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Disposal, Stabilization, and Conditional Valorization of Arsenic-Bearing Wastes Generated in Hydrometallurgical Processes: A Critical Review

Antonio Clareti Pereira, PhD

PhD in Chemical Engineering
University of São Paulo (USP)
Belo Horizonte, Minas Gerais, Brazil
E-mail: claretipereira@gmail.com
ORCID: https://orcid.org/0000-0001-8115-4279

Abstract

Arsenic is a persistent process impurity in hydrometallurgy because metal extraction commonly transfers, rather than destroys, arsenic between mineral, aqueous, precipitated, and encapsulated forms. This critical review evaluates arsenic-bearing wastes generated during leaching, pressure oxidation, solution purification, neutralization, effluent treatment, and secondary-residue processing, emphasizing the relationship between aqueous speciation, precipitate mineralogy, long-term stability, and realistic end-of-life options. The evidence shows that process performance cannot be judged solely by short-term arsenic removal from solution: a route is robust only when the resulting solid has a defensible mineralogical sink, controlled redox sensitivity, acceptable leachability under relevant exposure scenarios, manageable dewatering behavior, and a credible regulatory destination. Crystalline scorodite remains a central stabilization target under acidic oxidizing conditions, while ferric coprecipitates, calcium arsenates, arsenic sulfides, cementitious matrices, hydrothermal products, and vitrified materials occupy distinct stability domains and carry different secondary-waste burdens. Valorization is therefore conditional. Recovery of Cu, Zn, Pb, sulfur, alkali, acid, or metallic arsenic can improve material efficiency, but only when it reduces total risk rather than shifting arsenic into a more mobile stream. The review proposes an integrated process–environment framework in which arsenic mass balance, speciation control, targeted phase formation, residue aging, multi-condition leaching, and life-cycle assessment are treated as one design problem. The resulting hierarchy favors prevention and early arsenic separation, followed by phase-specific stabilization, and reserves material reuse for cases supported by long-term evidence and a defined regulatory pathway.

Keywords: Hydrometallurgy; arsenic-bearing waste; scorodite; arsenic stabilization; hazardous residues; resource recovery

Highlights

- Arsenic management is a phase-control problem, not only a solution-removal problem.
- Scorodite, Fe–As coprecipitates, As–Ca, and As–S residues have distinct aging risks.
- Valorization is credible only when recovery lowers the total arsenic risk and residue burden.

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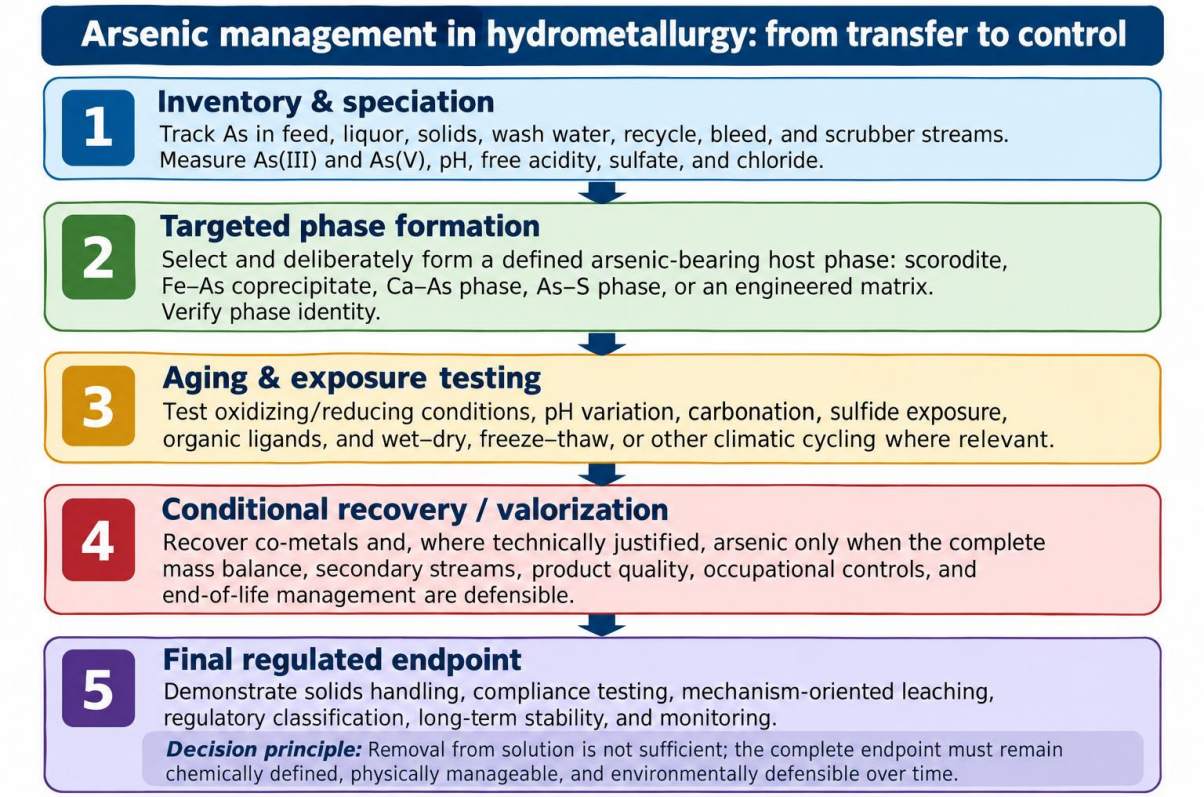
• Integrated mass balance, long-term leaching, TRL, and life-cycle evidence should govern route selection.

