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Recent Advances in Gallium Recovery from Zinc Metallurgical Residues and Integrated Zn–Pb Materials: From Process Deportment to Selective Recovery and Industrial Integration (2020–2026)

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ABSTRACT **Review Article**

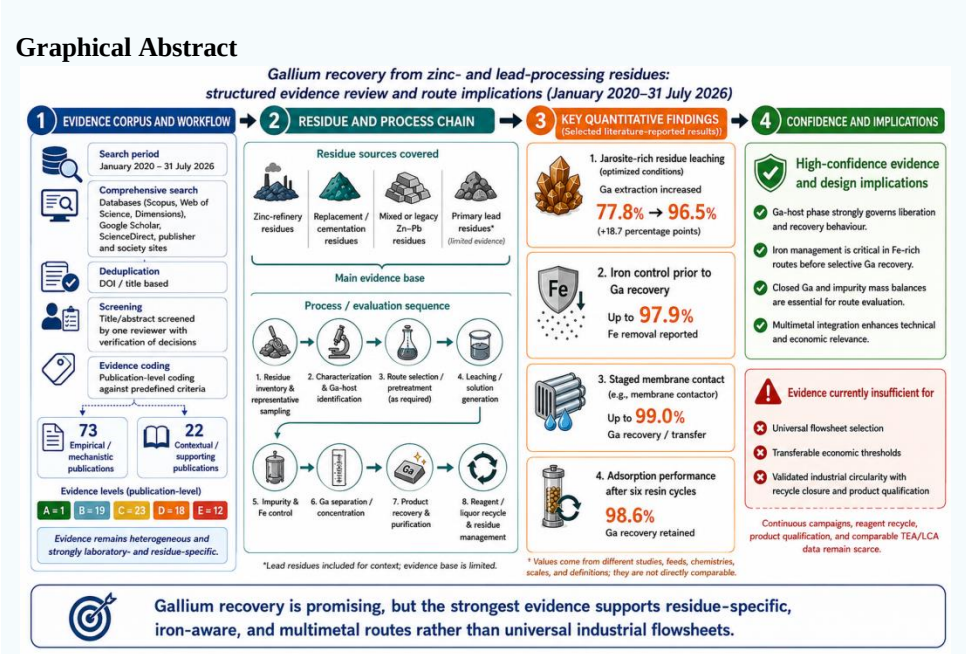
Gallium recovery from zinc-processing residues has expanded rapidly, yet the evidence remains heterogeneous and heavily weighted toward laboratory studies. This structured critical narrative review examines 95 publications issued from January 2020 to July 2026 on gallium deportment, residue formation, characterization, pretreatment, leaching, purification, separation, and product recovery in zinc metallurgical residues and integrated Zn–Pb materials. The corpus was assembled using reproducible keyword combinations, DOI- and title-based deduplication, single-reviewer screening, and study-level evidence coding. Seventy-three empirical or mechanistic publications were graded by evidence type (A = 4, B = 8, C = 20, D = 22, and E = 19), while 22 review, contextual, thesis, or proceedings publications were retained as supporting evidence; only a small minority used continuous, factory, or industrially representative operations. Quantitative comparisons show that host-phase control is decisive: industrial optimization increased gallium leaching from 77.83% to 96.46% when jarosite-associated gallium was addressed, while selected downstream operations achieved 97.9% iron removal before gallium extraction, up to 99% gallium recovery in staged membrane contact, and 98.6% adsorption after six resin cycles. Zinc-refinery and replacement residues provide the strongest evidence. Data for primary lead residues remain insufficient and are therefore treated as complementary evidence from integrated Zn–Pb materials rather than as an equivalent evidence base. High-confidence conclusions concern the importance of mineral hosting, iron control, complete mass balance, and multimetal integration. Claims regarding universal flowsheets, economic thresholds, and industrial circularity remain low confidence because continuous campaigns, reagent recycle, product qualification, and comparable techno-economic or life-cycle data are scarce.

Keywords: Gallium Recovery, Zinc-Refinery Residues, Integrated Zn–Pb Materials, Jarosite, Selective Separation, Critical Metals.

Highlights

- Gallium recovery depends primarily on residue mineralogy and process history.
- Zinc-refinery and replacement residues provide the strongest recent evidence.
- Iron control is essential before selective gallium concentration and recovery.
- Only four graded studies reached continuous, factory, or industrial scale.
- Universal flowsheets remain unsupported without recycle and product validation.

Graphical Abstract



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Introduction

Gallium is not generally mined from a discrete orebody. It is recovered as a companion element whose production depends on the mineralogy, throughput, and operating philosophy of much larger aluminum and zinc industries. This dependence creates a structural supply constraint: even when demand for gallium increases, primary zinc or alumina production may not expand proportionally. Consequently, metallurgical residues are increasingly considered technospheric resources rather than terminal wastes, particularly when they contain gallium together with germanium, indium, zinc, copper, silver, or lead (Huang et al., 2024; Kluczka, 2024; Pereira, 2026b; Robart et al., 2025; Robla et al., 2024; Zou et al., 2020).

The zinc industry is especially relevant because gallium may enter sphalerite concentrates through lattice substitution or submicroscopic inclusions and then be redistributed during roasting, pressure leaching, iron precipitation, solution purification, and electrowinning. It may report to neutral- or hot-acid-leach residues, jarosite, goethite, hematite, zinc-ferrite-rich solids, replacement residues, or process liquors. In integrated zinc–lead operations, the same solids can be transferred to lead smelters, where gallium may be retained in silicate slags or concentrated in recycled dusts. The resulting material is therefore defined as much by its process history as by its bulk chemical analysis (Dong et al., 2024; Dong et al., 2025; Ettler et al., 2021; Höber & Steinlechner, 2021; Hou et al., 2024; Taylor, 2020; Zhang, Li, et al., 2024).

Recent reviews cover gallium recovery from diverse wastes, ionic-liquid separation, jarosite valorization, and iron-precipitation residues. However, broad waste-centered syntheses can obscure the process-specific links among zinc metallurgy, gallium deportment, iron chemistry, and residue-dependent route selection. The 2020–2026 literature is also asymmetric: zinc-refinery residues are supported by increasingly detailed process studies, whereas primary lead residues are represented mainly by mineralogical and broader slag-valorization evidence. The present title and scope therefore treat integrated Zn–Pb materials as complementary to the zinc-centered evidence base (Dhiman et al., 2024; Höber & Steinlechner, 2021; Huang et al., 2024; Kluczka, 2024; Lim et al., 2024; Nowińska & Kokowska-Pawłowska, 2024; Silwamba et al., 2025; Singh et al., 2023).

The structured search and selection protocol is summarized in Table 1. The review questions then follow the full chain from process origin to a qualified gallium intermediate or product rather than treating maximum leach extraction as the endpoint.

Table 1. Structured search and selection protocol

Protocol element	Specification	Implementation
Review type	Structured critical narrative review	Transparent evidence synthesis; no claim of a prospectively registered systematic review.
Search period	1 January 2020–30 July 2026	Last search update: 30 July 2026.
Sources	Google Scholar; ScienceDirect; SpringerLink; ACS, Wiley, Taylor & Francis, MDPI and journal/publisher platforms	Publisher records were used to confirm bibliographic metadata and the version of record.
Search fields	Title, abstract, keywords, and full record where available; all fields in Google Scholar	Searches were repeated with material-, process-, and separation-specific terms.
Core Boolean strings	(gallium OR Ga (III)) AND (zinc refinery residue OR zinc leach residue OR jarosite OR goethite OR zinc ferrite OR replacement residue); AND (lead slag OR Zn–Pb slag OR smelter dust); AND (leaching OR chlorination OR solvent extraction OR ion exchange OR adsorption OR membrane OR electrowinning)	Exact term families were combined with spelling variants and individual technology names.
Eligibility	Peer-reviewed articles and reviews; proceedings and theses when uniquely informative; English or English-accessible metadata	Studies had to report feed/solution characteristics, Ga behavior, operating conditions, separation performance, product, mass balance, or scale.
Exclusion	Ga mentioned only incidentally; unrelated Bayer, coal, electronic, or photovoltaic matrices unless a transferable mechanism was essential; preprints when a version of record existed	Synthetic-solution studies were retained only for mechanisms directly relevant to Zn–Pb liquors.
Deduplication and screening	DOI first; exact title second; author–year–title third; version of record retained. Single reviewer at title/abstract and full-text stages	Multiple papers from one program were retained only when they reported distinct materials, unit operations, or evidence.

Note. Author's structured search protocol. The review is a structured critical narrative review, not a prospectively registered systematic review.

Table 1 makes the scope reproducible while avoiding a misleading PRISMA-compliance claim. Database-specific raw hit counts were not used as a denominator because the searches were iterative across overlapping discovery and publisher platforms; the final deduplicated corpus comprised 95 publications.

Accordingly, the review evaluates recent evidence on the occurrence, deportment, concentration, leaching, separation, recovery, and refining of gallium from zinc metallurgical residues and integrated Zn–Pb materials. The analysis follows the sequence feed – deportment – residue formation – characterization – liberation – leaching – purification – concentration – product recovery – secondary - residue management, with explicit separation between zinc residues containing lead and residues generated by primary or secondary lead metallurgy.

Review Methodology and Evidence Assessment

Search strategy, scope, and transparency

The review was conducted as a structured critical narrative review. The distinction among identification, screening, eligibility, and inclusion follows the reporting logic described by Page et al. (2021), but the article is not presented as a PRISMA-compliant systematic review because the search was iterative and was not prospectively registered. Searches were updated through 30 July 2026 using the sources, fields, and complete term families in Table 1. The principal period was deliberately restricted to 2020–2026; consequently, the title and objectives refer to recent advances rather than to the complete historical development of gallium recovery.

Inclusion, exclusion, deduplication, and reviewer procedure

Publications were included when they reported at least one auditable variable: feed or liquor composition, gallium grade,

host phase, operating conditions, gallium extraction or recovery, impurity behavior, product composition, mass balance, reagent demand, regeneration, or scale. Studies based solely on synthetic solutions were retained only when they addressed a separation mechanism directly transferable to sulfate, chloride, or alkaline liquors associated with zinc processing. DOI-, title-, and author–year–title matching were used sequentially for deduplication. The author performed title/abstract screening, full-text eligibility assessment, data extraction, and coding; this single-reviewer procedure is acknowledged as a limitation.

