. Complex phase management and multi-step circuits are also commonly required (Bagdaulet *et al.,* 2024; Qu *et al.,* 2024).

Acidic systems derived from zinc residues or coal fly ash generally show improved gallium extractability. However, the co-extraction of iron and zinc remains a major challenge. This often requires additional scrubbing or selective stripping stages, further increasing process complexity and operational costs (Zhao *et al.,* 2020; Zhang; Rao, 2024).

A recurring limitation of SX-based approaches is the lack of long-term stability and regenerability data. Many studies report only single-cycle extraction performance, often using synthetic or simplified solutions. In contrast, evidence of sustained operation under real-liquor conditions remains scarce (Losev *et al.,* 2024; Qi *et al.,* 2025). As a consequence, SX performance metrics reported in the literature are frequently not directly comparable and may also fail to represent industrially relevant operation.

Table 1 summarizes recent advances (2020–2025) in solvent extraction systems for gallium recovery from primary and secondary resources. The comparison emphasizes the chemistry of the extractant, feedstock characteristics, and solution conditions. It also highlights selectivity relative to major competing metals, including aluminum, iron, and zinc. Finally, practical operational constraints reported in the literature are critically assessed.

Table 1. Comparative performance of solvent extraction systems for gallium recovery. Adapted from Song et al. (2020), Zhang et al. (2021), Guo et al. (2024), Zhao et al. (2020), and Qi et al. (2025)

Extractant / System	Feedstock Type	Leach Solution Chemistry	Ga Selectivity vs. Al / Fe / Zn	Typical Operating Conditions	Key Advantages	Reported Operational Limitations
D2EHPA (Di-2-ethylhexyl phosphoric acid)	Bayer liquor, bauxite residue leachates	Strongly alkaline (NaOH)	Low vs Al; moderate vs Zn	pH > 12; O/A = 1–2	Industrially established; low cost	Severe co-extraction of Al; emulsification; high reagent consumption
EHEHPA / P507	Acidic bauxite leachates	H_2SO_4, pH 1–3	Moderate vs Al; low vs Fe	pH 1.5–2.5	Higher Ga affinity than D2EHPA	Poor Fe rejection; phase stability issues
P204 (HDEHP)	Secondary residues, fly ash leachates	HCl or H_2SO_4	Moderate vs Zn; low vs Al	pH 1–2	Simple stripping; good kinetics	Limited selectivity; organic degradation
Aliquat 336 (quaternary ammonium)	Zinc refinery residues, coal fly ash	Chloride media (HCl)	High vs Al/Fe; moderate vs Zn	$[Cl^-] > 4$ M	Strong Ga–Cl complex extraction	Corrosive environment; chloride management
TBP (Tributyl phosphate)	Chloride-based synthetic solutions	HCl	Moderate vs Al; high vs Fe	3–6 M HCl	Stable organic phase; low viscosity	Requires high acidity; poor loading capacity
Mixed extractants (D2EHPA + TOPO)	Bayer liquor, red mud leachates	Alkaline / weak acidic	Improved vs Al	pH 2–4	Synergistic Ga extraction	Complex formulation; regeneration issues
Task-specific ionic liquids (TSILs)	Synthetic & secondary liquors	Acidic & chloride media	Very high vs Al/Fe/Zn	Mild pH, low O/A	Exceptional selectivity; low volatility	High cost; limited scale-up data
Amide-based extractants	Electronic waste leachates	H_2SO_4, pH 1–2	High vs Zn; moderate vs Al	Ambient temperature	Lower environmental impact	Limited long-term stability

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Despite significant advances in extractant design and selectivity, solvent extraction systems for gallium remain highly sensitive to solution chemistry and impurity levels. These limitations have driven the growing integration of solvent extraction with complementary purification methods, including ion exchange, adsorption, and membrane-assisted separations, as discussed in the following section.ion.

3.3. Ion exchange and adsorption

Ion exchange and adsorption technologies have attracted growing interest as alternatives or complements to solvent extraction, particularly for dilute or chemically complex gallium-bearing solutions. Functionalized resins, biopolymers, inorganic sorbents, and hybrid materials have been proposed to enhance gallium selectivity. These materials rely on coordination chemistry, ion-exchange specificity, or size-exclusion effects (Guo *et al.,* 2020; Díez *et al.,* 2021; Ciocărlie *et al.,* 2024).

Several studies report on promising gallium adsorption capacities and high selectivity under controlled laboratory conditions. However, performance often deteriorates sharply when aluminum or iron concentrations are elevated (Saez *et al.,* 2024; Rudnik, 2024). Regeneration efficiency remains a critical concern. Repeated adsorption–desorption cycles may cause progressive capacity loss or structural degradation of the sorbent (Díez *et al.,* 2021; Ciocărlie *et al.,* 2024).

Biosorption and bio-assisted approaches represent a more exploratory branch of this research area. These include siderophore-mediated systems that exploit biologically driven selectivity mechanisms (Saikia *et al.,* 2022; Dhiman *et al.,* 2024). Despite their conceptual appeal, these approaches face significant challenges. Kinetic limitations, process control, and scalability remain unresolved. Although these methods align well with sustainability and circular-economy narratives, their integration into industrial hydrometallurgical circuits remains largely conceptual.

3.4. Membrane-based separations

Membrane-based technologies have been investigated as alternatives or complements to conventional separation methods. These include supported liquid membranes and hybrid membrane–solvent extraction (SX) systems. Their primary objective is to reduce solvent losses and improve phase-contact efficiency (Asadian; Ahmadi, 2020; Bayır, 2023). Under optimized conditions, these systems can achieve high gallium selectivity, particularly in streams with low gallium concentrations.

Despite these advantages, several technical barriers persist. Membrane fouling continues to constrain operational stability. Mechanical robustness is often inadequate for prolonged use. In addition, membrane performance is highly sensitive to solution chemistry and impurity levels (Kamran; Irannajad, 2024). As a result, most reported studies remain confined to the laboratory scale. Convincing demonstrations of long-term operation under realistic feed compositions are still lacking.

3.5. Electrochemical separation and polishing

Electrochemical techniques are typically used as final purification steps rather than primary separation tools. These methods include conventional electrowinning and hybrid electrochemical polishing. Recent studies show that pulse-assisted electrowinning can improve current efficiency. Cyclone-enhanced electrochemical configurations have also been reported to reduce energy consumption. These advances have been demonstrated for gallium recovery from zinc hydrometallurgical solutions and from GaAs-derived liquors (Liu *et al.,* 2023; Liu *et al.,* 2024a; Wang *et al.,* 2024a).

Despite these developments, electrochemical routes require relatively clean feed solutions. Impurities can cause electrode poisoning and parasitic side reactions. This requirement underscores the need for effective upstream separation and purification steps (Illés; Kékési, 2023; Wang *et al.,* 2024b). Consequently, electrochemical methods are best regarded as complementary unit operations within integrated gallium recovery flowsheets.

3.6. Integrated and hybrid separation flowsheets

An emerging trend in recent literature is the development of hybrid flowsheets that integrate multiple separation techniques. These configurations are designed to overcome the limitations of individual unit operations. Reported examples include solvent extraction followed by ion exchange polishing, adsorption-assisted solvent extraction, and the incorporation of electrochemical finishing stages (Dhiman *et al.,* 2024; Liu *et al.,* 2024b; Huang *et al.,* 2025).

The need for such hybrid approaches stems from the intrinsic complexity of gallium-bearing liquors. This complexity is especially pronounced in streams derived from secondary resources and residue-based feedstocks. In these systems, effective gallium recovery rarely relies on a single separation step. Instead, it requires integrating multiple separation and purification stages in sequence.

Figure 2 shows a conceptual integrated flowsheet for gallium recovery from complex liquors. The scheme highlights the complementary roles of solvent extraction, ion exchange or adsorption, membrane-assisted separation, and electrochemical polishing. Together, these unit operations enable progressive impurity removal and concentration, ultimately enabling the production of high-purity gallium products.

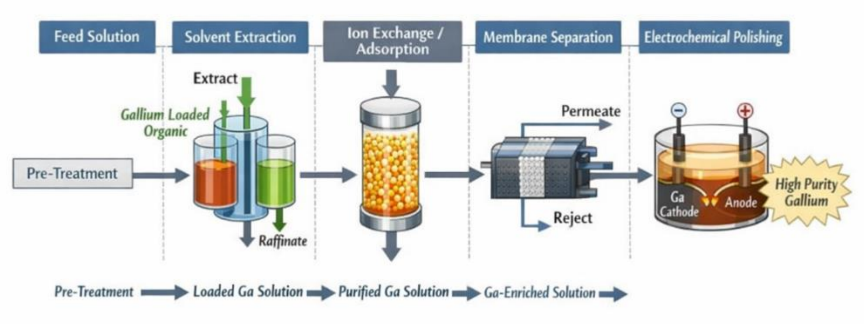

Figure 2. Conceptual integrated flowsheet for gallium recovery from complex liquors. Adapted from Qu et al. (2024).

As shown in Figure 2, gallium recovery performance is determined by the efficiency of sequential separation steps rather than by leaching alone. Hybrid configurations progressively reduce impurity loads but at the cost of increased process complexity and capital intensity, underscoring the need for selectivity-driven flowsheet optimization.

3.7. Critical assessment and technology readiness

Despite the broad range of separation technologies reported between 2020 and 2025, few studies provide convincing evidence of industrial readiness. Many investigations rely heavily on synthetic or simplified solutions. Complete mass balances are often missing, and analyses of reagent recycling and consumption are frequently absent. In addition, scale-up constraints are rarely discussed systematically (Losev *et al.,* 2024; Pavón *et al.,* 2025).