Graphical abstract



Note. Simplified author-developed conceptual synthesis for this review. The diagram distinguishes arsenic transfer through hydrometallurgical circuits from true long-term risk reduction and is intended for journal-size readability.

1. Introduction

Hydrometallurgical flowsheets increasingly process complex concentrates, secondary residues, refractory gold feeds, and metallurgical dusts that contain arsenic together with Cu, Zn, Pb, Co, Ni, Sb, and other value or penalty elements. Under these conditions, arsenic is not a single impurity with a single removal step. It changes oxidation state, complexes with solution ligands, partitions into ferric or calcium solids, precipitates as sulfide, incorporates into sulfate-bearing phases, and may later be released when redox state, acidity, ionic strength, or mineralogy changes. This is why high instantaneous removal from solution does not

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automatically mean low environmental risk (Coudert et al., 2020; Du et al., 2024; Liu et al., 2025; Ng, Liu, et al., 2023; Strauss et al., 2021).

The engineering challenge is therefore dual. The primary circuit must protect metal recovery and product quality, while the environmental circuit must convert arsenic into a form whose long-term behavior is demonstrably controlled. Recent work has expanded beyond conventional lime neutralization toward seeded scorodite crystallization, hydrothermal transformation, ferric coprecipitation control, mineral reconstruction of As–Ca and As–S residues, cementitious stabilization, vitrification, bio-assisted fixation, and selective recovery of arsenic or coexisting metals (Hu et al., 2024; Jiang et al., 2022; Kimura & Okibe, 2025; Li et al., 2024; Ma et al., 2020; Peng et al., 2025; Wang, Ptacek, et al., 2025; Wang et al., 2026).

Figure 1 maps the principal points at which arsenic-bearing residues are generated, and Table 1 links process stage, residue type, dominant arsenic form, and the key control question. Figure 2 provides a qualitative pH–redox framework for interpreting As(III)/As(V) behavior, while Table 2 summarizes the principal solid-phase sinks and their vulnerabilities. Table 3 compares common leaching and regulatory frameworks and explains why results from different extraction protocols should not be treated as interchangeable.

Figure 3 and Table 4 develop the treatment hierarchy, distinguishing chemical conversion, crystallization, mineral reconstruction, encapsulation, solidification, and vitrification. Figure 4 and Table 5 then reposition recovery and valorization inside the complete hydrometallurgical mass balance rather than treating reuse as an isolated end-of-pipe objective. Finally, Figure 5 and Table 6 compare technology maturity with the evidence burden required for scale-up, emphasizing that a high laboratory removal efficiency is only one component of readiness.

This review adopts a deliberately critical position: arsenic valorization should not be presumed to be preferable to disposal. A route is environmentally meaningful only if it produces a comparatively low-leachability arsenic sink under the evaluated pH–redox–aging conditions, avoids excessive generation of secondary liquids or solids, preserves a practical

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dewatering and handling pathway, and has a credible regulatory destination. This framing is consistent with recent life-cycle analyses and long-term mineralogical studies showing that short-term tests can miss transformations that become important during storage, weathering, or reuse (Abbasi et al., 2026; Wan et al., 2025; Warchulski et al., 2025; Yuan et al., 2020; Zhang et al., 2020; Zhang, Xia, et al., 2024).