Data normalization, evidence grading, and reporting completeness

Primary experimental studies were coded separately from reviews, contextual papers, theses, and proceedings. Evidence level describes study type and scale, whereas reporting completeness records whether mineralogy, multi-element balance, final product, replication or uncertainty, and recycle or durability were reported. These two dimensions were kept separate to avoid equating a real-residue experiment with high methodological quality. The study-level matrix is provided in the accompanying Supplementary File S1: Evidence Matrix.

$$E_{\mathrm{Ga,leach}}(\%) = 100 \times \frac{\sum_i C_{\mathrm{Ga},i}\, V_i}{m_{\mathrm{feed,dry}} w_{\mathrm{Ga,feed}}} \quad (1)$$

$$R_{\mathrm{Ga,stage}}(\%) = 100 \times \frac{m_{\mathrm{Ga,product}}}{m_{\mathrm{Ga,stage\ feed}}} \quad (2)$$

$$R_{\mathrm{Ga,overall}}(\%) = 100 \times \prod_j \frac{R_j(\%)}{100} \quad (3)$$

$$CF_{\mathrm{solution}} = \frac{C_{\mathrm{Ga,out}}}{C_{\mathrm{Ga,in}}}; \qquad EF_{\mathrm{solid}} = \frac{w_{\mathrm{Ga,out}}}{w_{\mathrm{Ga,in}}} \quad (4)$$

$$S_{\mathrm{Ga/Fe}} = \frac{R_{\mathrm{Ga}}}{R_{\mathrm{Fe}}}; \qquad \beta_{\mathrm{Ga/Fe}} = \frac{D_{\mathrm{Ga}}}{D_{\mathrm{Fe}}} \quad (5)$$

$$\text{Mass-balance closure}(\%) = 100 \times \frac{\sum m_{\mathrm{Ga,outputs}}}{\sum m_{\mathrm{Ga,inputs}}} \quad (6)$$

where C is gallium concentration in a solution stream (mass per unit volume); V is solution volume; m is mass; w is gallium mass fraction; R is stage or overall recovery (%); D is the dimensionless distribution ratio; CF and EF are the dimensionless solution concentration factor and solid enrichment factor, respectively; S is recovery-based Ga/Fe selectivity; β is the equilibrium Ga/Fe separation factor; i indexes solution or output streams; and j indexes sequential recovery stages. Concentration, volume, mass, and mass-fraction units must be internally consistent so that recoveries and mass-balance closure are dimensionless percentages.

Table 2 defines the evidence levels, keeps study type separate from reporting completeness, and reports the corpus distribution used in the synthesis.

Table 2. Evidence hierarchy, reporting-completeness domains, and corpus distribution

Level	Study type	Minimum defining evidence	Main limitation	Corpus interpretation
A	Continuous pilot, factory, demonstration, or industrial campaign	Real feed/liquor, duration or campaign basis, product or recycle evidence	Plant confidentiality and incomplete public balances	Rare; strongest evidence for operability, not automatically for economics.
B	Real-residue bench study with downstream separation	Feed characterization, leaching/pretreatment, separation, and defined intermediate/product	Batch operation may not predict impurity accumulation	Strongest laboratory basis for integrated flowsheets.
C	Real-residue characterization, leaching, or pretreatment	Real material, operating conditions, Ga transfer and residual solid	No demonstrated downstream product	Supports mineralogical and liberation conclusions.
D	Real-liquor separation or product-recovery study	Realistic matrix, selectivity, loading/stripping or product behavior	Upstream recovery and solid-residue behavior outside boundary	Supports separation-train design.
E	Synthetic-solution or conceptual/mechanistic study	Defined chemistry, equilibrium/kinetics or selectivity	Matrix effects and scale-up unverified	Useful for mechanism; weak for industrial claims.
Reporting completeness	Five independent domains	Mineralogy/host; multi-element balance; final product; replication/uncertainty; recycle/durability	NR is not scored as evidence of absence	Study-level Y/P/NR coding is supplied in the Supplementary File S1: Evidence Matrix.

Note. Author's evidence-coding framework. Y = reported; P = partially reported; NR = not reported or not applicable. Evidence level and reporting completeness are independent descriptors.

The 95-publication corpus contained 73 empirical or mechanistic publications eligible for evidence grading and 22 review, contextual, thesis, or proceedings publications, which were retained as supporting evidence. The graded distribution

was A = 4, B = 8, C = 20, D = 22, and E = 19. Evidence was concentrated in real-residue bench studies, real-liquor separation, and synthetic mechanistic studies; only a small minority involved factory, continuous, or industrially representative operation. This distribution supports strong conclusions about host-phase control and iron management, but only conditional conclusions about economics, long-term recycle, and industrial circularity.

Figure 1 summarizes the transparent evidence-selection and coding workflow used for the 95-publication corpus.

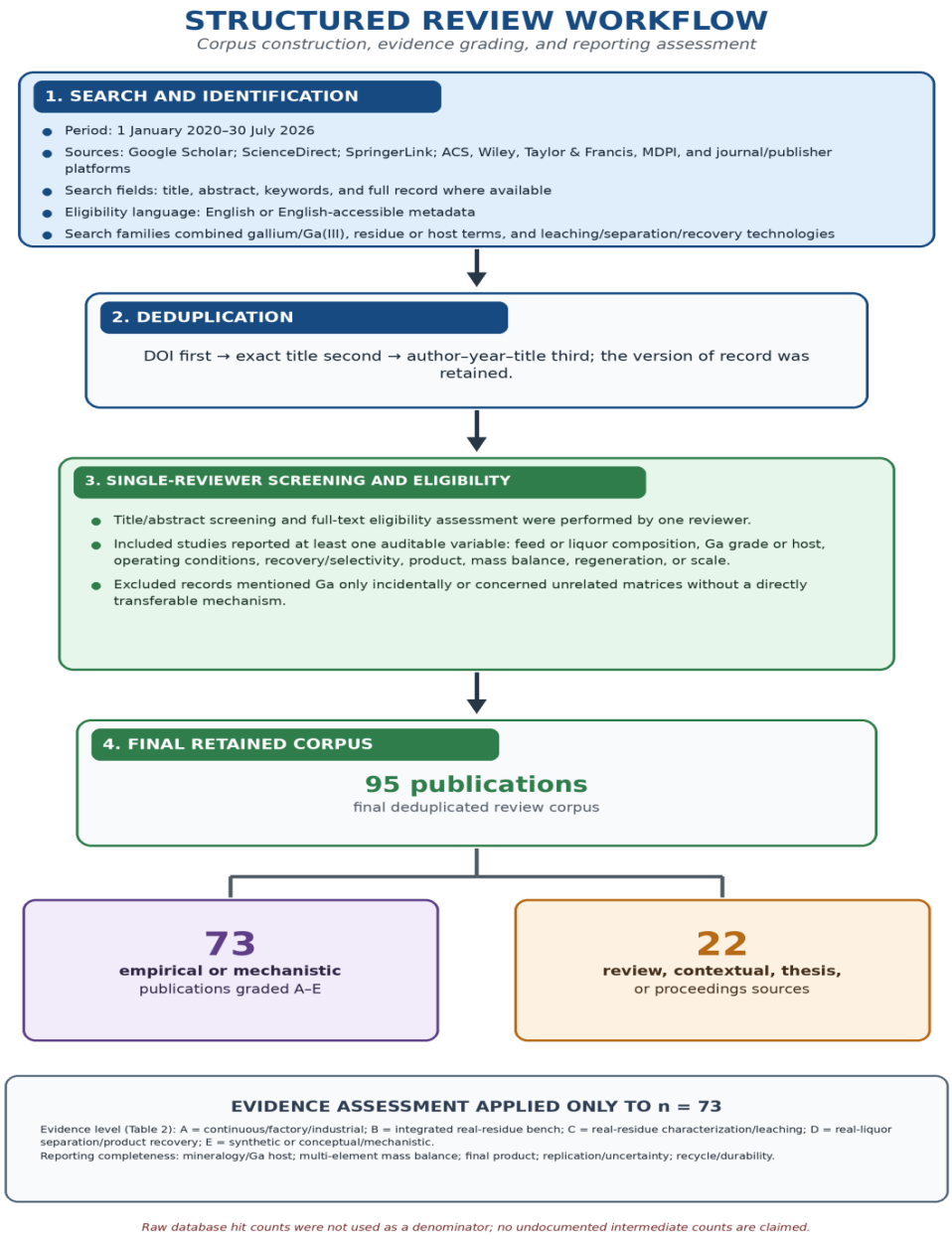

Figure 1. Structured literature-selection and evidence-coding workflow

Note. Author's elaboration based on Tables 1 and 2 and the reporting sequence described by Page et al. (2021). Raw database hit counts were not prospectively recorded and are therefore not shown as intermediate denominators.

The workflow distinguishes corpus construction from evidence grading. Reviews and contextual publications informed framing but were not treated as equivalent to primary experimental evidence.

Methodological limitations include single-reviewer screening, heterogeneous reporting, incomplete access to some plant data, and the absence of prospectively recorded database hit counts. These are addressed by transparent scope restriction, explicit NR coding, separating study type from reporting completeness, and cautious confidence statements.

Metallurgical Origins and Classification of Ga-Bearing Residues

Zinc hydrometallurgical circuits

Conventional zinc hydrometallurgy turns sulfide concentrate into oxide calcine, dissolves zinc via neutral and acid leaching, removes impurities, and electrowins zinc. Direct

oxygen-pressure leaching alters sulfur and iron separation points but leaves iron-rich residues. Gallium can follow dissolved zinc, stay with ferrites and silicates, or be scavenged by iron precipitates. Outcomes depend on acidity, temperature, redox, iron hydrolysis, and seed mineralogy (Chen, 2020; Höber & Steinlechner, 2021; Peng et al., 2026; Y. Z.-Y. Wang et al., 2020; Z.-Y. Z.-Y. Wang et al., 2020; Zhang, Rao, et al., 2024).

Iron-precipitation and purification residues

Jarosite, goethite, and hematite processes were developed to remove ferric iron from zinc sulfate liquors while limiting zinc loss and producing filterable solids. These solids are not chemically inert repositories. Their crystal structures, surface sites, pore liquids, and fine-grained intergrowths can retain gallium, indium, germanium, lead, silver, arsenic, and residual zinc. Industrial jarosite control therefore affects both the purity of the zinc electrolyte and the recoverability of companion metals (Asimi et al., 2020; De Souza Buriti et al., 2024; Cruells & Roca, 2022; Dong et al., 2025; Höber & Steinlechner, 2021; Peng et al., 2026; Pereira, 2025).

Zinc pyrometallurgical and secondary residues

Pyrometallurgical zinc routes, Waelz processing, selective fuming, and secondary-zinc treatment generate oxide dusts, slags, kiln accretions, and iron-rich residues. High-temperature treatment can either concentrate gallium in nonvolatile condensed phases or transfer it to dust through chloride-assisted volatilization and entrainment. Zinc ferrite is especially important because it can retain zinc, gallium, and indium in a spinel-type structure resistant to mild acid leaching (Iriarte Aguirre, 2023; Q. Chen et al., 2025; Grudinsky et al., 2021; Höber et al., 2022; Kashyap & Taylor, 2021; Kashyap et al., 2021; Steinlechner & Witt, 2023).

Lead metallurgy and integrated Zn–Pb residues

Primary and secondary lead operations produce slag, flue dust, matte, speiss, dross, anode residues, and sulfate-rich leach cakes. Evidence of direct gallium-recovery from these streams (2020–2026) is limited. Most evidence relates to integrated Zn–Pb operations, old polymetallic slags, and zinc-based materials used in lead furnaces. Gallium may be in complex oxide, spinel, silicate, or glassy forms, with accessibility affected by process history and weathering (Ettler et al., 2021–2024; Kamberović et al., 2021–2023; Lim et al., 2024; Nowińska & Kokowska-Pawłowska, 2024; Peng et al., 2023; Taylor, 2020).

Table 3 classifies residues according to their generation mechanism rather than by a single dominant element. This process-based classification is necessary because similarly named “zinc residues” may have fundamentally different gallium hosts.