From a separation-engineering perspective, future progress depends less on discovering new extractants or sorbents. Instead, it hinges on demonstrating robust, selective performance under realistic operating conditions. These demonstrations must be supported by integrated process evaluation, realistic feed compositions, and lifecycle-aware design approaches (Karali; Shah, 2022; Zuo *et al.,* 2025).

Although separation and purification technologies ultimately determine the technical feasibility of gallium recovery, their performance is constrained by feedstock characteristics and gallium speciation. These upstream factors directly influence impurity co-dissolution and separation selectivity. Accordingly, the next section examines how gallium occurrence, mineralogical associations, and matrix composition govern separation efficiency and process integration across primary and secondary resources.

4. FEEDSTOCKS AND GALLIUM OCCURRENCE

The effectiveness of gallium separation and purification technologies is intrinsically linked to the nature of the feedstock and to the physicochemical form in which gallium occurs. Unlike base metals, gallium is rarely present as a discrete mineral phase.

Instead, it typically substitutes for aluminum, iron, or zinc within host matrices. As a result, gallium occurs in low-grade, highly dispersed forms (Rudnik, 2024; Qu *et al.,* 2024).

Between 2020 and 2025, the literature identifies four dominant categories of gallium-bearing feedstocks. The first comprises Bayer process liquors from bauxite processing. The second comprises solid residues, such as red mud and coal fly ash. The third comprises zinc and lead metallurgical residues. The fourth comprises secondary resources, including electronic waste and GaAs-related scrap (Zhao *et al.,* 2021; Bagdaulet *et al.,* 2024; Liu *et al.,* 2024b). Each feedstock presents distinct challenges related to gallium concentration, chemical speciation, and impurity profile. These factors directly influence the selection and performance of downstream separation strategies (Abdulvaliev *et al.,* 2021).

4.1. Primary and secondary gallium-bearing feedstocks

4.1.1. Bayer liquor and bauxite-derived streams

Bayer liquor remains the most established industrial source of gallium and accounts for the majority of global primary gallium production. In this system, gallium occurs predominantly as soluble gallate species under strongly alkaline conditions. These species coexist with extremely high concentrations of aluminate ions (Qu *et al.,* 2024; Bagdaulet *et al.,* 2024). Typical gallium concentrations range from a few tens to several hundreds of $mg \cdot L^{-1}$. Consequently, Al/Ga ratios can exceed 10^4–10^5.

This extreme compositional imbalance explains why separation, rather than extraction, is the critical bottleneck in Bayer-based gallium recovery. Gallium speciation in alkaline media is highly sensitive to pH, temperature, and liquor composition. These variables strongly influence selectivity in solvent extraction or ion exchange processes (Zhang *et al.,* 2021; Rudnik, 2024). Moreover, long residence times and continuous liquor recycling introduce kinetic and stability constraints. These effects are rarely captured in laboratory-scale studies (Archambo; Kawatra, 2021; Mi *et al.,* 2022).

Table 2 compiles typical compositions of Bayer process liquors reported in gallium recovery studies published between 2020 and 2025. Particular emphasis is placed on gallium concentration, and aluminum-to-gallium ratios are also highlighted. In addition, alkalinity and major metallic impurities are reported. These parameters critically influence separation efficiency and reagent selectivity.

Table 2. Typical composition of Bayer liquors reported in gallium recovery studies (2020–2025), including Ga concentration, Al/Ga ratio, alkalinity, and major impurities. Table 2. Typical composition of Bayer liquors reported in gallium recovery studies. Adapted from Qu et al. (2024) and Dhiman et al. (2024)

Parameter	Typical Range	Units	Notes / Relevance for Ga Recovery
Gallium (Ga)	100–300	mg L^{-1}	Accumulates during repeated Bayer cycles; low absolute concentration requires high selectivity
Aluminum (Al)	80–150	g L^{-1} (as Al_2O_3)	Dominant component; primary competitor in extraction systems
Al/Ga mass ratio	300,000–800,000	–	Key challenge for selective separation and purification
Free Na_2O (caustic)	150–250	g L^{-1}	Governs Ga speciation and extractant performance
Total alkalinity	200–300	g L^{-1} Na_2O	Strongly alkaline environment (pH > 13)
Silicon (Si)	1–5	g L^{-1}	Forms sodalite/cancrinite; affects liquor stability
Iron (Fe)	10–100	mg L^{-1}	Minor impurity but problematic in acidic downstream routes
Zinc (Zn)	50–300	mg L^{-1}	Competes with Ga in several extractant systems
Vanadium (V)	50–200	mg L^{-1}	Often co-extracted; may require selective removal
Organic carbon (TOC)	0.5–3.0	g L^{-1}	Degradation products affect phase separation
Temperature (operation)	50–80	°C	Influences Ga solubility and extraction kinetics

The extremely high Al/Ga ratios and strong alkalinity summarized in Table 2 clearly illustrate why gallium recovery from Bayer liquors remains technically challenging. These compositional constraints help explain the growing preference for multi-stage purification strategies. Such strategies include pre-neutralization, selective complexation, and hybrid separation schemes. These approaches are discussed in the following subsection.

4.1.2. Red mud and coal fly ash

Red mud is an increasingly attractive secondary source of gallium, owing to its high generation volumes and strategic relevance in circular-economy frameworks. In this residue, gallium is predominantly associated with aluminosilicate phases and is also finely dispersed within iron oxides. As a result, gallium exhibits limited natural liberation and strong mineralogical locking (Zhao *et al.,* 2021; Saikia *et al.,* 2022).

Leaching of red mud commonly results in extensive co-dissolution of aluminum, iron, and silica. This process produces chemically complex liquors with unfavorable separation characteristics (Dhiman *et al.,* 2024; Rudnik, 2024). Acidic leaching generally enhances gallium solubilization but substantially increases impurity loads. In contrast, alkaline leaching limits iron dissolution at the expense of gallium recovery.

From a separation perspective, red mud–derived liquors impose more stringent requirements for selectivity and impurity tolerance than conventional Bayer liquors. This is especially true for adsorption- and membrane-based systems (Ciocărlie *et al.,* 2024; Kamran; Irannajad, 2024). As a result, gallium recovery from red mud is more effectively achieved using integrated or hybrid flowsheets. These flowsheets combine bulk impurity removal with highly selective downstream polishing stages (Li *et al.,* 2023).

4.1.3. Coal-derived materials and fly ash

Coal-derived materials, including coal fly ash and coal gangue, have become increasingly relevant secondary sources of gallium. This relevance stems from their large global inventories and gallium enrichment during coal combustion and beneficiation. In these materials, gallium typically occurs as a trace element substituted within aluminosilicate phases. It may also be finely dispersed in glassy matrices. As a result, gallium exhibits low natural liberation and a strong association with aluminum-bearing components (Rudnik, 2024; Zhao *et al.,* 2021).

Gallium concentrations in coal fly ash typically range from a few tens to several hundreds of $mg \cdot kg^{-1}$. These values depend on coal provenance, combustion conditions, and ash fractionation. Although these concentrations are lower than those in semiconductor wastes, the sheer volume of coal-derived residues makes them attractive from a resource availability perspective. This aspect is particularly relevant within circular economy frameworks (Saikia *et al.,* 2022; Rudnik, 2024).

From a separation standpoint, gallium recovery from coal-derived materials poses challenges similar to those in red mud processing. Acidic leaching promotes gallium dissolution but also mobilizes aluminum, iron, and silicon, forming chemically complex liquors with poor selectivity for downstream separation. In contrast, alkaline leaching tends to suppress iron dissolution but often limits gallium recovery because of gallium's strong association with refractory aluminosilicate phases (Zhao *et al.,* 2020; Dhiman *et al.,* 2024).

Consequently, liquors derived from coal fly ash typically require hybrid separation flowsheets. These flowsheets combine bulk impurity removal with highly selective polishing stages, such as ion exchange, adsorption, or membrane-assisted separation. These requirements further

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underscore that gallium recovery from coal-derived materials is governed less by dissolution efficiency than by the ability to manage matrix-driven competition during separation and purification.

4.1.4. Zinc and lead metallurgical residues

Zinc-refinery residues, flue dusts, and leach solutions constitute another important class of gallium-bearing feedstocks. In these systems, gallium is typically present at low concentrations, yet it can be partially enriched during zinc processing (Zhao *et al.,* 2020; Liu *et al.,* 2023).

In zinc-derived liquors, gallium commonly coexists with high concentrations of Zn^{2+}, Fe^{3+}, and other trace metals. This coexistence requires careful control of redox conditions and solution chemistry during separation (Illés; Kékési, 2023; Liu *et al.,* 2024b). Acidic conditions generally favor gallium solubilization but exacerbate iron interference. Consequently, selective extraction or electrochemical polishing steps become necessary.

Recent studies show that electrochemical methods are particularly well suited as downstream purification stages for zinc-related gallium recovery. This is especially true when upstream separation steps sufficiently reduce impurity loads (Wang *et al.,* 2024b; Liu *et al.,* 2024a).

4.1.5. Electronic waste and semiconductor-related residues

Secondary resources, including electronic waste, GaAs scraps, and spent LEDs, have attracted growing attention. This interest stems from their relatively high gallium content compared with mineral sources. In these feedstocks, gallium typically occurs in compound semiconductors. As a result, aggressive pre-treatment or highly selective leaching is required to dissolve gallium (Zhang; Rao, 2024; Pavón *et al.,* 2025).