2. Review scope and critical methodology

2.1 Scope of the evidence base

The initial evidence corpus comprised 144 records assembled by the author through iterative, topic-focused searches and reference chaining for this critical review. The core evidence window was 2020 to September 2026, with earlier foundational or regulatory sources retained when needed to establish long-standing concepts, test methods, or legal frameworks. The corpus was screened as a structured critical-narrative dataset rather than as a formal systematic-review database. Of the 144 records, 104 were retained for direct citation because they provided unique mechanistic relevance, direct arsenic endpoints, complementary residue classes, industrial or pilot proximity, long-duration stability information, or nonredundant regulatory/LCA/TEA evidence. Records not cited directly were not excluded because of manuscript length; they were primarily redundant, indirect to the arsenic endpoint, or less informative than a retained source addressing the same mechanism. Regulatory sources were checked separately against official repositories. Because the search process was iterative rather than a prospectively registered, reproducible multi-database protocol, this review does not claim bibliographic exhaustiveness and is not a PRISMA systematic review.

The screening logic favored studies that connected at least two of the following: arsenic speciation, mineralogy, process chemistry, leaching behavior, residue transformation, scale, duration, solids handling, co-product recovery, final disposal, or a directly measurable arsenic endpoint. Evidence directness was considered explicitly as: (i) direct hydrometallurgical process evidence; (ii) residue-transformation or aging evidence; (iii) pilot/field evidence; (iv)

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laboratory mechanistic evidence; (v) regulatory/institutional evidence; and (vi) LCA/TEA evidence. We used this classification qualitatively to interpret transferability, not to assign an artificial numerical quality score. We retained purely descriptive studies when they provided long-duration weathering evidence or field/pilot validation, whereas studies focused mainly on non-arsenic purification or value-metal recovery without a defensible arsenic endpoint were deprioritized. We retained conflicting findings when feed mineralogy, solution composition, test duration, scale, or exposure conditions plausibly explained the difference.

Evidence appraisal and synthesis were performed by a single reviewer/author rather than by independent duplicate assessors. Accordingly, no inter-rater reliability statistic was calculated. This is a limitation of the narrative evidence synthesis and reinforces the need to interpret the proposed framework as an author-developed critical synthesis rather than a formal evidence-grading system.

2.2 Critical comparison framework

The author-developed conceptual decision framework assessed each technology using six linked questions: (i) where arsenic enters and leaves the process; (ii) whether As(III) is oxidized to As(V), or otherwise transferred into a defined chemical form with condition-specific low mobility; (iii) what crystalline, amorphous, sulfide, or encapsulated phase actually hosts arsenic; (iv) how that host responds to pH, redox change, aging, and competing ions; (v) what secondary liquid and solid streams are created; and (vi) whether the route has a credible path from laboratory evidence to regulated disposal or reuse. This framework places coprecipitation and acidity control alongside solids handling and technology readiness (Pereira, 2026a; Pereira, 2026b).

The hierarchy used throughout this review is therefore an author-developed conceptual decision framework synthesized from the reviewed evidence; it is not a validated regulatory standard or a universal process-selection rule.

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The review does not assign a universal rank to stabilization routes because the correct endpoint depends on feed mineralogy, solution chemistry, climate, regulatory jurisdiction, and the availability of long-term containment. Instead, the analysis identifies conditions under which a route is defensible and failure modes that should trigger additional testing.

3. Hydrometallurgical sources and generation pathways of arsenic-bearing wastes

3.1 Leaching, pressure oxidation, and metallurgical dust processing

Arsenic-bearing feeds enter hydrometallurgy through several industrial pathways. Refractory gold ores and arsenopyrite-bearing materials release arsenic during oxidative pretreatment, while copper and lead–zinc operations encounter arsenic in flue dusts, waste acids, slags, sublimates, and secondary smelting residues. Alkali-rich arsenic streams also arise when NaOH-based systems selectively leach dusts or slags. These sources differ not only in arsenic concentration, but also in Fe/As ratio, sulfur form, chloride and sulfate load, particle size, and the inventory of recoverable metals (Che et al., 2024; Che et al., 2022; Chen et al., 2020; Chen et al., 2024; Davoudi & Kamran Haghighi, 2026; Du et al., 2024; Zhang, Liu, et al., 2023; Zhang, Guo, et al., 2021; Zhang, Che, et al., 2021; Zhang, Feng, et al., 2021).