Table 3. Classification of gallium-bearing residues in zinc and lead metallurgy

Residue class	Generation point	Likely Ga host or mechanism	Main process concern	Preferred first investigation
Neutral/hot-acid leach residue	Calcine or concentrate leaching	Zinc ferrite, iron oxides, silicates, unreacted particles.	Refractoriness and high Fe/Zn dissolution.	Mineralogy plus staged acid leaching.
Jarosite/goethite/hematite residue	Iron removal from Zn liquor	Structural incorporation, sorption, coprecipitation, pore liquor.	Ga loss during precipitation and difficult Fe separation.	Sequential extraction and microanalysis.
Zinc powder replacement residue	Cementation or Ga/Ge enrichment	Metallic/oxide assemblages, adsorbed or co-cemented Ga.	Heterogeneity and oxidation state.	Redox-sensitive leaching and phase mapping.
Zinc oxide or baghouse dust	Roasting, fuming, Waelz, gas cleaning	Fine oxides, chlorides, sulfates, entrained condensates.	Soluble salts, Pb/As/Cd, variable chloride.	Water wash followed by selective leaching.
Lead slag/matte/speiss	Lead smelting and slag cleaning	Glassy silicate, spinel, sulfide or arsenide phases.	Low Ga grade and refractory matrix.	Automated mineralogy and phase-specific tests.
Mixed historical residue	Cross-plant recycling or legacy storage	Multiple generations and weathered phases.	Poor traceability and variable leachability.	Sampling campaign and material genealogy.

Note. Author's synthesis based on Dong et al., 2024; Dong et al., 2025; Ettler et al., 2021; Höber & Steinlechner, 2021; Hou et al., 2024; Kamberović et al., 2021; Lim et al., 2024; Nowińska & Kokowska-Pawłowska, 2024; Rao et al., 2021; Singh et al., 2023; Z.-Y. Wang et al., 2020.

The classification shows why a universal gallium flowsheet is unlikely. Iron-precipitation residues invite selective phase decomposition and careful iron control, replacement residues invite redox-controlled leaching, and lead slags may require prior pyrometallurgical concentration or mineral-phase transformation.

Figure 2 maps the principal solid and liquid streams to their metallurgical origins and connects residue formation with subsequent gallium recovery options.

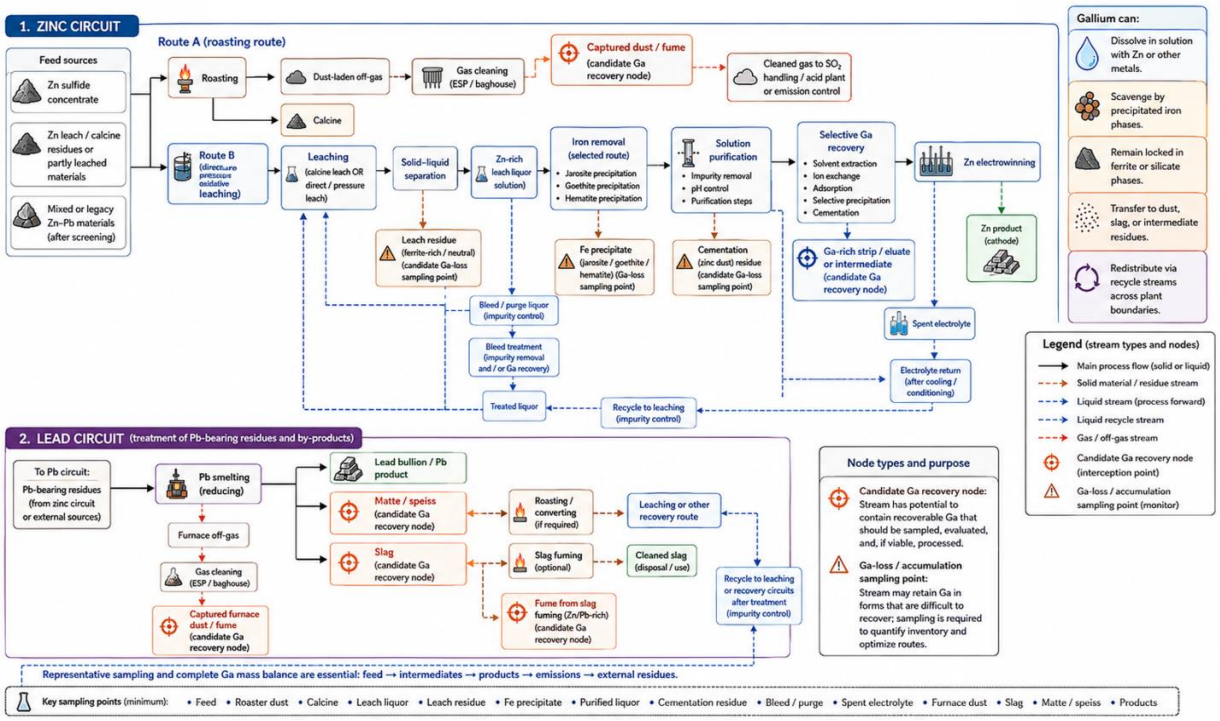

Figure 2. Plant-wide gallium deportment in integrated zinc and lead metallurgical flowsheets

Note. Author's synthesis based on Chen, 2020; Dong et al., 2025; Höber & Steinlechner, 2021; Hou et al., 2024; Rao et al., 2021; Taylor, 2020; Z.-Y. Wang et al., 2020; Zhang, Li, et al., 2024.

Figure 2 demonstrates that gallium can circulate between zinc and lead operations rather than follow a single linear path. Sampling only a final residue can therefore conceal earlier losses to dust, iron precipitates, recycle liquors, or intermediate metal-bearing solids.

Gallium Occurrence, Speciation, and Process Deportment

Initial occurrence and substitution mechanisms

Gallium commonly occurs as a dispersed substituent rather than as a discrete mineral. Its trivalent state and ionic size favor substitution in Al- and Fe-bearing phases, while its association with sphalerite can be controlled by coupled substitutions, inclusions, or nanoscale domains. After oxidation and leaching, the original ore-scale association may be destroyed, but Ga's chemical affinity for the hydrolyzed iron and aluminum phases remains important. Structural studies of ferrihydrite and goethite demonstrate that Ga substitution can modify local order and surface behavior, reinforcing the need to distinguish incorporated Ga from surface-sorbed Ga (Buist et al., 2024; Dong et al., 2024; Dong et al., 2025).

Roasting, ferrite formation, and residue refractoriness

During roasting or high-temperature oxidation, zinc and iron may form zinc ferrite, while gallium and indium can become incorporated in spinel-related or iron-rich phases. Mild sulfuric leaching then dissolves readily reactive zinc oxide but leaves a ferrite-rich residue. Reduction of zinc ferrite, sulfating roasting, and selective chlorination have therefore been investigated as ways to alter the host phase before leaching or to transfer valuable metals to more separable products (Geng et al., 2025; Grudinsky et al., 2021; Höber et al., 2022; Kashyap & Taylor, 2021; Kashyap et al., 2021).

Deportment during iron precipitation

Jarosite precipitation may enrich gallium in the solid by structural incorporation, surface retention, occlusion, or entrainment of mother liquor. The same process can be deliberately exploited to concentrate scattered metals from zinc liquor, but recovery then depends on breaking the iron sulfate framework without redissolving an excessive iron load. Goethite and ferrihydrite similarly provide reactive

surfaces and substitution sites. Hematite generally offers a more stable, lower-sulfate iron product, but its formation conditions and aging history can still influence trace-metal partitioning (Asimi et al., 2020; Buist et al., 2024; De Souza Buriti et al., 2024; Cruells & Roca, 2022; Dong et al., 2025; Pereira, 2025; Pereira, 2026a).

Lead smelting and slag retention

In lead metallurgy, gallium distribution depends on oxygen potential, sulfur activity, slag basicity, iron and zinc contents, and the presence of matte or speiss. Historical slags from polymetallic operations show that Ga may be associated with spinel-group phases, glass, or complex oxidized domains. Such mineralogy can limit direct acid extraction even where total Ga grades appear attractive. Fine-grained weathering products may improve apparent leachability while simultaneously increasing environmental mobility of Pb, As, and other hazardous elements (Ettler et al., 2021; Ettler et al., 2022; Lim et al., 2024; Nowińska & Kokowska-Pawłowska, 2024; Peng et al., 2023).

The principal gallium-retention mechanisms and the evidence required to distinguish them are compiled in Table 4.

Table 4. Gallium-retention mechanisms and diagnostic evidence

Mechanism	Typical residue	Diagnostic evidence	Processing implication
Structural substitution	Jarosite, goethite, ferrihydrite, spinel/ferrite	Lattice-parameter change, spectroscopy, microprobe correlation.	Requires phase dissolution or transformation.
Surface sorption	Fresh Fe–Al hydroxides and fine dusts	Desorption response, pH dependence, surface spectroscopy.	Potentially recoverable by controlled complexation.
Coprecipitation/occlusion	Iron-removal residues	Ga follows precipitate growth; losses depend on supersaturation and aging.	Precipitation control may prevent loss or intentionally enrich Ga.
Discrete oxide/sulfate domain	Roasted or pressure-leach residue	Micro-XRF/EPMA hotspots, selective dissolution.	Targeted leach chemistry may be feasible.
Glassy or silicate incorporation	Lead/Zn slag	Diffuse microanalysis signal and limited acid response.	Thermal reduction, chlorination, or fine grinding may be required.
Entrained process liquor	Filter cake and sludge	Water-wash release of soluble Ga and salts.	Wash recovery should precede aggressive treatment.

Note. Author's synthesis based on Buist et al., 2024; De Souza Buriti et al., 2024; Cruells & Roca, 2022; Dong et al., 2024; Dong et al., 2025; Ettler et al., 2021; Geng et al., 2025; Hou et al., 2024; Nowińska & Kokowska-Pawłowska, 2024; Pereira, 2026a.

Table 4 demonstrates that "gallium in jarosite" or "gallium in slag" is not a sufficient mineralogical description. Structural incorporation, sorption, and entrainment can coexist, and each fraction responds differently to washing, complexing agents, acid strength, and thermal pretreatment.

Figure 3 illustrates gallium-retention mechanisms that cannot be resolved from bulk chemical composition alone.

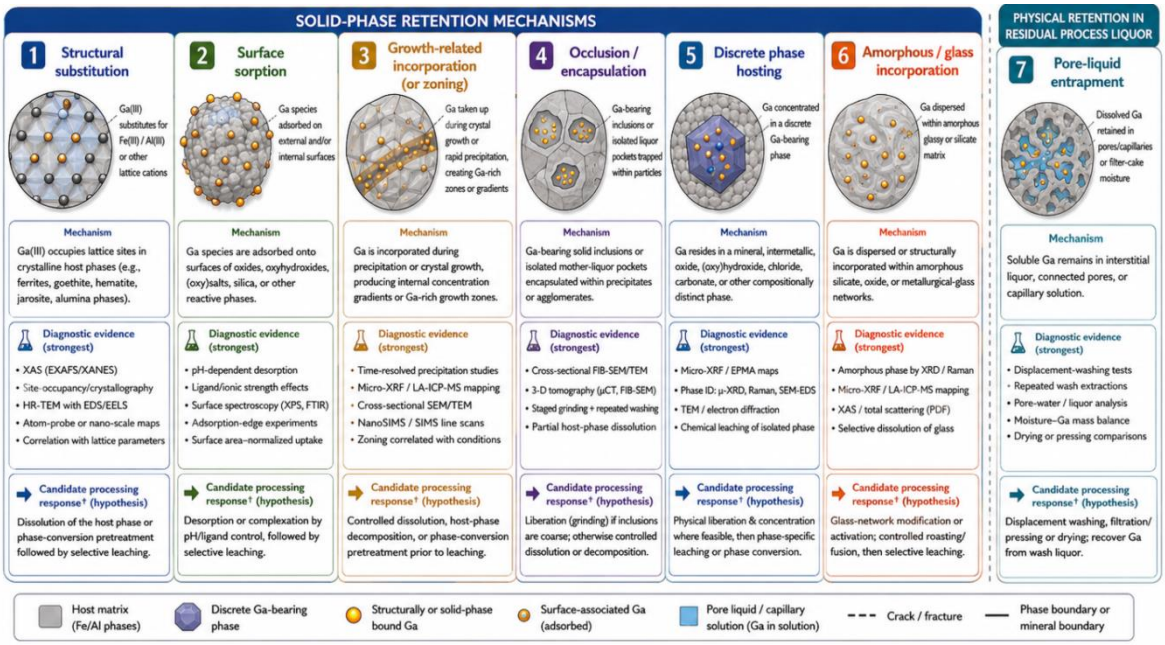

Figure 3. Mechanisms of gallium retention in metallurgical residues

Note. Author's synthesis based on Buist et al., 2024; De Souza Buriti et al., 2024; Cruells & Roca, 2022; Dong et al., 2024; Dong et al., 2025; Ettler et al., 2021; Pereira, 2026a.