Although these materials offer favorable gallium grades, their heterogeneous composition complicates separation and purification. The presence of toxic and precious metals further increases process complexity. Consequently, flowsheets for electronic waste often prioritize selectivity and flexibility over throughput. In these systems, solvent extraction and ion exchange play dominant roles (Losev *et al.,* 2024; Qi *et al.,* 2025).

4.2. Thermodynamics and speciation: Ga (III) as a chemical “chameleon”

The separation behavior of gallium is intrinsically governed by its complex thermodynamic and speciation characteristics. These features justify describing Ga(III) as a chemical “chameleon”. In aqueous systems, Ga^{3+} readily forms strong hydroxo, chloro, fluoro, and organo-complexes. The dominant gallium species shifts sharply with pH, ligand availability, ionic strength, and redox conditions. This pronounced adaptability leads to substantial changes in coordination chemistry across acidic, neutral, and alkaline environments. These effects are particularly relevant in chloride-rich Bayer liquors and zinc hydrometallurgical streams (Qu *et al.,* 2024; Rudnik, 2024).

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As shown in Figure 3, the qualitative dominance of gallium over aluminum, iron, and zinc varies markedly with pH. This variation directly influences separation selectivity and process robustness in real industrial liquors. The dominance diagram indicates that the most severe selectivity constraints occur in strongly alkaline systems. Under these conditions, gallium and aluminum exhibit highly similar hydroxo-complex chemistry. Significant constraints also occur under acidic to weakly acidic conditions, where iron competition and hydrolysis-driven precipitation dominate. These transitions explain why gallium separation efficiency is rarely governed by solubility limitations. Instead, it is primarily controlled by matrix-driven competitive interactions.

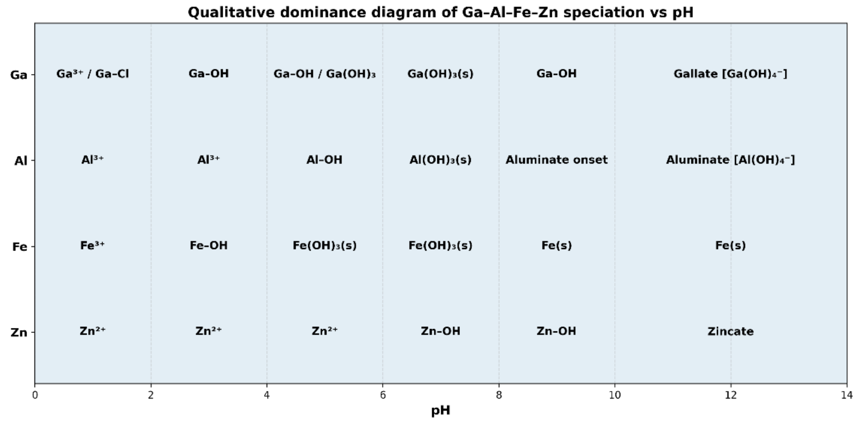

Figure 3. Qualitative dominance diagram illustrating the prevailing aqueous speciation of gallium, aluminum, iron, and zinc as a function of pH and its implications for separation selectivity in complex process liquors. Adapted from Qu et al. (2024) and Rudnik (2024).

Gallium recovery is rarely governed by solubility in strongly alkaline media. This behavior is primarily due to overwhelming competition from aluminate species. A similar limitation occurs in acidic systems, where iron hydrolysis and complexation dominate. These effects underscore the need for speciation-aware separation strategies.

A critical consequence of this speciation flexibility is the frequent discrepancy between laboratory-scale studies and industrial performance. Many laboratory studies rely on simplified synthetic solutions, whereas real process liquors exhibit far greater chemical complexity. In these matrices, gallium competes directly with chemically similar, far more abundant species, such as Al^{3+}, Fe^{3+}, and Zn^{2+}, for extractants, ion-exchange sites, and adsorption surfaces.

As a result, separation schemes that appear highly selective under idealized conditions often lose selectivity in real-world liquors. They may consume excessive amounts of reagents or saturate prematurely. This behavior reflects the dominance of competitive equilibria and mass-transfer limitations in multicomponent systems.

To translate these thermodynamic effects into process-relevant insights, Table 3 summarizes qualitative speciation trends for Ga, Al, Fe, and Zn across representative pH ranges

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and highlights the associated separation constraints. It organizes dominant species into discrete operating windows. These windows are explicitly linked to critical consequences for solvent extraction, ion exchange, adsorption, membrane separation, and downstream polishing steps.

Table 3. Qualitative speciation trends of Ga, Al, Fe and Zn as a function of pH and implications for separation and purification. (Adapted from Qu et al., 2024; Rudnik, 2024.) *

pH range	Ga(dominant behavior/species)	Al(dominant behavior/species)	Fe(dominant behavior/species)	Zn(dominant behavior/species)
0–1 (strongly acidic)	Ga remains soluble as Ga^{3+} / Ga–chloro complexes (if Cl^- high)	Al^{3+} soluble; competitive in SX/IX	Fe^{3+} strongly competitive; may form complexes; high interference	Zn^{2+} soluble; co-extracted depending on extractant
1–3 (acidic)	Increasing tendency to hydrolyze; still soluble; Ga^{3+} ↔ hydroxo complexes	Al^{3+} soluble; hydrolysis starts slowly	Fe^{3+} hydrolysis/colloids begin; risk of gel/precipitation	Zn^{2+} soluble and mobile
3–5 (weakly acidic)	Stronger hydrolysis; Ga may approach precipitation depending on matrix	Al begins hydrolysis; still soluble in many systems	Fe^{3+} tends to precipitate as hydroxides/oxyhydroxides	Zn^{2+} still soluble
5–7 (near-neutral)	Ga hydrolysis significant; risk of $Ga(OH)_3$ precipitation	Al hydroxide formation increasingly likely	Fe largely precipitated; colloids possible	Zn^{2+} soluble but can form $Zn(OH)_2$ near upper range
7–9 (mildly alkaline)	Ga predominantly hydroxo species; solubility depends on ligands	Al amphoteric; can re-dissolve as aluminate above ~9	Fe remains insoluble	Zn begins hydroxo complexes
>10–14 (strongly alkaline; Bayer-type)	Ga as gallate ($[Ga(OH)_4]^-$ / gallate) highly soluble	Al as aluminate ($[Al(OH)_4]^-$) overwhelmingly dominant	Fe insoluble (mostly removed)	Zn can form zincate in very alkaline

Note: This table provides qualitative trends intended for separation-process interpretation; rigorous speciation should be verified via thermodynamic modeling for each liquor (ionic strength and ligand composition dependent).

From a separation and purification perspective, the chameleonic behavior of Ga(III) has significant implications for process design. Robust processes must be grounded in realistic thermodynamic modeling and rely on speciation-aware experimentation. Extrapolation from simplified synthetic systems is often insufficient.

Effective gallium recovery therefore requires strategies that explicitly account for competitive complexation and conditional stability constants. These strategies must also account for speciation

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shifts driven by upstream process fluctuations. Together, these factors underscore the need for integrated, multistage separation flowsheets. Such approaches are generally more effective than single-step solutions.

4.3. Comparative assessment of gallium occurrence

Across the diverse range of primary and secondary feedstocks, gallium occurs in three dominant modes. The first mode comprises soluble gallate species in strongly alkaline liquors. The second involves lattice-substituted gallium within aluminosilicate or oxide matrices. The third corresponds to compound-bound gallium associated with semiconductor materials. This classification provides a practical framework for linking feedstock characteristics to the selection and expected performance of separation and purification strategies (Qu *et al.*, 2024; Karali; Shah, 2022).

To translate these occurrence modes into process-relevant insights, Figure 3 schematically summarizes the dominant forms of gallium in representative feedstocks, including Bayer liquors, red mud and fly ash, zinc-derived residues, and electronic waste. The figure highlights how gallium distribution within each matrix directly constrains achievable selectivity and dictates the need for pre-treatment or bulk impurity removal. It also governs the complexity of downstream separation flowsheets.

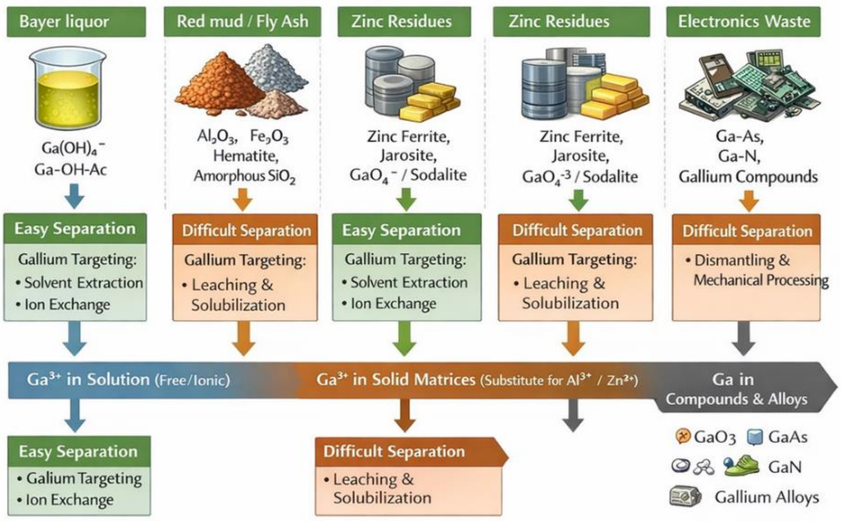

Figure 4. Schematic representation of gallium occurrence modes in major feedstocks (Bayer liquor, red mud/fly ash, zinc residues, and electronic waste) and their implications for separation and purification pathways. Adapted from Qu et al. (2024) and Rudnik (2024).