Pressure oxidation deserves separate treatment because arsenic fixation occurs simultaneously with sulfide oxidation and iron hydrolysis. The fate of arsenic depends on pyrite/arsenopyrite proportions, oxygen demand, dissolved Fe species, acidity, curing, sulfate activity, and the kinetics of phase evolution. A residue that appears well fixed immediately after POX can still transform during curing or subsequent storage, especially when reduced iron or organic ligands become available (Liu et al., 2022; Liu et al., 2025; Ng, Clarke-Hannaford, et al., 2023; Ng, Liu, et al., 2023; Strauss et al., 2021; Yuan et al., 2020; Zhou et al., 2022).

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3.2 Purification, neutralization, and effluent treatment

Solution purification converts a dissolved impurity problem into a solids-management problem. Ferric salts, iron-bearing slags, magnetite, limonite, siderite, lime, and aluminum-bearing residues have all been used as arsenic sinks or iron sources. The resulting precipitates can include crystalline scorodite, hydrous ferric arsenate, ferrihydrite-associated arsenate, calcium arsenates, mixed Fe–Ca phases, and poorly crystalline products. Process variables that improve solution polishing can therefore worsen filterability or long-term stability if phase formation is not controlled (Li, Qi, Shi, et al., 2022; Li, Cai, et al., 2021; Li, Qi, Li, et al., 2022; Li et al., 2024; Li, Zhu, Qi, Shu, Zhang, Li, Wei, Hao, et al., 2020; Ma, Su, et al., 2022; Mendes et al., 2021; Qi et al., 2020; Su et al., 2021; Yang et al., 2023).

Arsenic sulfide precipitation remains relevant where reducing sulfide chemistry is advantageous, but it produces a residue whose subsequent oxidation is a central risk. Alkaline oxidative leaching and hydrothermal treatment can convert sulfide-rich residues into alternative forms or recover arsenic, but these routes introduce their own reagent, redox, and secondary-salt burdens (Hu et al., 2024; Li et al., 2023; Liu et al., 2021; Miao et al., 2025; Ouyang et al., 2023; Peng et al., 2025; Xu et al., 2020; Xu et al., 2022; Zhang, Lu, et al., 2021).

The practical implication is that every arsenic-removal step should be represented as an explicit unit operation in the overall arsenic mass balance. Disappearing arsenic from the pregnant leach solution is not a valid endpoint if it reappears in a high-volume neutralization sludge, a difficult-to-dewater gel, a soluble bleed stream, or a residue that lacks a regulated destination.

Table 1 summarizes the principal residue-generation points and the control question associated with each process stage.

Table 1
Process origin, residue type, arsenic form, and the principal control question

Process stage	Typical arsenic-bearing output	Likely As host/form	Critical control question

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Oxidative leaching / POX	Leach residue; acidic liquor	Fe–As–S–O phases; dissolved As(III)/As(V)	Is arsenic being fixed during oxidation, or merely transferred to downstream neutralization?
Flue-dust / secondary-residue leaching	Alkaline or acidic leachate; insoluble residue	Arsenite/arsenate; sulfides; oxide-associated As	Can valuable metals be recovered without generating a more mobile As-rich liquor?
Fe-based purification	Ferric arsenate/ferrihydrite sludge	Scorodite, HFA, adsorbed/coprecipitated arsenate	Is the target phase crystalline and stable under the expected pH–redox envelope?
Lime neutralization	Gypsum-rich or Ca–As sludge	Calcium arsenates; mixed Ca–Fe–As phases	Will carbonation, sulfate exchange, or acidification remobilize arsenic?
Sulfide precipitation	As–S sludge	As_2S_3/As–S phases, elemental S	How will oxidation during storage change leachability?
Polishing / adsorptive treatment	Spent Fe/Mn sludge or media	Surface-bound or coprecipitated As(V)	Can the spent medium be regenerated, stabilized, or safely disposed?