Figure 3 compares structural substitution, surface sorption, coprecipitation, occlusion, discrete phase hosting, glass incorporation, and pore-liquid entrainment, and links each mechanism to diagnostic tests and likely responses to washing, leaching, or thermal conversion.

Characterization and Mass-Balance Requirements

Chemical and physical characterization

A defensible recovery study begins with representative sampling and total digestion for Ga, Ge, In, Zn, Pb, Fe, Al, Cu, Cd, As, Sb, Si, Ca, Mg, sulfur, and alkalis. Because gallium is often present at trace levels, contamination control, certified reference materials, duplicates, blanks, and method detection limits are essential. Particle-size distribution, moisture, porosity, surface area, bulk density, permeability, and filtration behavior are equally important because many zinc residues are fine, gel-forming, or agglomerated.

Mineralogical and microanalytical characterization

Bulk X-ray diffraction (XRD) identifies major crystalline phases but can miss amorphous iron phases and trace gallium hosts. A tiered strategy should combine Rietveld-refined XRD with scanning electron microscopy–energy-dispersive spectroscopy (SEM–EDS), electron-probe microanalysis (EPMA), automated mineralogy, laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), micro–X-ray fluorescence (micro-XRF), and, where necessary, X-ray absorption spectroscopy (XAS), including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). Microanalytical work on zinc-refinery residues and Zn–Pb slags illustrates the value of mapping Ga with Fe, Zn, In, Ge, Si, and S rather than interpreting isolated spot analyses (Buist et al., 2024; Dong et al., 2024; Ettler et al., 2021).

Sequential extraction and process genealogy

Selective washing and sequential dissolution can distinguish soluble salts, surface-bound fractions, iron-hosted gallium, ferrite-hosted gallium, and silicate- or glass-hosted fractions. These tests should be interpreted alongside process genealogy: feed source, roasting conditions, leach stage, precipitation reagent, recycle history, and storage weathering. Without this information, two residues with similar bulk grades may be incorrectly treated as equivalent.

Complete multi-element mass balance

Gallium recovery must be reconciled through feed, wash liquor, pregnant leach solution, solid residue, purification precipitates, organic phase, strip solution, intermediate product, and final raffinate. The balance should include Ga, Ge, In, Zn, Pb, Fe, Al, Cu, As, and water or solution volumes. Studies that report only solution concentration without accounting for solid mass change or wash streams may overstate extraction.

Table 5 links each analytical method to a process decision rather than presenting characterization as an isolated descriptive exercise.

Table 5. Characterization toolkit for residue-specific gallium recovery

Method	Primary information	Critical limitation	Best decision supported
Total digestion + ICP-MS/OES	Bulk Ga and impurity inventory.	Incomplete digestion of spinel or silicate can bias grade.	Resource screening and mass balance.
XRD/Rietveld	Major crystalline phases and transformations.	Low sensitivity to trace and amorphous hosts.	Pretreatment selection.
SEM–EDS/EPMA	Textural association and local composition.	Detection limits may exceed dispersed Ga concentration.	Liberation and host-phase mapping.
LA-ICP-MS/micro-XRF	Trace-element distribution at micro-scale.	Requires standards and careful matrix correction.	Ga–Ge–In deportment.
XAS methods	Oxidation state and local coordination.	Limited access and complex interpretation.	Distinguishing substitution from sorption.
Sequential extraction	Operationally defined Ga fractions.	Fractions are method-dependent, not unique minerals.	Leach sequence design.
Filtration/rheology tests	Thickening, washing, and solid–liquid separation behavior.	Often omitted in batch chemistry studies.	Scale-up and water balance.

Note. Author's synthesis based on Buist et al., 2024; Dong et al., 2024; Ettler et al., 2021; Geng et al., 2025; Hou et al., 2024; Nowińska & Kokowska-Pawłowska, 2024; Peng et al., 2023; Zhang, Li, et al., 2024.

The combined toolkit reduces the risk of selecting a route solely from bulk gallium grade. In particular, microanalysis and sequential extraction determine whether gallium can be released by washing, requires dissolution of the iron phase, or remains locked in ferrite, spinel, or glass.

Figure 4 summarizes the quantitative evidence landscape by material basis, evidence level, reporting completeness, and corpus role.

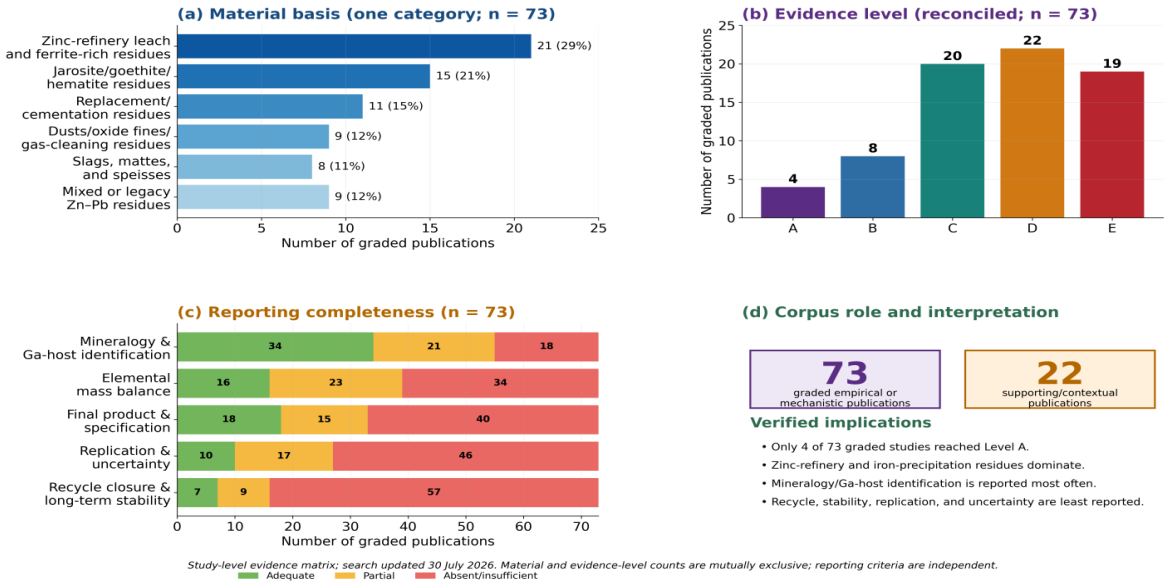

Figure 4. Evidence landscape of the 2020–2026 gallium-recovery corpus

Note. Author's synthesis from Supplementary File S1: Evidence Matrix. Each graded publication received one material category and one evidence level; reporting-completeness criteria were coded independently. Search updated 30 July 2026.

The material basis is dominated by zinc-refinery and iron-precipitation residues. Evidence grading is reconciled to A = 4, B = 8, C = 20, D = 22, and E = 19. Reporting is strongest for mineralogy and Ga-host identification and weakest for recycle closure, long-term stability, replication, and uncertainty. The 22 contextual and supporting publications inform interpretation but are not included in the graded counts.

Pretreatment and Gallium Liberation

Washing, sizing, and physical conditioning

Water washing is the lowest-complexity pretreatment for filter cakes and dusts. It removes entrained sulfate or chloride liquors, soluble alkalis, acid, and a potentially recoverable fraction of dissolved gallium. Desagglomeration and controlled grinding can improve reagent access, but ultrafine grinding may worsen filtration, entrainment, and downstream clarification. Physical concentration is generally limited because gallium is dispersed; nevertheless, size classification or selective recovery of magnetic or dense phases can be useful when Ga is associated with spinel-rich or fine dust fractions.

Thermal decomposition and selective roasting

Thermal treatment can decompose jarosite, drive off sulfate, transform goethite to hematite, alter zinc ferrite, and create phases more responsive to leaching. Sulfating roasting with iron sulfates, oxidizing roasting followed by reduction, and selective chlorination have all been proposed for zinc residues. The technical objective must be explicit: either retain gallium in a leachable nonvolatile phase, transfer it to a volatile chloride-enriched dust, or separate iron and zinc through controlled phase formation (Iriarte Aguirre, 2023; Q. Chen et al., 2025; Grudinsky et al., 2021; Höber et al., 2022; Kamberović et al., 2023; Pereira, 2025; Steinlechner & Witt, 2023; Xing et al., 2024; Zhu et al., 2025).

Reduction and ferrite destruction

Reducing zinc ferrite can separate zinc from an iron-rich product and improve access to gallium and indium. However, the reduction conditions may also produce metallic iron, complex spinels, or sintered material, which can reduce subsequent leachability. Process selection must therefore consider not only metal extraction but also gas composition, dust capture, reductant demand, and the intended disposition of iron (Kashyap & Taylor, 2021; Kashyap et al., 2021; Zhu et al., 2025).

Hydrothermal, pressure, and assisted pretreatments

Hydrothermal and oxygen-pressure treatments provide intensive chemical access without complete melting. Ultrasound can improve boundary-layer transport, particle breakage, and gas–liquid–solid contact in replacement

residues, while oxygen pressure promotes oxidation and dissolution of reactive phases. These benefits are material-specific and should be separated from simple increases in temperature, mixing, or energy input (Ding et al., 2026; Liang et al., 2026; Xi et al., 2022).

Table 6 compares pretreatments according to their intended mineralogical effect. The same thermal label may conceal very different objectives, from sulfate decomposition to chloride volatilization.

Table 6. Pretreatment options for gallium-bearing Zn–Pb residues

Pretreatment	Best-suited feed	Primary effect	Main risk	Evidence base
Water washing/desagglomeration	Filter cake, jarosite, dust	Recovers entrained liquor and removes soluble salts.	Water demand and contaminated wash solution.	Industrial solids handling and residue studies.
Jarosite/goethite calcination	Iron-precipitation residue	Sulfate removal and phase conversion.	Ga encapsulation by sintering or hematite growth.	Thermal decomposition and transformation studies.
Sulfating roasting	Ferrite-rich zinc residue	Converts selected metals to sulfates.	SO_x control and nonselective sulfate formation.	Mechanistic roasting studies.
Controlled chlorination	Hot-filter residue, iron residue, dust	Forms volatile or leachable chlorides.	Corrosion, chloride recycle, Pb/As volatilization.	Thesis, laboratory, and integrated process studies.
Ferrite reduction	Zinc refinery residue	Destroys spinel and separates Zn/Fe behavior.	Sintering, reductant demand, complex product phases.	Zn–Ga–In extraction studies.
Oxygen-pressure/ultrasound assistance	Replacement residue or refractory leach feed	Enhances oxidation, transport, and phase opening.	CAPEX and uncertain incremental energy benefit.	Factory-condition and mechanistic studies.