As shown in Figure 4, soluble gallate species in alkaline liquors favor liquid-phase separation techniques. However, these systems face severe competition from aluminum. In contrast, lattice-substituted gallium in solid residues requires aggressive leaching, which increases impurity loads.

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Compound-bound gallium in semiconductor materials presents a different scenario. These feedstocks offer higher intrinsic gallium grades. Nevertheless, they require highly selective dissolution and flexible separation schemes.

Collectively, these distinctions reinforce that gallium recovery cannot be approached with a uniform strategy. Instead, separation and purification routes must be tailored to feedstock-specific modes of gallium occurrence.

4.4. Critical implications for process design

The diversity of gallium-bearing feedstocks underscores the inherent limitations of universal recovery strategies. Many separation technologies reported in the literature rely on idealized assumptions about gallium speciation. Others assume simplified impurity systems. These assumptions often yield optimistic performance metrics. Such results are unlikely to be reproduced under industrial conditions (Losev *et al.,* 2024; Pavón *et al.,* 2025).

From an engineering perspective, effective gallium recovery requires early and explicit integration of several elements, including feedstock characterization, analysis of gallium occurrence, and selection of appropriate separation and purification strategies. Failure to account for these interdependencies remains a primary reason for the persistent gap between laboratory-scale demonstrations and industrial implementation.

These findings reinforce that separation performance is constrained not only by feedstock origin but also by the thermodynamic speciation behavior of Ga(III) in multicomponent liquors. Consequently, robust process design must prioritize speciation-aware experimentation and realistic impurity matrices. Integrated separation flowsheets should be favored over isolated, single-step solutions.

While feedstock chemistry and gallium occurrence fundamentally constrain separation performance, these factors become operationally relevant only when incorporated into hydrometallurgical processing routes. The following section therefore examines how different leaching strategies interact with gallium speciation and impurity matrices. It also explains why selectivity, rather than dissolution, ultimately governs process viability.

5. HYDROMETALLURGICAL ROUTES FOR GALLIUM RECOVERY: SELECTIVITY-DRIVEN PERSPECTIVES

Hydrometallurgical processing remains the dominant approach for gallium recovery from both primary and secondary resources. Across all reported routes, however, selectivity consistently emerges as the critical bottleneck. It governs technical feasibility, operating costs, and process scalability. Dissolution efficiency alone is rarely the limiting factor (Agrawal; Dhawan, 2022; Changju *et al.,* 2024).

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This section critically reviews alkaline, acidic, halide-based, and assisted leaching methods. Particular emphasis is placed on solution chemistry and impurity matrices. The discussion also highlights how downstream separation constraints ultimately determine overall process performance.

5.1. Alkaline leaching routes (Bayer-type and related systems)

Alkaline leaching is the most mature hydrometallurgical method for gallium recovery, as gallium exists as gallate species in Bayer liquors and alkaline streams. This allows integration with alumina refineries, reducing additional separation steps and capital costs (Hua *et al.,* 2024; Qu *et al.,* 2024).

Selectivity collapse from extreme Al/Ga ratios limits alkaline routes. Under strongly alkaline conditions, gallium and aluminum show similar hydroxo-complex chemistry, making most extractants and resins insufficiently selective. Only specialized functional groups can overcome this (Bagdaulet *et al.,* 2024; Pang *et al.,* 2025a).

High caustic concentrations and high temperatures limit separation materials, accelerating degradation, fouling, and capacity loss (Guo *et al.,* 2020; Pang *et al.,* 2025b). Alkaline leaching is rarely restricted by gallium solubilization but by the availability of separation technologies. capable of Sustaining long-term operation under Bayer process conditions relies on overcoming challenges in separation and purification, as alkaline leaching seldom fails during dissolution. The similar chemistry of gallate and aluminate species limits selectivity, making multistage purification necessary instead of single-step extraction.

Table 4. Alkaline leaching routes for gallium recovery: controlling factors, advantages, limitations, and implications for separation and purification

Feedstock / System	Operating conditions (typical)	Gallium speciation	Main advantages	Main limitations	Separation & purification implications
Bayer liquor (industrial)	pH > 13; 50–80 °C; NaOH 150–300 g L^{-1}	Gallate, $[Ga(OH)_4]^-$	Ga already in solution; direct industrial integration; no solid handling	Extremely high Al/Ga ratios; similar Ga/Al hydroxo chemistry	Selectivity collapse in SX/IX; extractants and resins must tolerate hot caustic; multi-stage purification mandatory
Aged Bayer liquor (recycled)	Long residence times; cyclic chemistry	Stable gallate complexes	Natural Ga enrichment over time	Organic degradation products; kinetic instability	Phase disengagement problems; fouling of resins and membranes

Alkali-treated red mud	pH 12–14; NaOH leaching	Partial gallate formation	Suppresses Fe dissolution; compatible with Bayer flowsheets	Low Ga extraction efficiency; silica dissolution	Low-grade liquors still separation-limited; polishing steps dominate CAPEX
Alkali leaching of coal fly ash	High NaOH; elevated temperature	Gallate + aluminosilicate complexes	Avoids Fe co-dissolution	Strong silica interference; low selectivity	Membrane and IX performance severely affected by silicates

Table 4 shows that performance differences among alkaline systems are driven primarily by separation chemistry rather than leaching efficiency, underscoring the need for downstream selectivity-oriented design.

5.2. Acidic leaching routes (red mud, fly ash, metallurgical dusts)

Acidic leaching is common for gallium-rich residues like red mud, coal fly ash, zinc residues, and metallurgical dusts, where gallium is in lattice-substituted or dispersed phases. Under acidic conditions, gallium dissolves quickly, even at moderate temperatures and short times (Zhao *et al.,* 2020; Nakamura *et al.,* 2024; Zhu *et al.,* 2024; Gao *et al.,* 2025).

However, this advantage is offset by extensive co-dissolution of aluminum, iron, zinc, and silica. The resulting liquors are chemically complex. Downstream separation becomes the main challenge (Dhiman *et al.,* 2024; Pan *et al.,* 2023). Iron hydrolysis, colloid formation, and silica polymerization worsen fouling. These also hinder phase disengagement during solvent extraction, adsorption, and membrane separation (Petrova, 2021; 2023; Karimi; Rahbar-Kelishami, 2023; Teng *et al.,* 2024).

Acidic routes often need multi-stage flowsheets, combining impurity removal like iron precipitation with selective polishing for gallium (Zhang *et al.,* 2021; Zhu *et al.,* 2024; Qi *et al.,* 2025). Although acid leaching effectively releases gallium, it increases process complexity by moving it from leaching to separation (Singh *et al.,* 2025).

Figure 5 shows gallium dissolution under acidic conditions rarely limits the process. Instead, costs and complexity are driven by managing co-dissolution of aluminum, iron, and other elements during separation and purification. Impurity control, not leaching efficiency, is the main bottleneck in acidic gallium recovery.

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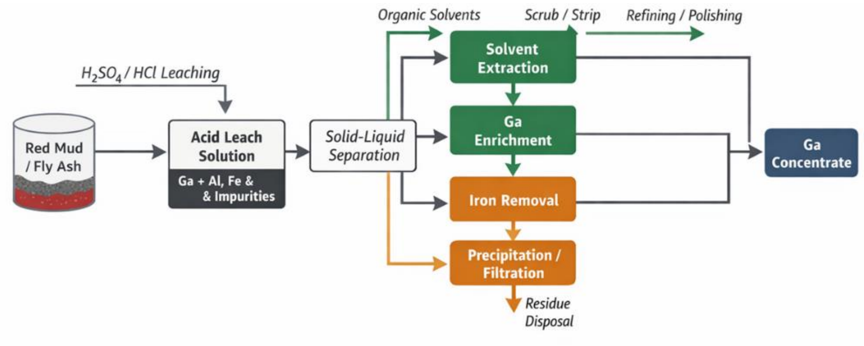

Figure 5. Conceptual acidic leaching–separation flowsheet for gallium recovery from red mud and fly ash, illustrating the shift of complexity from dissolution to downstream purification. Adapted from Dhiman et al. (2024) and Pan et al. (2023).

Figure 5 shows that, in acidic systems, overall process viability is governed by the efficiency of impurity management rather than by gallium dissolution.elf.

5.3. Chlorination and halide-based routes (dry and hybrid processes)

Halide-based processing routes, like dry chlorination, chlorination roasting, and hybrid halide–hydrometallurgical schemes, are gaining interest as alternatives for gallium recovery. They aim to bypass aqueous speciation by converting gallium into volatile or soluble halide species, partially separating it from aluminum and iron matrices.

Chlorination approaches effectively separate gallium using chemical volatility or complexation before aqueous purification (Aguirre, 2023; Okabe *et al.,* 2021). Yet, they face engineering and environmental challenges like corrosive atmospheres, Cl_2 and HCl emissions, material issues, and strict emission controls (Okabe *et al.,* 2020).

Halide-based routes are niche or hybrid solutions, suited to specific feedstocks or high-value residues, not as universal alternatives to aqueous hydrometallurgy.

Figure 6 compares aqueous hydrometallurgical and halide-based routes. Aqueous selectivity depends on pH and competition with Al, Fe, and Zn, while halide methods use volatility, complex stability, and phase transfer. Halide routes can bypass some aqueous limitations but raise issues like corrosion, reagent handling, environmental impact, and material choice, illustrating the trade-off between chemical selectivity and engineering challenges.