Note. Synthesized from the process and residue evidence reviewed in Sections 3–5; representative sources include (Coudert et al., 2020; Du et al., 2024; Jiang et al., 2022; Li, Qi, Li, et al., 2022; Ouyang et al., 2023; Qi et al., 2020; Yao et al., 2020).

Figure 1 maps where arsenic-bearing residues are generated across a generic hydrometallurgical circuit.

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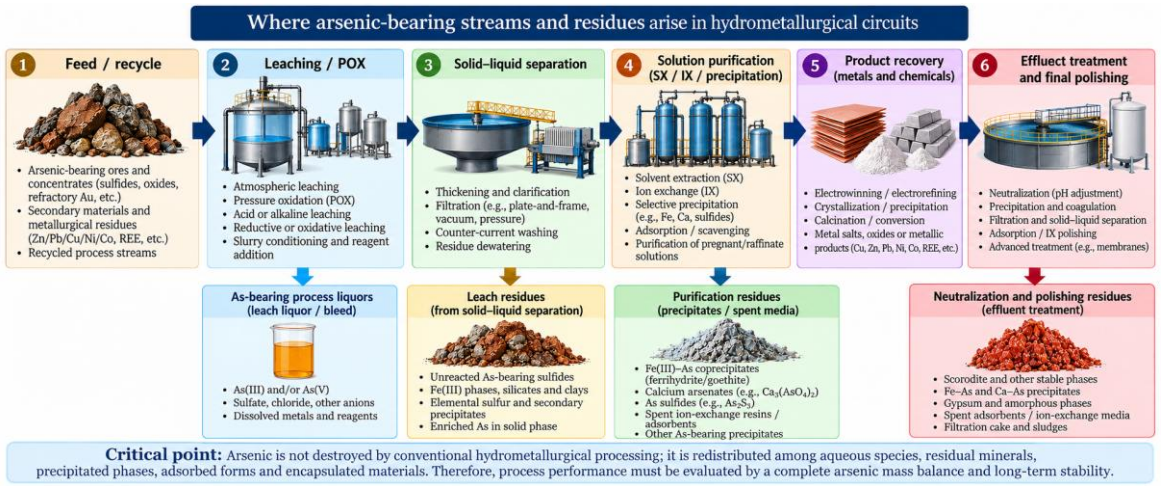

Figure 1. Conceptual generation map for arsenic-bearing residues in hydrometallurgical circuits.
Note. Original schematic based on the residue-generation logic described by (Che et al., 2022; Coudert et al., 2020; Du et al., 2024; Ng, Liu, et al., 2023; Zeng et al., 2021; Zhang, Liu, et al., 2023).

4. Arsenic speciation, aqueous chemistry, and precipitation control

4.1 As(III), As(V), acidity, and redox state

Arsenic control begins with oxidation state. As(III) and As(V) differ in protonation, affinity for Fe-bearing surfaces, sulfide behavior, and the chemistry required for stable precipitation. In acidic metallurgical solutions, oxidation of As(III) before or during ferric precipitation is frequently necessary to access the most robust Fe(III)–As(V) sinks. Researchers have investigated pressurized oxygen, ozone, biological oxidation, and catalytic systems for this purpose (Jiang et al., 2022; Li, Zhang, et al., 2022; Vega-Hernandez et al., 2021; Vega-Hernandez et al., 2020; Yuan et al., 2023).

Free acidity is a separate control variable from pH. Highly saline sulfate or chloride liquors can exhibit similar measured pH while containing very different acid inventories and buffering capacities. This distinction matters because iron hydrolysis, seed dissolution, gypsum formation, and alkali demand depend on titratable acidity and speciation, not on pH alone. Misinterpreting pH as a complete acidity descriptor can therefore shift the precipitation

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window and increase reagent consumption (Pereira, 2026b; Qi et al., 2020; Wang, Su, et al., 2025).

4.2 Fe/As ratio, sulfate, chloride, and competing ions

Ferric arsenic systems are especially sensitive to Fe/As ratio and sulfate activity. Insufficient iron can leave dissolved arsenate, whereas excessive iron can generate large volumes of ferric hydroxide-like solids that dilute arsenic, increase sludge mass, and complicate dewatering. Sulfate may be structurally incorporated into scorodite-related phases or influence transformation of hydrous ferric arsenates; chloride and other dissolved metals can modify precipitation kinetics and phase stability (Ma, Qi, et al., 2022; Ma et al., 2024; Ma et al., 2021; Ng, Clarke-Hannaford, et al., 2023; Wang, Su, et al., 2025; Zhang et al., 2020; Zhang, Xia, et al., 2024).