Note. Author's synthesis based on Iriarte Aguirre, 2023; Q. Chen et al., 2025; Ding et al., 2026; Grudinsky et al., 2021; Höber et al., 2022; Kamberović et al., 2023; Kashyap et al., 2021; Liang et al., 2026; Steinlechner & Witt, 2023; Xi et al., 2022; Xing et al., 2024; Zhu et al., 2025.

No pretreatment should be selected without a downstream mass balance. A roasting step is justified only when the altered phase assemblage improves overall gallium recovery, reduces impurity loading, or produces valuable zinc, lead, or iron coproducts sufficient to offset energy and gas-treatment requirements.

Leaching Technologies

Sulfuric-acid leaching

Sulfuric acid is the default lixiviant for zinc hydrometallurgical integration because sulfate liquors can often be returned to existing circuits. Its performance depends on free acidity, temperature, residence time, liquid-to-solid (L/S) ratio, redox potential, particle size, and iron speciation. Strong acid or pressure conditions improve dissolution of refractory phases but also increase Fe, Al, Zn, and silica loading. Gallium extraction must therefore be optimized against impurity dissolution rather than maximized independently (Chen, 2020; Geng et al., 2025; Rao et al., 2021; Y. Wang et al., 2020; Zhang, Rao, et al., 2024).

Mixed inorganic–organic acid systems

Complexing organic acids can change selectivity by stabilizing dissolved gallium and germanium or by precipitating iron as an oxalate. Sulfuric–tartaric and organic-acid routes have been evaluated for zinc residues and jarosite cakes, with the central challenge being to dissolve Ga and Ge while controlling Fe and avoiding excessive reagent loss to the matrix. Organic acids may offer lower volatility and tunable coordination, but their recovery, degradation, and impact on downstream extraction remain decisive (Mondal et al., 2025; Song et al., 2021; Qi et al., 2026).

Chloride leaching

Hydrochloric- and chloride-rich media can convert gallium into extractable chloride complexes and support selective solvent extraction, anion exchange, liquid membranes, or ketone-based separations. Chloride routes are attractive after chlorination roasting or for chloride-bearing dusts, but corrosion, volatile emissions, $PbCl_2$ precipitation, and chloride management must be incorporated into the flowsheet. High iron concentrations are particularly problematic because Fe(III) and Ga(III) can form similarly

extractable chloride species (Anpilogova et al., 2022; Asadian & Ahmadi, 2020; Chen et al., 2026; Hashizume et al., 2024; Qi et al., 2026; Stankovic & Oshima, 2026; Xu et al., 2023; Zhou & Huang, 2022; Zhou et al., 2020).

Alkaline and pressure leaching

The amphoteric behavior of gallium enables alkaline dissolution as gallate while much of the iron remains solid. Alkaline routes can, however, co-dissolve aluminum and zinc and require careful caustic recovery. Oxygen-pressure leaching improves kinetics and can selectively attack replacement residues or pressure-leach intermediates. The practical advantage depends on whether the resulting liquor is compatible with purification and electrowinning (Ding et al., 2026; Hou et al., 2024; Liang et al., 2026; Liu, Guo, et al., 2023; Wang et al., 2024; Xu et al., 2024; D. Zhou et al., 2025).

Kinetic and scale-up interpretation

Reported extraction should be interpreted with particle-size change, solid mass loss, dissolved iron, and wash recovery. Apparent kinetic improvement under ultrasound or pressure may arise from enhanced mixing, surface renewal, or phase conversion; these contributions should be separated experimentally. Continuous countercurrent washing, autoclave discharge behavior, and silica management are rarely demonstrated but can determine whether a high batch extraction is operationally useful.

Table 7 provides the central quantitative comparison requested for critical synthesis. Values are reported only when they were explicitly available; NR denotes information that could not be consistently compared across the reviewed publications.

Table 7. Quantitative comparison of representative gallium-recovery studies

Reference	Material and Ga host	Route and conditions	Quantitative Ga and impurity results	Product and scale	Evidence level/source role
Zhang, Rao, et al. (2024)	Industrial zinc replacement residue; Ga embedded in jarosite; feed grade NR	Modified pressure plus atmospheric H_2SO_4 leaching	Ga leaching increased from 77.83% to 96.46%; Ga, Fe, and As dissolution were coupled	Ga-bearing process liquor; industrial-problem bench optimization	C
Song et al. (2021)	Zinc residue bearing Ga and Ge; grade NR	H_2SO_4–tartaric-acid leaching	Ga extraction >96% and Ge >99% under optimized conditions; Fe control remained a downstream issue	Mixed Ga–Ge liquor; real-residue batch study	C
K. Zhang et al. (2021)	Strongly acidic sulfate leach solution from zinc residue; Ga concentration NR	N235 acid/Fe removal followed by Cyanex 272 SX and stepwise stripping	97.9% Fe removal in three stages; other metals <3% in the first step; overall Ga recovery NR	Ga-rich strip solution; real-liquor batch SX	D
Pan et al. (2025)	Gallium electrolyte from a zinc-refinery plant	LSC-600P adsorption, elution, and lime precipitation	98.6% Ga adsorption after six cycles and >98% desorption; Al adsorption <4.5% and Al removal 93.12%	Ga strip/hydroxide route with alkali recycle; cyclic bench study	D
Asadian and Ahmadi (2020)	Defined synthetic Ga(III) chloride solution	Emulsion liquid membrane in staged contact	Up to 99% Ga recovery in three stages; real-matrix competition not demonstrated	Ga strip phase; synthetic-solution study	E
Wu et al. (2025)	Strongly acidic chloride model liquor, including 6 mol/L HCl	Acid-tolerant solvent-free extractant in multistage contact	99.9% Ga removal and 6.0 g/L loading; residue-derived liquor not demonstrated	Loaded organic and strip route; model-liquor study	E
Kashyap et al. (2021)	Ferrite-rich zinc-refinery residue; Ga and In associated with zinc ferrite	Ferrite reduction followed by extraction	Ga accessibility improved; comparable overall recovery NR; Fe disposition and sintering remained relevant	No final Ga product; real-residue bench study	C
Iriarte Aguirre (2023)	Zinc-plant residues; jarosite/ferrite-related Ga	Chlorination roasting followed by a hydrometallurgical refining concept	Ga transfer and recovery demonstrated; global recovery NR; chloride volatility and Fe/Pb behavior require closure	Ga chloride/SX–electrowinning concept; thesis-scale flowsheet	Supporting/contextual source; not graded

Liang et al. (2026)	Zinc powder replacement residue; Ga mainly in oxide and composite-oxide phases	Ultrasound-enhanced oxygen-pressure leaching	Ultrasound increased Ga leaching by more than 18 percentage points; Zn was less affected and Ge was jointly recovered	Ga–Ge liquor; mechanistic real-residue study	C
Q. Chen et al. (2025)	Zinc pressure-leach hot-filter residue containing Ga and Ge	Controlled-potential chlorination	High-efficiency multimetal recovery; directly comparable Ga value NR; selectivity governed by chloride volatilization	Chloride-enriched products; integrated real-residue bench route	B
Zhu et al. (2025)	Jarosite residue; Ga and In in an iron-rich matrix	Oxidizing roasting, reduction, smelting, and electrorefining	Ga separated from an Fe–Ga alloy; global Ga recovery NR; Zn/In volatilization and Fe-alloy formation integrated	Ga-rich electrorefining product; multistep real-residue bench route	B
J. Wang et al. (2024)	Purified Ga electrolyte from a complex zinc-hydrometallurgy system with Al, Zn, and OH^- impurities	Gallium electrowinning	Cathodic Ga obtained; Al, Zn, and OH^- affected current efficiency and deposit quality	Metallic Ga cathode; complex-liquor bench electrolysis	D

Note. Author's synthesis based on the cited studies. NR = not reported in a directly comparable form; SX = solvent extraction; IX = ion exchange. Percentages refer to the experimental boundary stated in each row and are not necessarily overall process recoveries.

The table reveals two recurring limitations. First, studies frequently report high extraction or separation percentages without corresponding Fe extraction, product purity, or overall recovery. Second, numerical results obtained from synthetic solutions cannot be transferred directly to heterogeneous residues. Sulfate routes remain the most compatible with zinc plants when iron and silica are controlled; chloride, organic-acid, and intensified routes are conditional options for specific hosts and downstream separation trains.

Critical synthesis and confidence assessment

High-confidence conclusions. Gallium leachability is controlled by host phase and process history, not by bulk grade alone. Jarosite association, ferrite encapsulation, and glass or spinel hosting explain why similar feeds can respond differently. Industrially grounded optimization can materially improve extraction, as shown by the increase from 77.83% to 96.46% when jarosite-associated gallium and the leaching sequence were addressed (Zhang, Rao, et al., 2024).

Moderate-confidence conclusions. Pressure, ultrasound, mixed-acid complexation, and phase-conversion pretreatments can improve recovery for selected residues, but their incremental benefit must be separated from temperature, mixing, and reagent-intensity effects.

Low-confidence or unverified claims. No universal Fe/Ga threshold, minimum economic Ga grade, or preferred lixiviant can be established from the current corpus. A route should be rejected when host-phase liberation is unproven, impurity dissolution overwhelms Ga concentration, or wash, filtration, and secondary-residue balances remain open.

Solution Purification and Impurity Management

Iron as the principal separation barrier

Iron commonly exceeds gallium by two or three orders of magnitude in leach liquors. It consumes extractant capacity, controls hydrolysis behavior, colors and contaminates precipitates, and promotes crud or third-phase formation. Conventional neutralization, jarosite, goethite, and hematite precipitation can remove iron, but gallium may be adsorbed, incorporated, or occluded during precipitation. The process window must therefore balance iron removal against gallium retention in solution (Asimi et al., 2020; Buist et al., 2024; De Souza Buriti et al., 2024; Cruells & Roca, 2022; Peng et al., 2026; Pereira, 2026a).

Redox, complexation, and selective scrubbing

Iron–gallium separation can be improved by changing oxidation state or ligand environment. In chloride systems, co-extraction of Fe(III) and Ga(III) may be followed by selective reductive scrubbing of iron while retaining gallium in the organic phase. In oxalate systems, controlled precipitation of ferrous oxalate can remove iron before Ga–Ge extraction. These approaches avoid indiscriminate pH elevation but require redox control and management of reducing or complexing reagents (Chen et al., 2026; Helbig et al., 2024; Zhang et al., 2021).

Zinc, aluminum, lead, and hazardous impurities

Zinc should be recovered or recycled rather than discarded with a gallium concentrate. Aluminum can follow gallium in acidic or alkaline media and may require partial neutralization or precipitation from barren electrolyte. Lead can be rejected as sulfate in sulfuric systems or as chloride-bearing solids in chloride systems, while arsenic, antimony, cadmium, and copper require stable product destinations.

Purification must therefore be designed as a multi-element sequence, not as an isolated Fe-removal step (Kamberović et al., 2021; Pan et al., 2025; Peng et al., 2023; Rao et al., 2021; Tagiyeva & Geidarov, 2022; Zhang et al., 2022).