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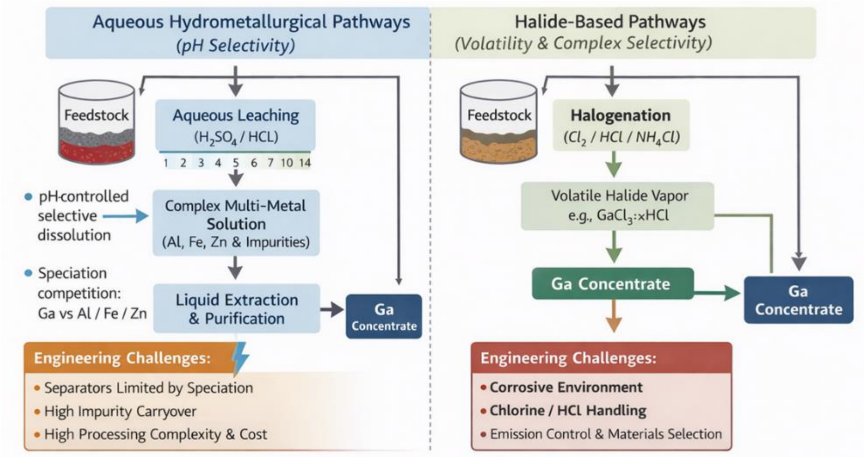

Figure 6. Comparison between aqueous hydrometallurgical and halide-based gallium recovery pathways, highlighting selectivity mechanisms and engineering trade-offs. Adapted from Aguirre (2023) and Okabe et al. (2021).

5.4. Assisted leaching routes (mechanochemical, microwave, bio-assisted)

Assisted leaching techniques, like mechanochemical activation, microwave heating, ultrasonic treatment, and bio-assisted processes, are increasingly used to improve gallium extraction from refractory matrices. They often boost leaching efficiency by disrupting mineral structures or speeding up reactions (Sun *et al.,* 2025; Liu *et al.,* 2025).

Improved extraction often reduces selectivity because matrix disruption causes aluminum, iron, and other impurities to dissolve simultaneously. Assisted leaching can shift bottlenecks downstream, raising reagent use, separation challenges, and waste (Saikia *et al.,* 2022; Wu *et al.,* 2025).

From a separation-centric perspective, assisted leaching should not be evaluated solely based on extraction yield. Its net impact on downstream purification performance and overall flowsheet robustness must also be considered.

As summarized in Table 5, assisted leaching shows a paradox: higher gallium extraction often reduces downstream separation performance. While these techniques improve matrix disruption and mass transfer, they also increase impurity release. This highlights that hydrometallurgical innovation should be evaluated at the flowsheet level, not just during leaching.

Table 5. Assisted leaching strategies for gallium recovery: extraction benefits versus downstream separation penalties. Adapted from Sun et al. (2025), Saikia et al. (2022), and Wu et al. (2025)

Assisted technique	Target feed stocks	Main mechanism	Extraction benefit	Hidden drawbacks	Impact on downstream separation
Mechanochemical activation	Red mud;	Lattice disorder;	Higher Ga leachability at	Releases Al, Fe, Si simultaneously	Increases impurity load; SX/IX

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	coal gangue	surface area increase	lower reagent consumption		selectivity deteriorates
Microwave-assisted leaching	Fly ash; red mud; CIGS waste	Selective heating of Ga-bearing phases	Faster kinetics; reduced leaching time	Poor selectivity control	Generates chemically complex liquors; requires intensive polishing
Ultrasonic-assisted leaching	Low-grade residues	Cavitation-enhanced mass transfer	Improved Ga dissolution	Promotes colloid formation	Fouling of membranes and adsorbents
Bioleaching / biosorption	E-waste; zinc residues	Biogenic complexation	Mild conditions; selective at low concentrations	Slow kinetics; scale-up uncertainty	Often requires post-treatment before SX or electrowinning
Siderophore-assisted systems	Red mud; zinc residues	Strong Ga-complex formation	High Ga affinity	Co-complexation of Fe and Al	Selectivity gains upstream may be lost downstream

Across all hydrometallurgical routes, gallium recovery is rarely limited by dissolution kinetics but is mainly constrained by matrix-driven selectivity. The next section discusses separation and purification technologies.

This section examines how solvent extraction, adsorption, membrane processes, and electrochemical polishing aim to overcome these constraints. It also discusses where these approaches ultimately succeed and where they fail.

6. SEPARATION AND PURIFICATION: THE CORE OF GALLIUM RECOVERY

Gallium recovery depends on feedstock, leaching, separation, and purification. Separation, often challenged by competition from abundant metals like aluminum, iron, and zinc, influences process viability, selectivity, and scalability.

This section critically reviews the dominant separation and purification strategies for gallium. The discussion is organized by the fundamental mechanisms that govern selectivity rather than by feedstock alone.

6.1. Solvent extraction (SX)

Solvent extraction remains the most mature and widely studied separation method for gallium, particularly in Bayer liquors, zinc refinery solutions, and acidic leachates from red mud and fly ash. Its dominance stems from flexibility, scalability, and compatibility with continuous operation.

Extractant families and selectivity mechanisms

Classical gallium extractants include organophosphorus acids (e.g., D2EHPA, P204, P507), neutral organophosphorus compounds (TOPO, TBP), amines, and oxine-based chelators. Recent studies increasingly explore ionic liquids (ILs) and deep eutectic solvents (DES) to enhance selectivity and stability (Zhang *et al.,* 2021; Guo *et al.,* 2024; Pang *et al.,* 2025a).

Selectivity in SX is governed by:

- conditional stability constants of Ga complexes,
- pH-dependent speciation (Ga–Al overlap),
- extractant resistance to high ionic strength and alkalinity,
- suppression of third-phase formation and emulsification.

Despite promising distribution coefficients in synthetic solutions, Ga/Al selectivity remains the primary bottleneck, especially in Bayer liquors where Al/Ga ratios exceed 10^5 (Grigorieva *et al.,* 2020; Qu *et al.,* 2024; Chen *et al.,* 2025).

Engineering constraints

High reagent consumption, extractant degradation under hot caustic conditions, and inefficient stripping remain persistent challenges, often shifting complexity downstream rather than eliminating it (Guo *et al.,* 2020; Losev *et al.,* 2024).

Table 6 shows that improvements in gallium selectivity using novel extractants often come at the expense of chemical robustness, underscoring why SX alone rarely constitutes a complete purification solution.

Table 6. Representative solvent extraction systems for gallium recovery, highlighting extractant family, operating medium, selectivity drivers, and key limitations. Adapted from Zhang et al. (2021), Guo et al. (2024), Pang et al. (2025b), and Chen et al. (2025)

Extractant family	Representative extractant	Operating medium	Main selectivity drivers	Typical advantages
Organophosphorus acids	D2EHPA, P204	Acidic sulfate or chloride	pH-dependent cation exchange; stronger affinity for Ga^{3+} than Zn^{2+}	Industrial maturity; fast kinetics; scalable
Neutral organophosphorus	TBP, TOPO	Chloride-rich acidic media	Solvation of $GaCl_4^-$ / $GaCl_3$ species	Effective in Cl^- systems; mild pH control
Tertiary amines	N235, Alamine 336	Acidic chloride systems	Anion exchange of Ga chloro-complexes	Good Ga/Zn discrimination; high loading
Hydroxamic acids	Novel hydroxamate extractants	Mildly acidic to neutral	Specific chelation with Ga^{3+}	Improved Ga/Al selectivity; lower Fe interference

Oxine-type chelators	8-hydroxyquinoline derivatives	Weakly acidic	Strong Ga–N,O coordination	High intrinsic selectivity
Amide-based extractants	Halogenated secondary amides	Acidic sulfate/chloride	Hydrogen bonding + soft donor effects	Tunable selectivity; reduced third phase
Ionic liquids (ILs)	Phosphonium-based ILs	Acidic or alkaline	Tailored coordination environment	High selectivity; low volatility
Deep eutectic solvents (DES)	ChCl–organic acid systems	Mild acidic	Combined solvation and complexation	Low toxicity; tunable chemistry

Table 6 demonstrates that solvent extraction performance for gallium is governed more by speciation-controlled selectivity windows than by extractant strength. Across extractant families, the dominant limitations stem from aluminum competition in alkaline systems. In acidic media, iron interference is the primary constraint. These trends reinforce the need for upstream conditioning and downstream polishing. Reliance on single-step solvent extraction is rarely sufficient.

6.2. Adsorption and ion-exchange

Adsorption and ion-exchange processes have attracted growing attention as selective, modular alternatives or complements to solvent extraction, particularly for polishing steps and low-concentration streams (Díez *et al.,* 2021).

Functional materials and performance metrics

Functional resins containing phosphonate, iminodiacetate, oxime, or amide groups show strong affinity for Ga(III). In addition, hybrid inorganic–organic sorbents provide alternative separation platforms. Examples include $MgFe_2O_4$ spinels and mesoporous carbons. These materials offer enhanced chemical stability and tunable selectivity (Díez *et al.,* 2021; Ciocărlie *et al.,* 2024; Saez *et al.,* 2024).

Critical performance metrics include:

- adsorption capacity (mg $Ga \cdot g^{-1}$),
- uptake kinetics,
- resistance to fouling,
- regeneration efficiency and cycle stability.

Although adsorption systems can outperform solvent extraction in selectivity, capacity utilization, and regeneration losses, real-liquor conditions still pose major challenges (Cui *et al.,* 2022; Kluczka, 2024).

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Table 7 shows adsorption and ion-exchange systems that favor gallium recovery within specific pH ranges suited to Ga(III) speciation. While they often have lower capacities than solvent extraction, they better discriminate against zinc and sometimes iron. However, aluminum competition is a major limitation, along with fouling from hydrolysis products and declining integrity over cycles.