Iron source is therefore not a trivial reagent-selection question. Solid iron sources such as magnetite, limonite, siderite, copper slag, or Fe(OH)3 can couple dissolution kinetics to arsenic precipitation, sometimes promoting controlled crystallization while reducing soluble-iron dosing. The advantage is conditional: mineral impurities, dissolution rate, surface passivation, and residual gangue must still be incorporated into the solids balance (Li, Qi, Shi, et al., 2022; Li, Cai, et al., 2021; Li, Zhu, Qi, Shu, Zhang, Li, Wei, Hao, et al., 2020; Su et al., 2021; Tang et al., 2024c).

4.3 Coprecipitation versus crystallization

Coprecipitation can remove arsenic rapidly, but the resulting amorphous or nanocrystalline Fe–As solids can age substantially. Crystallization toward scorodite or other defined phases reduces uncertainty because the arsenic host can be characterized explicitly, yet this requires a narrower operating window, seeding strategy, residence time, and often elevated temperature. Recent kinetic studies emphasize that nucleation, iron release, oxidation state, and mixing history can control whether the process produces a durable crystal or a metastable

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precursor (Ma, Su, et al., 2022; Pereira, 2026a; Takaya et al., 2021; Tang et al., 2024a; Tang et al., 2024b; Tang et al., 2024c; Tang et al., 2024d).

Figure 2 should therefore be read as a process-control map rather than a quantitative Pourbaix diagram. Actual phase boundaries vary with temperature, activities, Fe/As ratio, sulfate and chloride concentration, dissolved metals, and the presence of pre-existing solids. The critical review conclusion is not that one pH–Eh point is universally optimal, but that arsenic stabilization must define and verify the chemical window that leads to a known solid phase.

Figure 2 provides a qualitative process-control framework for interpreting the combined influence of pH and redox state.