Prevention of secondary gallium losses

Gallium losses during impurity precipitation should be measured by analyzing both precipitate and supernatant after washing. High local pH, uncontrolled supersaturation, long aging, and large fresh iron-hydroxide surface area favor scavenging. Seeded precipitation, staged neutralization, temperature control, complexant addition, and redissolution of a gallium-bearing precipitate are possible countermeasures, but each creates an additional recycle stream.

Table 8 summarizes impurity-management choices and explicitly identifies how each operation can generate a secondary gallium loss.

Table 8. Impurity-management options before gallium concentration

Impurity/problem	Control method	Potential Ga loss mechanism	Required verification
Fe (III) in sulfate liquor	Controlled hydrolysis, goethite/hematite precipitation, SX pretreatment.	Sorption, coprecipitation, entrainment.	Washed precipitate balance and aging tests.
Fe (III) in chloride liquor	Co-extraction plus reductive scrubbing or selective complexation.	Organic capacity consumed by Fe; Ga stripping during scrub.	Loading/scrubbing isotherms and Fe redox balance.
Al in acidic/alkaline liquor	Partial neutralization, precipitation, or selective extraction.	Ga hydrolysis near the Al precipitation window.	Ga/Al separation factor and redissolution test.
Zn and Cu	Cementation, extraction, or return to main circuit.	Ga co-cementation or organic competition.	Value-metal balance and recycle compatibility.
Pb, As, Sb, Cd	Sulfate/chloride precipitation and stabilized solids.	Entrained liquor or adsorption on fresh precipitate.	Leaching stability and hazardous-residue classification.
Silica and fine solids	Preclarification, aging, flocculation, controlled leach conditions.	Ga entrainment in gel or filter cake.	Wash efficiency and filterability.

Note. Author's synthesis based on Chen et al., 2026; Helbig et al., 2024; Kamberović et al., 2021; Pan et al., 2025; Peng et al., 2023; Pereira, 2026a; Rao et al., 2021; Tagiyeva & Geidarov, 2022; Zhang et al., 2022; Zhang et al., 2021; Peng et al., 2026.

The preferred sequence depends on solution chemistry. Sulfate liquors favor controlled precipitation and organophosphorus extraction, whereas chloride liquors favor anionic complex extraction, ketones, or membranes. In both cases, gallium should remain in a defined stream whose volume and impurity inventory are progressively reduced.

Gallium Separation, Concentration, and Product Recovery

Solvent extraction

Within the reviewed 2020–2026 corpus, solvent extraction (SX) has the broadest evidence base for concentrating Ga from acidic liquors. Cyanex 272, P507-type reagents, and D2EHPA are relevant to sulfate media, whereas amines, ketones, solvating reagents, hydroxamic acids, and ionic liquids extend the operating window to strongly acidic sulfate or chloride solutions. Performance must be judged by loading, Ga/Fe and Ga/In separation, phase disengagement, scrubbing, stripping, extractant loss, and repeated-cycle stability (Fleitlikh & Grigorieva, 2025; Guo et al., 2024; Hashizume et al., 2024; K. Zhang et al., 2021). Ketone, ionic-liquid, and acid-tolerant systems remain less validated with dirty real liquors (Dhiman et al., 2024; Song et al., 2020; Stankovic & Oshima, 2026; Wu et al., 2025; Xu et al., 2023).

Stepwise extraction is often preferable to a single nominally selective contact. N235 can first remove free acid and Fe before Cyanex 272 concentrates Ga, whereas chloride systems may co-extract Ga and Fe and then selectively scrub Fe. Sulfate-polymetallic separation and controlled-potential chlorination provide complementary examples (F. Chen et al., 2025; Q. Chen et al., 2025; Q. Chen et al., 2026; K. Zhang et al., 2021). New hydroxamic and acid-tolerant extractants should be compared with conventional reagents using real liquors, loading–stripping cycles, and phase-stability data (Guo et al., 2024; Wu et al., 2025; Zhang, Zhou, et al., 2024).

Ion exchange, adsorption, and hybrid sorbents

Ion exchange (IX) and adsorption are attractive for dilute solutions or polishing after bulk impurity removal. Carbon,

cellulose, hydroxamic resin, solvent-impregnated resin, silica-supported P507–TBP, and catechol-functionalized materials demonstrate diverse coordination and ion-exchange mechanisms (Díez et al., 2021; Guo et al., 2020; He et al., 2023; Li et al., 2024; Meng et al., 2021; Raj et al., 2023a, 2023b). Clinoptilolite, biogenic Se/Te sorbents, mesoporous materials, and extractant-loaded nanofibers extend the material range, but the industrially relevant metrics are capacity at realistic acidity, Ga/Fe/Zn/Al selectivity, column breakthrough, regeneration, pressure drop, and fouling resistance (Protsak et al., 2024; Sáez et al., 2021; Saikia, Costa, et al., 2022; Saikia et al., 2026; Saikia, Sinharoy, et al., 2022; Segala et al., 2022, 2023).

Liquid membranes and intensified contactors

Emulsion and supported liquid membranes combine extraction and stripping in a compact transport step. They can be effective for low-concentration Ga chloride solutions, including systems based on organophosphorus or bifunctional ionic-liquid carriers. Their main scale-up concerns are membrane stability, carrier loss, emulsion breakage, module lifetime, and sensitivity to suspended solids (Asadian & Ahmadi, 2020; Zhou & Huang, 2022; Zhou et al., 2022; Zhou et al., 2020).

Precipitation and electrowinning

Selective precipitation can produce $Ga(OH)_3$, basic salts, or Ga-rich mixed intermediates suitable for redissolution and oxide production. Adsorption–precipitation has also been proposed for recovering gallium, aluminum, and alkali from zinc-refinery gallium electrolyte. Metallic gallium recovery by electrowinning is favored after substantial purification and concentration. Alkaline electrolytes suppress some impurity pathways but hydrogen evolution, cathode material, electrode geometry, pretreatment, and mass transfer strongly influence current efficiency (Liu, Guo, et al., 2023; Liu et al., 2025; Liu, Tian, et al., 2023; Pan et al., 2025; Wang et al., 2024; Xu et al., 2024).

Product definition and refining

A complete study should define whether the target is a Ga-rich solution, hydroxide, Ga_2O_3, technical-grade metal, or high-purity gallium. The purity required for semiconductor applications is far beyond that demonstrated by most residue-leaching studies. Consequently, the practical objective of a residue plant may be a transportable Ga-rich intermediate that can be refined in an existing specialist facility. Product specifications must include Fe, Zn, Al, Pb, Ge, In, alkali, chloride, sulfate, and organic carryover (Liu et al., 2025; Liu, Xu, et al., 2023; Robart et al., 2025).

Table 9 organizes separation technologies by the concentration and chemistry of the feed liquor. Its purpose is not to identify a universally superior reagent, but to show the appropriate operating window for each technology family.

Table 9. Separation and product-recovery technologies for gallium-bearing liquors

Technology	Best application	Strength	Critical scale-up issue	Representative evidence
Acidic organophosphorus SX	Sulfate liquors after Fe control	High concentration factor and established equipment.	Fe/Al/Zn competition, stripping, organic loss.	Cyanex 272, P507, D2EHPA studies.
Amine/solvating/ketone SX	High-acid chloride or complexed liquor	Exploits anionic Ga complexes and ion solvation.	Fe co-extraction, water balance, corrosion.	N235, ketone, and chloride studies.
Hydroxamic/ionic-liquid SX	Difficult Ga–Ge–In separation	Tunable selectivity and synergistic chemistry.	Cost, viscosity, synthesis, long-term stability.	Hydroxamic and ionic-liquid studies.
Chelating resin/adsorbent	Dilute or polished solution	Low solvent inventory and column operation.	Capacity loss, regeneration, suspended solids.	Hydroxamic, catechol, cellulose, silica, zeolite systems.
Supported/emulsion liquid membrane	Low-concentration chloride stream	Simultaneous extraction and stripping.	Carrier loss and module/emulsion stability.	Supported and emulsion membrane studies.
Selective precipitation	Concentrated purified Ga solution	Simple equipment and oxide precursor production.	Coprecipitation and poor filterability.	Hydroxide and adsorption–precipitation routes.
Electrowinning	Purified gallate or concentrated Ga electrolyte	Direct metallic product and process intensification.	Hydrogen evolution, cathode fouling, energy efficiency.	Pulse/cyclone and conventional electrowinning.

Note. Author's synthesis based on Anpilogova et al., 2022; Asadian & Ahmadi, 2020; F. Chen et al., 2025; Dhiman et al., 2024; Díez et al., 2021; Fleitlikh & Grigorieva, 2025; Guo et al., 2020; Guo et al., 2024; Hashizume et al., 2024; He et al.,

2023; Ito et al., 2020; Li et al., 2024; Liu, Guo, et al., 2023; Liu et al., 2025; Liu, Tian, et al., 2023; Meng et al., 2021; Pan et al., 2025; Protsak et al., 2024; Qiu et al., 2021; Raj et al., 2023a; Raj et al., 2023b; Sáez et al., 2021; Saikia, Costa, et al., 2022; Saikia et al., 2026; Saikia, Sinharoy, et al., 2022; Segala et al., 2022; Segala et al., 2023; Silwamba et al., 2025; Song et al., 2020; Stankovic & Oshima, 2026; Wang et al., 2024; Wu et al., 2025; Xu et al., 2023; Xu et al., 2024; Zhang et al., 2021; Zhang, Zhou, et al., 2024; Zhou & Huang, 2022; Zhou et al., 2022; Zhou et al., 2020.

Solvent extraction remains the leading bulk-concentration option, while ion exchange and adsorption are strongest at lower concentrations or as polishing steps. Membranes offer intensified transport but have less evidence for dirty real liquors. Electrowinning becomes credible only after the impurity inventory has been reduced and a stable electrolyte has been demonstrated.

Figure 5 distinguishes bulk impurity removal from gallium concentration and final product recovery.

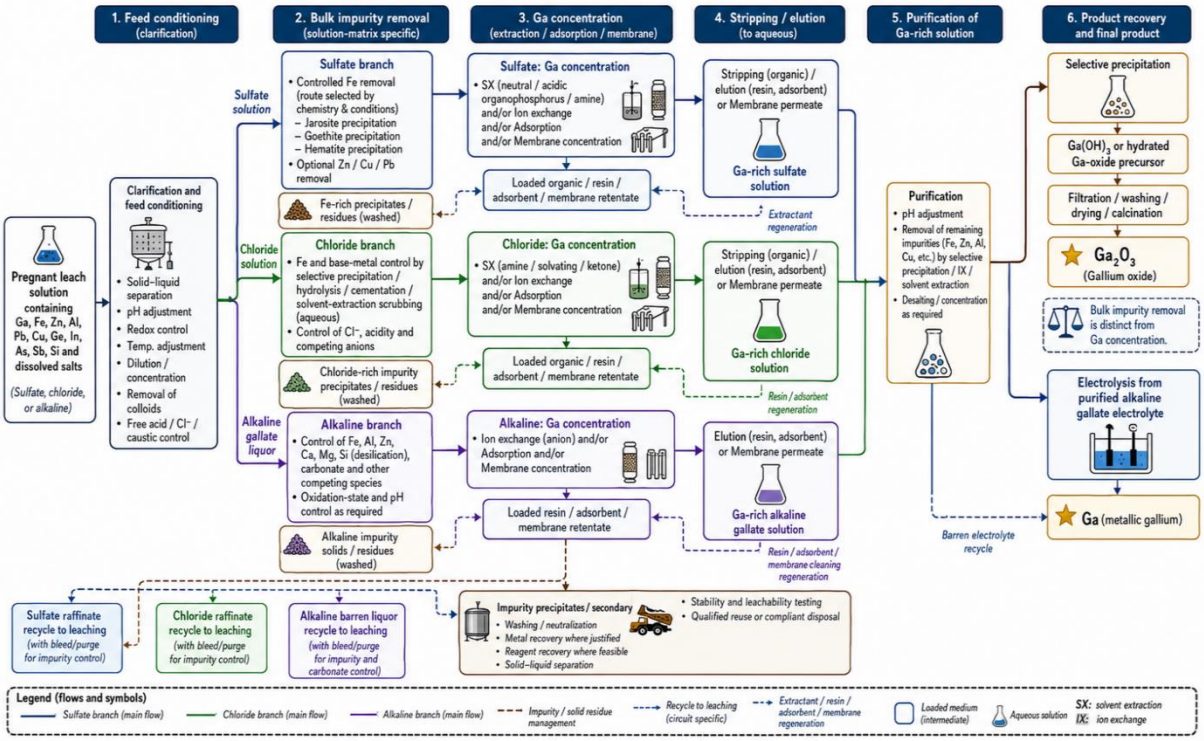

Figure 5. General separation train from pregnant leach solution to gallium product

Note. Author's synthesis based on F. Chen et al. (2025), Q. Chen et al. (2026), Liu, Xu, et al. (2023), Pan et al. (2025), J. Wang et al. (2024), and K. Zhang et al. (2021).