Table 7. Adsorbents and ion-exchange materials applied to gallium separation, including functional groups, capacity, operating pH, and regeneration performance. Adapted from Díez et al. (2021), Ciocărlie et al. (2024), Saez et al. (2024), and Kluczka (2024)

Adsorbent / material type	Functional group / active site	Typical operating pH	Reported Ga capacity (mg Ga g^{-1})	Selectivity features	Regeneration & stability
Mesoporous carbon	Oxygenated surface groups	2–4	5–15	Moderate Ga selectivity over Zn; poor vs Al	Regenerable by acid elution; gradual capacity loss over cycles
$MgFe_2O_4$ spinel	Surface metal–oxygen sites	3–6	20–35	Strong affinity for Ga^{3+} via surface complexation	Good chemical stability; regeneration by dilute acid
Chelating resins (iminodiacetate)	$–N(CH_2COO^-)_2$	2–5	10–25	Ga/Fe discrimination under controlled pH	Multi-cycle regeneration possible; Fe fouling risk
Phosphonate resins	$–PO_3H^-$ groups	1–4	15–40	High affinity for trivalent metals including Ga^{3+}	Acid regeneration effective; Al competition significant
Oxime-functionalized polymers	–C=N–OH	3–6	8–20	Improved Ga/Zn selectivity	Limited alkaline stability; gradual degradation
Hybrid inorganic–organic adsorbents	Metal oxide + chelating ligand	3–7	25–50	Tunable selectivity; reduced Fe interference	Promising cycling stability; scale-up data limited
Biosorbents / biopolymers	Carboxylate / hydroxyl groups	3–5	3–12	Low selectivity; mainly pre-concentration	Low cost; poor long-term stability
Ion-exchange membranes (fixed sites)	Sulfonic / phosphonic sites	2–6	— (flux-based)	High selectivity when coupled with speciation control	Fouling-sensitive; regeneration depends on liquor purity

Adsorption and ion exchange are best as intermediate or polishing steps, most effective after bulk impurity removal. Their success depends on upstream liquor conditioning and controlled speciation, complementing, not replacing, solvent extraction or electrochemical purification in gallium flowsheets (Hua *et al.,* 2024; Saez *et al.,* 2024).

6.3. Selective precipitation and co-precipitation

Selective precipitation is primarily used as a pre-purification step. Its main objective is to remove iron, aluminum, or silica before fine gallium separation. Common techniques include controlled pH adjustment, sulfide precipitation, and hydroxide formation.

Although precipitation can simplify downstream separation, it carries inherent risks. Gallium co-precipitation and irreversible losses may occur. These effects are particularly pronounced near neutral pH, where gallium hydrolysis becomes significant (Zhu *et al.,* 2024; Pan *et al.,* 2023).

As a result, precipitation is rarely used as a standalone method for gallium recovery. Instead, it remains a valuable tool for managing bulk impurities in integrated flowsheets.

6.4. Membrane-based separation (ED, NF/RO, SLM)

Membrane processes offer attractive selectivity and potential for process integration. These include electrodialysis (ED), nanofiltration/reverse osmosis (NF/RO), and supported liquid membranes (SLMs).

Supported liquid membranes combine extraction and stripping, allowing high selectivity under controlled conditions (Asadian; Ahmadi, 2020; Bayır, 2023). However, issues such as fouling, limited stability, and high costs hinder widespread adoption.

As a result, membrane systems are best suited as niche or hybrid components. They are better suited as complementary units rather than as primary separation steps.

6.5. Electrochemical methods (electrodeposition, electroextraction, electrorefining)

Electrochemical routes play a crucial role in the final purification of gallium, particularly when producing high-purity metal.

Electrowinning and electrorefining are most effective when applied to already purified solutions. In these systems, concentrations of competing ions are minimized. Recent advances have reported improved current efficiency and energy performance. These improvements are achieved through pulse electrolysis and cyclone-assisted configurations (Liu *et al.,* 2023; Wang *et al.,* 2024b).

Electrochemical methods are therefore best understood as terminal purification or polishing steps. They are not suited to serve as primary separation technologies.

Figure 7 outlines the roles of separation tech in a gallium recovery flowsheet, showing no single method covers all selectivity needs. This highlights the need for staged purification, advancing from impurity-tolerant bulk steps to highly selective ones tailored to Ga(III) speciation.

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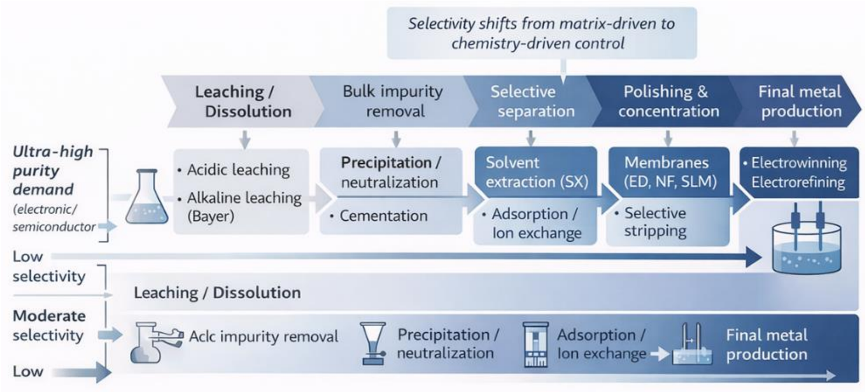

Figure 7. Positioning of gallium separation and purification technologies along the process chain, illustrating how selectivity requirements evolve from bulk impurity removal to final metal production. Adapted from Kluczka (2024), Qu et al. (2024), and Robla et al. (2024).

Gallium separation is not solely governed by extraction efficiency but also by the ability to maintain selectivity under extreme chemical imbalance, making integrated, multi-step purification flowsheets unavoidable for industrial implementation.

7. ENVIRONMENTAL AND ECONOMIC ASSESSMENT (2020–2025)

Environmental and economic assessments of gallium hydrometallurgical routes vary greatly, and results often can't be compared. To aid process choice and scale-up, recent studies highlight the importance of harmonized KPIs, which should be reported consistently (Gunawardhana *et al.,* 2024; Wu *et al.,* 2025).

Results should be normalized per tonne of feed processed, with metrics such as kg t^{-1} feed, kWh t^{-1} feed, and m^3 t^{-1} feed. Normalization per unit of gallium recovered is also required, including kg kg^{-1} Ga, kWh kg^{-1} Ga, and m^3 kg^{-1} Ga. This dual normalization reduces bias from high extraction efficiencies without indicating reagent, energy, or waste usage, allowing fair comparison across different feedstocks like Bayer liquors, red mud, fly ash, zinc residues, and electronic waste (Jia *et al.,* 2022; Song *et al.,* 2022; Zuo *et al.,* 2025; Sverdrup; Haraldsson, 2025).

From a circular-economy view, gallium recovery depends less on solubilization and more on controlling losses and recycling reagents. Important aspects include regenerating lixiviant, reusing process water, and closed-loop solvent extraction or adsorption. Stabilizing solid residues also matters. These factors significantly impact costs (OPEX) and environmental footprint.

Studies on sustainability in gallium- and indium-waste show that downstream purification and residue management dominate life-cycle impacts, especially for secondary resources like LEDs, CIGS photovoltaics, and GaAs scraps (Harazin, 2020; Theocharis *et al.,* 2021; Ravilla *et al.,* 2024; Huang *et al.,* 2024a; Wu *et al,* 2025).025).

7.1. Harmonized Indicators and Reporting Basis

To enable cross-route comparability, a minimum environmental–economic inventory should include:

(i) reagent consumption (acids, bases, complexants, extractants, oxidants/reductants),

(ii) water use (make-up, recycling rate),

(iii) energy demand (heating, mechanical activation, pumping, electrochemical steps),

(iv) residues generated (kg t^{-1} feed and kg kg^{-1} Ga, classification and treatability), and

(v) Closed-loop potential (regeneration of NaOH/HCl/solvents, adsorbent or resin lifetime, water reuse). Circular-economy analyses of critical raw materials repeatedly highlight that omitting these parameters severely limits the relevance of laboratory-scale demonstrations for industrial implementation (Petrova, 2021; 2023; Valero *et al.,* 2021; Song *et al.,* 2022; Zuo *et al.,* 2025).

To standardize environmental and economic comparisons across gallium recovery routes, Table 8 summarizes a minimum inventory set and the recommended normalization basis for reporting performance metrics.

Table 8. Minimum inventory and harmonized KPIs for environmental and economic assessment of gallium recovery routes (2020–2025), including reporting basis and recommended normalization. Adapted from Petrova (2021, 2023), Valero et al. (2021), Ravilla et al. (2024), and Zuo et al. (2025)

Category	Indicator	Unit	Reporting basis	Recommended normalization
Feedstock	Gallium grade	mg Ga/kg feed or ppm	As received feed	—
	Feed throughput	t feed/h or t feed/y	Process scale	—
Leaching / Dissolution	Leaching yield	% Ga dissolved	Leaching step	—
	Acid/alkali consumption	kg reagent/t feed	Leaching stage	kg reagent/kg Ga recovered
	Leaching water demand	m³/t feed	Leaching stage	m³/kg Ga recovered
	Leaching energy demand	kWh/t feed	Leaching stage	kWh/kg Ga recovered
Separation & Purification	Selectivity (Ga/Al, Ga/Fe, Ga/Zn)	Dimensionless ratio	Separation step	—
	Extractant / sorbent consumption	kg/t feed or kg/m³ liquor	SX / IX / adsorption	kg/kg Ga recovered
	Phase ratio / loading capacity	g Ga/L organic or mg Ga/g sorbent	Separation unit	—
	Regeneration efficiency	% capacity retained per cycle	Cyclic operation	—

Electrochemical / Final Recovery	Current efficiency	%	Electrowinning / electrorefining	—
	Specific electricity consumption	kWh/kg Ga	Metal recovery stage	kWh/kg Ga
Residues & Emissions	Solid residue generation	kg/t feed	Overall process	kg/kg Ga recovered
	Liquid effluent volume	m³/t feed	Overall process	m³/kg Ga recovered
	Secondary waste (spent solvents, resins)	kg/y or kg/t feed	Separation stages	kg/kg Ga recovered
Circularity & Integration	Reagent recyclability	Qualitative / %	Process-wide	—
	By-product valorization	Qualitative	Process-wide	—
Economic Indicators	Estimated OPEX	USD/kg Ga	Overall process	USD/kg Ga
	Estimated CAPEX (order of magnitude)	USD/t feed·y	Installed capacity	—

Table 8 shows that without dual normalization (per ton of feed and per kilogram of Ga), routes with high extraction efficiency may appear competitive despite excessive reagent use, energy consumption, or waste generation.

7.2. Feedstock-Dependent Environmental and Cost Drivers

For Bayer liquors, dissolution is already achieved upstream. As a result, environmental and economic burdens shift toward aluminum selectivity. Additional challenges include material stability under hot, concentrated NaOH and the management of purge streams enriched in impurities. Long-term liquor recycling amplifies even small inefficiencies. Consequently, solvent stability and circuit closure become central to sustainability (Jia *et al.,* 2022; Song *et al.,* 2022; Zainudeen *et al.,* 2023; Sverdrup; Haraldsson, 2025).

In red mud and coal fly ash, acidic leaching often enhances gallium solubilization. However, it also promotes extensive co-dissolution of aluminum, iron, and silicon. As a result, downstream purification and effluent treatment dominate both operating costs and environmental impacts. Several reviews of bauxite residues indicate that maximizing gallium extraction alone can worsen overall process performance when impurity management is considered (Mi *et al.,* 2022; Pan *et al.,* 2023; Jiu *et al.,* 2024; Li *et al.,* 2024; Fernández-Pereira *et al.,* 2024; Singh *et al.,* 2025).

For zinc-refinery residues and metallurgical slags, sustainability is governed by ionic complexity. Effective management of co-metals such as Zn, Fe, Ge, and In is required. Electrochemical steps are often effective for final purification, but they introduce additional energy demand that must be balanced against gains in product purity (Ettler *et al.,* 2022; Wang *et al.,* 2024a; Qi *et al.,* 2025; Sun *et al.,* 2025; Zhou *et al.,* 2025).

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In electronic waste streams, including LEDs, CIGS, and GaAs, relatively high gallium grades are offset by other challenges, including heterogeneous composition, hazardous constituents, and energy-intensive pre-treatment steps. Life-cycle-oriented studies indicate that strong process integration and the minimization of specialized reagents are essential to achieving favorable environmental and economic outcomes (Gunawardhana *et al.,* 2024; Theocharis *et al.,* 2021; Ravilla *et al.,* 2024; Mustafa *et al.,* 2025; Wu *et al.,* 2025).

7.3. Critical perspective: incomplete inventories and overestimated viability

Despite significant experimental progress between 2020 and 2025, many publications still fail to report a minimum environmental–economic inventory. Two recurring issues are:

(i) Extraction-driven optimization, where aggressive leaching increases impurity loads, reagent consumption, and waste volumes, shifting the burden to downstream stages without quantification (Mi *et al.,* 2022; Pan *et al.,* 2023); and

(ii) Selectivity without durability, where solvent extraction, adsorption, or membrane systems are evaluated under idealized conditions that ignore stability, fouling, regeneration losses, and multi-cycle performance, which ultimately dominate OPEX and environmental footprint (Petrova, 2021; Valero *et al.,* 2021; Wu *et al.,* 2025).

Figure 8 reinforces that robust gallium recovery strategies require complete inventories, highlighting the systematic increase in complexity from dissolution through purification, recycling, and residue management.

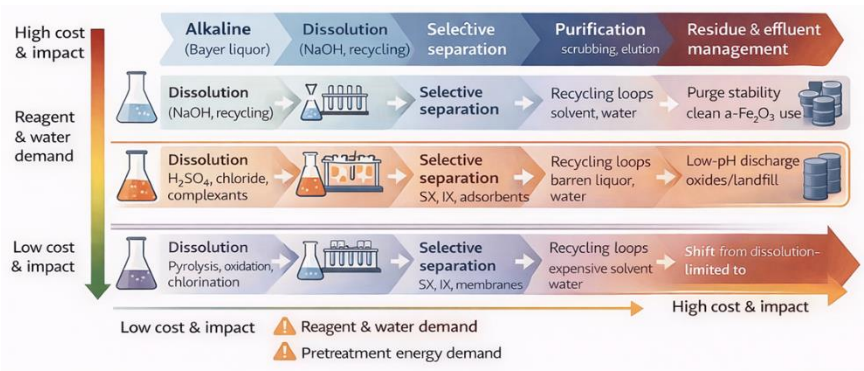

Figure 8. Hotspots of cost and environmental burden across gallium recovery pathways, illustrating the transition from dissolution-limited to purification- and residue-management-limited process viability. Adapted from Mi et al. (2022), Pan et al. (2023), Ravilla et al. (2024), and Wu et al. (2025).

Figure 8 reinforces that robust gallium recovery strategies require complete inventories and closed-loop thinking. Without these elements, laboratory-scale successes are unlikely to translate into industrial processes that are both economically and environmentally viable.

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Although environmental and economic assessments identify dominant hotspots and reporting gaps across gallium recovery routes, these impacts cannot be fully interpreted in isolation. They must be considered within the context of the overall process structure. In practice, reagent consumption, energy demand, water use, and residue generation are not intrinsic properties of individual unit operations. Instead, they emerge from how dissolution, separation, purification, and recycling steps are integrated into a flowsheet.

Meaningful comparison of gallium recovery requires an architectural perspective beyond isolated steps. The next section compares different process architectures, examining how combinations of leaching, separation, polishing, and recycling stages spread technical, environmental, and economic risks. This framework explains why similar chemistries perform differently in various configurations.

8. COMPARISON BY FLOWSHEET ARCHITECTURES

Instead of comparing individual units, a more meaningful assessment of gallium recovery routes occurs at the flowsheet architecture level. Literature from 2020-2025 identifies four recurring, conceptually distinct flowsheet archetypes. Each redistributes chemical selectivity, environmental burdens, and economic risks in characteristic ways, largely independent of the specific extractants or materials used.

8.1. Bayer liquor–based architecture: selective capture from alkaline media

Bayer liquor → selective capture → stripping → polishing → product

This architecture reflects the most mature gallium recovery pathway, integrated into alumina refineries. Gallium exists as gallate under alkaline conditions, eliminating the need for a dissolution step (Qu *et al.,* 2024; Hua *et al.,* 2024). The main challenge is now selective capture from liquors with extreme Al/Ga ratios and high ionic strength.

Selective sorption or solvent extraction is first, followed by stripping into a lower-volume stream. Then, polishing with ion exchange or electrochemical refining achieves electronic-grade gallium (Bagdaulet *et al.,* 2024; Kluczka, 2024). While this method generates minimal waste and offers high integration, it faces limitations from aluminate competition and the long-term stability of capture media in hot caustic conditions (Ott, 2021).

From an architectural standpoint, this route exemplifies a system with limited separation. In such systems, even marginal gains in selectivity translate directly into disproportionate improvements in overall process viability.

8.2. Acid leach–based architecture for residues: impurity-driven complexity

Acid leach (red mud / fly ash) → Fe/Al removal → SX/IX → polishing

Acidic flowsheets dominate studies of red mud, coal fly ash, and metallurgical residues. In these systems, gallium dissolution is typically rapid and efficient. However, it is accompanied by extensive co-leaching of aluminum, iron, and other matrix elements (Pan *et al.,* 2023; Dhiman *et al.,* 2024). As a result, the architectural bottleneck shifts from leaching to bulk impurity management.

Pre-removal of iron and aluminum is often required before selective gallium separation is feasible. Common approaches include controlled hydrolysis, precipitation, or cementation (Zhu *et al.,* 2024; Saikia *et al.,* 2022). After this conditioning step, solvent extraction or ion exchange can be applied. These stages operate on partially purified liquors and are typically followed by polishing to meet final purity specifications.

This architecture is inherently purification-dominated. Its environmental and economic performance is governed more by residue generation and reagent recycling than by the gallium recovery yield. Studies that do not explicitly integrate impurity management into the flowsheet often overestimate scalability and underestimate downstream costs (Mi *et al.,* 2022; Li *et al.,* 2024).

8.3. Halogenation and chlorination-based architecture: matrix bypass strategies

Halogenation / chlorination → volatilization or absorption → purification

Halide-based architectures offer an alternative for gallium recovery by bypassing aqueous constraints. Using dry or hybrid chlorination, gallium becomes volatile or soluble halides, facilitating separation from refractory matrices like bauxite residues, copper tailings, or zinc wastes (Borisov *et al.,* 2021; Aguirre, 2023; Ji *et al.,* 2023).

After chlorination, gallium vapors or condensates are captured by absorption or dissolution, then purified. While this offers high selectivity and separates gallium recovery from aluminum chemistry, it faces engineering challenges like corrosion, complex gas handling, and environmental controls (Okabe *et al.,* 2020, 2021; Usuki *et al.,* 2024).

Halogenation routes are highly chemoselective but infrastructure-intensive, making them suitable for niche or high-value applications. Large-scale use is unlikely without robust containment and recycling strategies (Smolenski *et al.,* 2022).