Figure 5 presents alternative sulfate, chloride, and alkaline branches, including raffinate or barren-electrolyte recycle, extractant or resin regeneration, treatment of impurity precipitates, and the point at which a Ga-rich intermediate or metallic product is obtained.

Critical synthesis and confidence assessment

High-confidence conclusions. Bulk Fe removal must precede or be integrated with Ga concentration, and reported Ga loading without stripping, regeneration, and a defined product is incomplete evidence. The strongest real-liquor example used staged N235/Cyanex 272 extraction, with 97.9% Fe removal while limiting first-stage co-extraction of other metals to below 3% (K. Zhang et al., 2021).

Moderate-confidence conclusions. SX currently has the broadest evidence base for bulk concentration; IX and adsorption are technically credible for dilute or polishing duties when column behavior and regeneration are demonstrated. Electrowinning is credible only after a stable, sufficiently pure electrolyte has been produced.

Low-confidence or unverified claims. Synthetic-solution capacity, single-contact extraction, or short-cycle adsorption do not establish robustness in real liquors. Routes should be rejected when stripping is incomplete, organic or resin loss is unmeasured, pressure drop or fouling is unresolved, or the eluate cannot be converted to a specified Ga intermediate or metal.

Residue-Specific Integrated Flowsheets

Zinc refinery leach residue

A rational flowsheet begins with washing, mineralogical classification, and recovery of readily soluble zinc. Ferrite-rich material then requires reduction, sulfating roasting, stronger acid leaching, or pressure treatment. The resulting Ga–Ge liquor should be clarified and subjected to iron control before joint or sequential Ga–Ge separation. Zinc and lead should return to their principal circuits where feasible, and the final iron-rich residue should be assessed as a potential

hematite product or stable disposal material (Geng et al., 2025; Kashyap & Taylor, 2021; Kashyap et al., 2021; Rao et al., 2021; Z.-Y. Wang et al., 2020; Zhang, Li, et al., 2024).

Jarosite, goethite, and Pb–Ag sludge

For jarosite-rich residues, initial washing separates entrained electrolyte and alkalis. Thermal or hydrothermal decomposition can reduce sulfate and convert the host phase, after which selective acid or complex-acid leaching extracts Ga, Ge, In, Zn, and Cu, leaving a more stable iron product. Pb–Ag-bearing sludge requires separate management of lead and silver and tighter control of sulfur and arsenic. Integrated routes that combine roasting, reduction, smelting, and electrorefining can recover multiple metals but carry a higher energy and equipment burden (Kamberović et al., 2021; Kamberović et al., 2023; Mondal et al., 2025; Singh et al., 2023; Xing et al., 2024; Q. Zhou et al., 2025; Zhu et al., 2025).

Zinc powder replacement residues and pressure-leach intermediates

Replacement residues can be attractive because cementation or precipitation has already enriched gallium and germanium relative to the original liquor. Oxygen-pressure leaching, ultrasound assistance, and controlled redox conditions can dissolve target phases while limiting zinc and iron transfer. Zinc powder cementation can also serve as an intentional enrichment step from pressure-leachate before downstream leaching or separation (Ding et al., 2026; Hou et al., 2024; Liang et al., 2026; D. Q. Zhou et al., 2025).

Zinc smelting slags, lead slags, and dusts

Dusts should normally be washed to remove soluble salts before selective acid or chloride treatment. Lead-rich and arsenic-bearing components require early stabilization or separation. Slags with Ga in glass or spinel may be unsuitable for direct leaching; an alternative is reductive smelting or selective chlorination followed by treatment of an enriched dust or leachate. Tartaric-acid coordination and anion exchange illustrate how a slag-derived acid leachate can be directed to a gallium-specific separation step (Q. Chen et al., 2025; Ettler et al., 2021; Ettler et al., 2022; Höber et al., 2022; Lim et al., 2024; Nowińska & Kokowska-Pawłowska, 2024; Qi et al., 2026; Steinlechner & Witt, 2023).

Multimetal integration

Gallium rarely carries the full economics of a complex residue project. The most credible flowsheets recover or preserve value from zinc, lead, germanium, indium, copper, and silver while producing an iron-rich residue with lower sulfate and leachability. Multimetal integration also changes the optimal order of operations: a step that is suboptimal for gallium alone may be justified if it prevents zinc loss, produces a germanium coproduct, or avoids hazardous waste disposal.

Table 10 consolidates the review into residue-specific process sequences. The proposed flowsheets are conceptual and should be treated as testable frameworks rather than ready-made designs.

Table 10. Proposed residue-specific gallium recovery flowsheets

Feed	Proposed sequence	Principal coproducts	Critical gate
Ferrite-rich Zn leach residue	Wash → Zn recovery → ferrite conversion/reduction → acid or pressure leach → Fe control → Ga–Ge separation.	Zn, Ge, In, Fe product.	Ga host liberation without excessive Fe dissolution.
Jarosite/goethite residue	Wash → thermal/hydrothermal decomposition → selective leach → Pb/Zn/Fe control → Ga concentration.	Zn, Pb/Ag where present, hematite-rich residue.	Sulfate removal and low Ga loss during Fe rejection.
Zn powder replacement residue	Characterize redox phases → ultrasound/O_2 pressure leach → cementation residue recycle → Ga–Ge separation.	Ge, Zn, Cu.	Continuous pressure operation and impurity stability.
Zinc/lead smelter dust	Water wash → selective acid/chloride leach → Pb/As/Sb stabilization → Ga recovery.	Zn, Pb, Cd, In/Ge.	Dust variability and hazardous volatile elements.
Lead or Zn–Pb slag	Mineralogy → direct leach test; if refractory, reduction/fuming or chlorination → enriched dust leach → Ga separation.	Zn, Pb, Ge, Fe-bearing slag product.	Tonnage-grade balance and energy intensity.
Mixed legacy residue	Campaign sampling → blending → modular pretreatment → multimetal recovery → stabilized residue.	Site-specific suite.	Representativeness, variability, and environmental liability.

Note. Author's synthesis based on Q. Chen et al., 2025; Ding et al., 2026; Ettler et al., 2022; Hou et al., 2024; Kamberović et al., 2021; Kamberović et al., 2023; Kashyap et al., 2021; Liang et al., 2026; Mondal et al., 2025; Qi et al., 2026; Rao et al., 2021; Singh et al., 2023; Steinlechner & Witt, 2023; Z.-Y. Wang et al., 2020; Xing et al., 2024; D. Q. Zhou et al., 2025; Q. Q. Zhou et al., 2025; Zhu et al., 2025.

The principal selection gate is different for each feed. Ferrite-rich residues require liberation, jarosite residues require controlled iron-phase decomposition, replacement residues require redox management, and slags require proof that the gallium grade and recoverable tonnage justify an energy-intensive concentration step.

Figure 6 integrates the principal author-derived synthesis of the review into a route-selection and qualification framework.

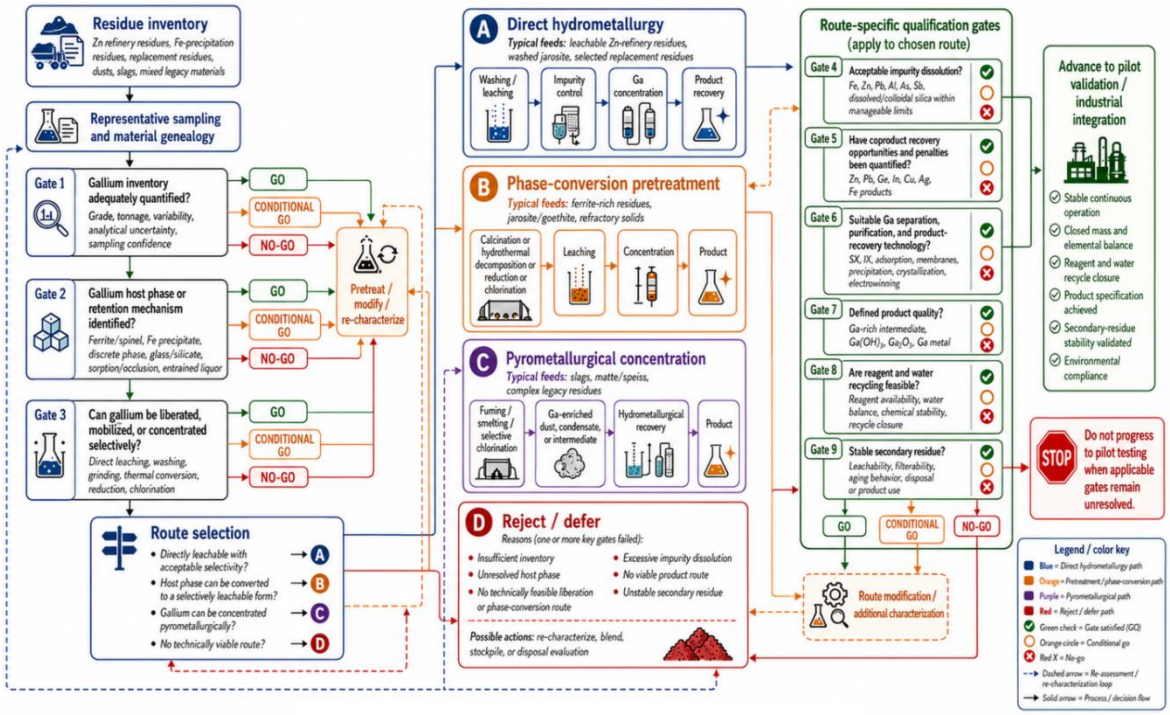

Figure 6. Residue-specific route-selection framework with measurable technical gates

Note. Author's synthesis based on Geng et al., 2025; Höber & Steinlechner, 2021; Lim et al., 2024; Pereira, 2026b; Rao et al., 2021; Singh et al., 2023; Z.-Y. Wang et al., 2020; Zhang, Li, et al., 2024.

The framework contains explicit stop/go gates for representative gallium inventory, identified host phase, feasible liberation, acceptable impurity dissolution, recoverable coproducts, suitable concentration technology, defined product quality, reagent recycle, and stable secondary residue. A route does not progress to pilot testing while these gates remain unresolved.