8.4. Secondary resource architecture: electronic waste and photovoltaics

E-waste / PV → selective leaching → SX/IX → electrorefining

Flowsheets targeting electronic waste, LEDs, and photovoltaic materials are characterized by relatively high gallium grades and extreme compositional heterogeneity. In these systems, the architectural emphasis is on the selective liberation of gallium-bearing phases.

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This is often achieved through oxidative or ligand-assisted leaching (Hu *et al.,* 2022; Huang *et al.,* 2024b; Maarefvand *et al.,* 2020).

Downstream separation usually combines solvent extraction or ion exchange with electrochemical refining to produce high-purity gallium at low throughputs (Gabriel, 2022; Illés; Kékési, 2023; Ravilla *et al.,* 2024). While effective, these methods are sensitive to feed variability and favor flexible, modular designs over continuous, large-scale processes.

From an architectural perspective, these flowsheets prioritize selectivity and adaptability over throughput. This approach aligns with circular-economy objectives. However, it also leads to higher unit processing costs (Mustafa *et al.,* 2025).

8.5. Cross-architecture comparison and design implications

Comparison of four flowsheet archetypes shows gallium recovery depends more on how chemical complexity is distributed than on separation technology. In alkaline Bayer flowsheets, complexity is at capture; in acidic residue routes, at impurity removal; in halogenation routes, in infrastructure and environmental controls; and in e-waste flowsheets, across leaching and downstream processes.

This perspective explains why technologies excel in one context but often fail elsewhere without structural changes. It also stresses the need to consider flowsheet configuration when reporting gallium recovery efficiencies. For relevant and robust comparison, gallium recovery routes should be evaluated as integrated architectures instead of isolated chemical steps.

To improve comparison of gallium recovery methods, representative flowsheet architectures that integrate dissolution, separation, and purification can be used. These architectures show how selectivity, impurities, and complexity change based on feedstock chemistry and gallium occurrence. Figure 9 summarizes four main flowsheet archetypes from 2020-2025.

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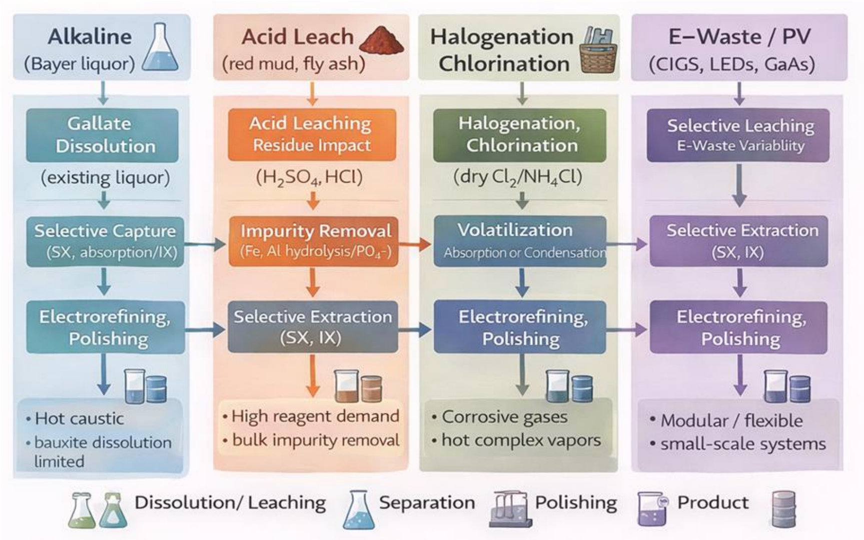

Figure 9. Comparison of representative flowsheet architectures for gallium recovery from different feedstocks. Adapted from Aguirre (2023), Ji et al. (2023), Hu et al. (2022), and Illés & Kékési (2023).

9. RESEARCH GAPS AND FUTURE PERSPECTIVES

Despite significant progress between 2020 and 2025, most gallium recovery technologies remain confined to laboratory-scale demonstrations and have limited industrial relevance. Based on a critical analysis of recent literature, several actionable research gaps emerge.

GAP 1 – Lack of standardized performance metrics.

Gallium recovery studies often report extraction efficiencies without using harmonized metrics. As a result, meaningful comparisons between different processes become difficult.

Essential parameters are often documented inconsistently, including gallium concentration in process liquors (mg Ga L^{-1}), selectivity ratios like Ga/Al and Ga/Fe, and reagent consumption per kilogram of recovered gallium. Cyclic stability is also rarely reported uniformly, despite its significance. Specifically, performance over at least 20 cycles for extractants or resins is seldom shown.

This lack of standardization hinders cross-study comparisons. It also obscures the true technical and economic performance of gallium recovery routes (Petrova, 2021; Kluczka, 2024; Qu *et al.,* 2024).

GAP 2 – Insufficient evaluation under real matrix conditions.

Most separation strategies are validated with synthetic solutions. In contrast, industrial liquors, including Bayer liquor, red mud leachates, coal-derived solutions, and zinc refinery streams, contain highly complex chemical matrices. These matrices typically include aluminum, iron, silicon, halides, and organic species.

Several studies show that competitive complexation and co-extraction significantly reduce selectivity in real-world process liquors. However, systematic tolerance testing under realistic conditions remains scarce (Losev *et al.,* 2024; Rudnik, 2024; Chen *et al.,* 2025).

GAP 3 – Absence of closed-loop chemical balances.

Only a limited number of publications report closed mass balances for key reagents, including NaOH, acids, extractants, and stripping agents. Without quantitative data on regeneration efficiency, chemical losses, and reagent composition, process evaluation remains incomplete.

As a result, both techno-economic and environmental assessments become unreliable. This information gap significantly limits the ability to assess process scalability and sustainability (Petrova, 2023; Ravilla *et al.,* 2024; Zuo *et al.,* 2025).

GAP 4 – Limited integration of multi-metal recovery.

Gallium commonly co-occurs with indium, germanium, rare-earth elements, or titanium. However, most reported flowsheets focus on gallium recovery in isolation.

Integrated strategies that recover multiple critical metals without compromising gallium selectivity remain underdeveloped. This gap persists despite the clear relevance of these approaches to circular-economy applications (Qin *et al.,* 2024; Robla *et al.,* 2024; Teng *et al.,* 2024; Huang *et al.,* 2024a).

GAP 5 – Neglect of materials selection and corrosion.

Halide-based routes and hot alkaline or acidic liquors impose severe constraints on materials of construction. Therefore, corrosion resistance, liner compatibility, and long-term material stability are critical considerations.

However, these aspects are rarely addressed in the literature. This omission is a major barrier to industrial scale-up (Okabe *et al.,* 2021; Aguirre, 2023; Usuki *et al.,* 2024).

GAP 6 – Low TRL and limited continuous validation.

Most reported gallium recovery processes remain at low technology readiness levels. Only a limited number have been demonstrated at continuous or pilot scale.

Long-term stability is rarely evaluated. Fouling behavior and operational robustness during extended operating campaigns are also seldom assessed. This lack of long-duration testing significantly limits confidence in industrial implementation (Ott, 2021; Robart *et al.,* 2024; Sverdrup; Haraldsson, 2025; Zuo *et al.,* 2025).

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Overall perspective.

Addressing these gaps requires a paradigm shift. Process development must move beyond isolated separation chemistry. Instead, it should adopt flowsheet-integrated, inventory-complete, and TRL-oriented approaches (Ott, 2021; Yandem; Jabłońska-Czapla, 2024).

Without this transition, advances in gallium recovery are unlikely to progress beyond laboratory-scale feasibility. Achieving economically and environmentally viable industrial applications will remain limited (Robart *et al.,* 2024; Sverdrup; Haraldsson, 2025).

10. CONCLUSIONS

This review critically examined gallium recovery technologies reported between 2020 and 2025 from the perspective of separation and purification science. Across all primary and secondary feedstocks, gallium recovery is governed less by dissolution efficiency and more by the ability to selectively separate Ga(III) from chemically similar, far more abundant competing species. The most critical competitors are aluminum, iron, and zinc.

Gallium is highly adaptable, with its aqueous speciation strongly changing with pH, ligands, and ionic strength. This flexibility causes loss of selectivity when separation systems designed in labs are used on industrial liquors. Therefore, methods like solvent extraction, adsorption, ion exchange, membranes, and electrochemical processes need testing beyond equilibrium, considering their resistance to competition, fouling, degradation, and cycling in real conditions.

Comparing feedstocks shows no single separation tech works universally. Effective gallium recovery depends on integrated flowsheets, combining impurity removal, selective capture, and polishing. Solvent extraction and ion exchange are primary, with membranes, precipitation, and electrochemical methods acting as auxiliary stages.

Literature shows inconsistencies in environmental and economic reporting, hindering comparisons among separation routes. However, a trend is clear: as feedstock complexity rises and gallium decreases, process performance depends more on purification, reagent regeneration, and residue management, not gallium solubilization. This highlights the need for complete mass balances and closed-loop processes.

Gallium recovery is a complex, separation-intensive challenge where selectivity, stability, and process integration are more crucial than extraction yield. Progress depends on creating separation systems tailored for real process liquors that can handle multicomponent competition and enable reagent recycling. Framing recovery through separation and purification principles offers a structured foundation for research and industrial development. A major barrier remains the absence of harmonized techno-economic and environmental metrics, hindering the transition from laboratory research to industrial application.

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Author Contributions (CRediT):

Antonio Clareti Pereira: Conceptualization; Methodology; Formal analysis; Investigation; Writing – original draft; Visualization; Project administration.

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