Comparative Performance, Environmental, and Industrial Integration

Performance metrics beyond extraction

A high gallium extraction is only one component of performance. Comparative assessment should include overall recovery, concentration factor, Ga/Fe selectivity, zinc and lead recovery, reagent consumption, solution volume, energy demand, product purity, solid–liquid separation, and the mass and stability of secondary residues. The appropriate benchmark is the complete integrated route rather than an isolated batch step (Pereira, 2026b; Robart et al., 2025; Z.-Y. Wang et al., 2020; Zhang, Li, et al., 2024).

Environmental performance and circularity

Zn–Pb residues may contain Pb, Cd, As, Sb, sulfate, chloride, and fine reactive iron phases. A gallium route can reduce liability if it recovers valuable metals and converts the remaining solids to a stable product. It can also transfer the liability to a more hazardous precipitate, spent sorbent, chloride dust, or organic-bearing raffinate. Circularity therefore requires a full mass balance, demonstrated reagent and water recycle, defined coproduct destinations, and leaching stability of every final solid (Kamberović et al., 2021; Lim et al., 2024; Nowińska & Kokowska-Pawłowska, 2024; Peng et al., 2023; Singh et al., 2023; Q. Zhou et al., 2025).

Industrial integration and technology readiness

The lowest-risk implementation uses existing plant assets: sulfate leaching and iron control at a zinc refinery, dust handling at a smelter, established SX equipment, or a specialized external gallium refinery. Autoclaves, chlorination reactors, membrane modules, or dedicated

electrowinning cells may be justified for enriched feeds but require stronger economic evidence. Continuous filtration, wash efficiency, organic-phase operation, electrode maintenance, and impurity accumulation are typical bottlenecks in scale-up (Ding et al., 2026; Liu et al., 2025; Robart et al., 2025; Wang et al., 2024; Xi et al., 2022).

Economic structure

The economic value of a residue route is jointly determined by gallium revenue, germanium and indium coproducts, recovered zinc and lead, avoided disposal cost, reagent and energy use, and the cost of managing hazardous impurities. Because gallium grades are often low, a multimetal refinery concept is more credible than a gallium-only plant. Historical stockpiles may offer large inventories but entail additional sampling, dewatering, transport, and environmental remediation costs.

Table 11 presents an author-assigned indicative maturity assessment. The classification is based on feed realism, scale and duration, mass-balance closure, product demonstration, recycle or durability, secondary-residue verification, and availability of economic data; it is not a formal TRL certification.

Table 11. Author-assigned indicative maturity and minimum industrial-readiness criteria

Route family	Indicative maturity	Main advantage	Main unresolved risk	Minimum evidence for scale-up
Direct sulfate hydrometallurgy	Bench to industrially compatible	Fits existing zinc circuits.	Fe/silica loading and dilute Ga.	Continuous leach/wash plus downstream Ga product.
Pressure/assisted leaching	Bench to pilot-oriented	Accesses refractory phases.	Autoclave cost and incremental energy benefit.	Continuous pressure campaign and discharge filtration.
Chlorination/chloride hydrometallurgy	Bench to integrated concept	Strong phase conversion and Ga complexation.	Corrosion, volatile Pb/As, chloride recycle.	Closed chloride balance and off-gas characterization.
SX/IX/adsorption concentration	Laboratory to industrially familiar unit operations	High concentration factor and modularity.	Real-liquor fouling and long-term reagent stability.	Multi-cycle or column campaign with mass balance.
Membrane separation	Laboratory/emerging	Process intensification for dilute streams.	Carrier loss and module lifetime.	Long-duration real-liquor module test.
Electrowinning/refining	Laboratory to specialized industrial practice	Direct metallic product.	Hydrogen evolution and impurity sensitivity.	Stable current efficiency and product-purity campaign.
Integrated pyro–hydrometallurgy	Bench/concept for specific residues	Recovers multiple metals and transforms Fe phases.	Energy, gas treatment, and capital intensity.	Pilot mass/energy balance and saleable coproducts.

Note. Author's synthesis based on the cited studies. Indicative maturity reflects predefined reporting and demonstration criteria and should not be interpreted as a formal technology readiness level (TRL) certification.

No universal route is favored. Direct sulfate processing is conditionally attractive when Ga is already leachable and Fe can be controlled. Chlorination and integrated pyro–hydrometallurgy are conditional options for refractory feeds with sufficient multimetal value. Adsorption and membranes are presently best supported as concentration or polishing operations rather than as substitutes for feed preparation and bulk impurity control.

Conditional industrial conclusions

High-confidence conclusions. The lowest-risk implementation leverages existing sulfate, solids-handling, purification, and refinery infrastructure and treats Ga as part of a multimetal value chain. A complete mass balance and a defined destination for every hazardous secondary stream are necessary conditions for circularity.

Moderate-confidence conclusions. Chlorination, pressure leaching, integrated pyro–hydrometallurgy, and dedicated electrowinning may be viable for enriched feeds, but their relative ranking depends on tonnage, coproduct credits, recycle performance, and residue stability.

Low-confidence or unverified claims. The reviewed literature does not support universal statements that one route is "most compatible," "leading," or "industrially ready" independent of feed and boundary conditions. Comparable techno-economic assessment (TEA) and life-cycle assessment (LCA) data remain too sparse to definitively rank routes.

Knowledge Gaps and Research Priorities

Plant-wide deportment and representative residues

The largest knowledge gap is the lack of comprehensive gallium deportment data across zinc and lead plants. Most studies begin with an isolated residue and do not reconstruct the fraction of gallium previously lost to solution, dust, iron precipitate, recycle, or final slag. Plant-wide sampling should include feed concentrates, calcines, leach liquors, iron residues, purification residues, dusts, slags, and products. This requirement is especially urgent for integrated Zn–Pb operations and secondary lead plants.

Mineral hosts below conventional detection limits

Gallium commonly lies below the practical detection limit of routine SEM–EDS and bulk XRD. Correlative microanalysis, synchrotron methods, and well-designed sequential extraction are needed to distinguish lattice substitution from sorption or occlusion. Research should report not only where gallium is detected, but what fraction of the total inventory is assigned to each host.

Standardized extraction and selectivity reporting

Studies should distinguish dissolution, recovery, and enrichment. Required variables include dry feed mass, solution volume, wash volume, final solid mass, dissolved and residual gallium, impurity extraction, and analytical uncertainty. Selectivity should be expressed using recoveries or distribution ratios for Fe, Zn, Al, Pb, Ge, and In rather than by gallium extraction alone.

Real-liquor durability of separation technologies

Many advanced extractants, resins, nanofibers, and membranes have been tested with synthetic solutions. The next priority is long-duration operation with real liquors containing suspended solids, silica, sulfate or chloride, organics, and changing oxidation states. Loading capacity, phase disengagement, pressure drop, regeneration, extractant loss, and spent-material treatment must be measured over repeated cycles (Díez et al., 2021; Guo et al., 2020; He et al., 2023; Li et al., 2024; Meng et al., 2021; Protsak et al., 2024; Raj et al., 2023a; Raj et al., 2023b; Sáez et al., 2021; Saikia et al., 2026; Segala et al., 2022; Segala et al., 2023; Wu et al., 2025; Zhou & Huang, 2022; Zhou et al., 2022).

Lead-metallurgical residues and hazardous-element control

Direct studies of gallium recovery from primary lead slags, lead dusts, speiss, and secondary lead residues remain limited. Future work should integrate gallium mineralogy with the behavior of Pb, As, Sb, Cd, and Ag. Any thermal concentration route must quantify volatile emissions and dust recycling; any hydrometallurgical route must demonstrate stable destinations for hazardous elements.

Product qualification, economics, and demonstration

Research programs should continue beyond a Ga-rich eluate. They should produce and analyze Ga_2O_3 or metal, define refinery compatibility, and calculate overall recovery. Techno-economic and environmental assessments require continuous data, reagent recycle, water balance, energy use, and residue classification. Demonstration campaigns should be designed around the most concentrated, mineralogically favorable residues rather than around average plant waste.

Table 12 provides a minimum reporting standard intended to make future studies comparable and to prevent incomplete laboratory evidence from being described as a circular industrial process.

Table 12. Minimum reporting standard for future gallium recovery studies

Reporting block	Mandatory information	Reason
Feed definition	Origin, generation step, sampling plan, dry mass, moisture, storage history.	Establishes representativeness and genealogy.
Chemistry/mineralogy	Ga plus major and hazardous elements; quantitative phases; host evidence.	Links grade to processability.
Operating conditions	Reagent concentration, L/S, temperature, pressure, redox, time, mixing, particle size.	Enables comparison and scale-up.
Mass balance	Feed, washes, solutions, residues, precipitates, organic/strip streams, products.	Separates true recovery from transfer.
Selectivity	Extraction/recovery of Fe, Zn, Al, Pb, Ge, In, Cu, As, and Ga.	Quantifies downstream burden.
Product quality	Ga concentration, impurity specification, phase, filterability, refining route.	Demonstrates a usable intermediate or product.
Recycle and durability	Reagentrecycle, water balance, multi-cycle SX/IX/membrane/electrode performance.	Tests industrial robustness.
Environmental/TRL	Secondary-residue leaching, emissions, energy, scale, continuous runtime.	Supports credible circularity and readiness claims.

Note. Author's synthesis based on Huang et al., 2024; Kluczka, 2024; Lim et al., 2024; Page et al., 2021; Pereira, 2026b; Robart et al., 2025; Robla et al., 2024; Singh et al., 2023; Xi et al., 2022; Zhang, Li, et al., 2024; Zou et al., 2020.

Adoption of these requirements would substantially improve the evidence base. It would also help identify instances in which gallium recovery is technically secondary to a broader objective, such as zinc recycling, germanium production, iron-residue stabilization, or remediation of a hazardous historical stockpile.

Conclusions

Recent evidence shows that Ga recovery from zinc metallurgical residues is controlled less by total grade than by process history, mineral host, impurity ratios, and integration with existing metal circuits. Zinc-refinery, iron-precipitation, and replacement residues provide the strongest evidence in the 2020–2026 corpus. Integrated Zn–Pb slags and historical materials are relevant complementary resources, but direct evidence of primary lead residues remains insufficient to support equivalent treatment in route selection. Sulfate and oxygen-pressure leaching are conditionally compatible with zinc hydrometallurgy when Fe, As, silica, and wash streams are controlled; chloride, chlorination, and pyro–hydrometallurgical routes are reserved for refractory hosts and require closed chlorine, gas, and hazardous-element balances. Iron management is the principal barrier to purification. SX has the broadest evidence for bulk concentration, while IX, adsorption, membranes, precipitation, and electrowinning are complementary operations whose value depends on real-liquor selectivity, stripping or elution, regeneration, and final product quality. The evidence supports residue-specific multimetal flowsheets, not a universal Ga route. Industrial-readiness and circularity claims should remain conditional until complete mass balances, continuous operation, reagent and water recycle, qualified Ga products, stable secondary residues, and comparable economic and environmental assessments are demonstrated.

Declarations

Conflict of interest

The author declares no conflict of interest.

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Data availability

All data analyzed in this review are derived from the cited literature. The study-level evidence coding is provided in the accompanying Supplementary File S1: Evidence Matrix.

Author contributions

The author: Conceptualization; Methodology; Investigation; Data curation; Formal analysis; Writing—original draft; Writing—review and editing; Visualization.

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