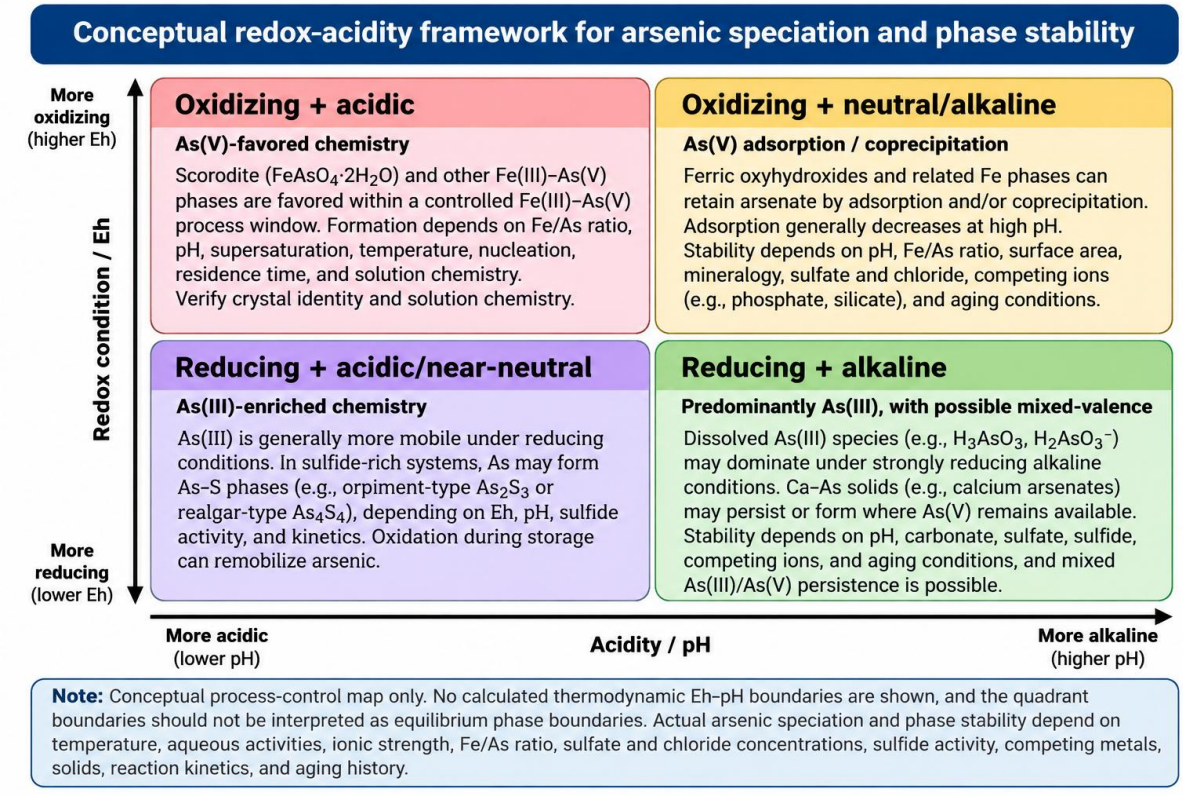

Figure 2. Qualitative redox-acidity process-control framework for arsenic speciation and fixation.
Note. Conceptual synthesis based on Jiang et al. (2022), Liu et al. (2022, 2025), Ma et al. (2024, 2021), Takaya et al. (2021), Tang et al. (2024d), and Wang, Su, et al. (2025). Redox and acidity are

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shown only as qualitative categories. This is not a calculated Pourbaix diagram and no quantitative phase boundary should be inferred.

5. Mineralogy, transformation, and characterization of arsenic-bearing residues

5.1 Scorodite and ferric arsenate systems

Scorodite ($FeAsO_4 \cdot 2H_2O$) is the most studied crystalline sink for arsenate in acidic hydrometallurgical systems because it combines relatively high arsenic content with a recognizable crystal structure and, under suitable conditions, comparatively low solubility. However, the term "scorodite" should not be applied to any Fe–As precipitate. Hydrous ferric arsenates, sulfate-bearing precursors, poorly crystalline ferric solids, and mixed phases can coexist and can evolve during aging (Bobos et al., 2026; Li et al., 2024; Ma, Qi, et al., 2022; Ma et al., 2024; Pozo et al., 2020; Tang et al., 2024a; Tang et al., 2024b; Tang et al., 2024c; Tang et al., 2024d).

Long-term evidence shows that scorodite stability is conditional rather than absolute. Organic ligands, Fe reduction, pH drift, sulfate changes, and other environmental perturbations can promote dissolution or transformation. The most defensible residue characterization therefore combines X-ray diffraction with spectroscopy or microscopy capable of detecting poorly crystalline and substituted phases, together with repeated leaching after controlled aging (Abbasi et al., 2026; Yuan et al., 2020; Zhou et al., 2022).

5.2 Calcium arsenates, arsenic sulfides, and mixed residues

Calcium arsenate residues are a common consequence of lime-based neutralization. Their attraction is operational simplicity, but several studies show that mineral phase reconstruction is often necessary to improve stability. Acid treatment plus iron addition can convert As–Ca solids toward ferric arsenate or scorodite-like products, while magnetite tailings, copper slag, or composite Fe stabilizers can supply iron and promote lower-mobility phases (Li, Yang, et al., 2021; Ma et al., 2025; Ma et al., 2020; Su et al., 2025; Sun et al., 2022;

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Wang, Xie, et al., 2025; Wang, Zhang, et al., 2023; Zhao, Du, et al., 2025; Zhao, Ma, et al., 2024; Zhao, Wang, et al., 2025).

Arsenic sulfide sludge presents the opposite redox problem. Under reducing process conditions it can be an effective sink, yet exposure to oxygen can convert sulfur and arsenic to more oxidized, mobile forms. Hydrothermal treatment, mechanochemical activation, surface modification, alkaline-oxidative conversion, and direct reduction to elemental arsenic are attempts to change this risk profile rather than merely store the original sulfide (Hu et al., 2024; Hu et al., 2026; Li et al., 2023; Ouyang et al., 2023; Peng et al., 2025; Xu et al., 2020; Xu et al., 2022; Yao et al., 2020; Zhang, Lu, et al., 2021).

5.3 Encapsulated, cementitious, and vitrified hosts

Solidification adds a physical or mineralogical barrier around the arsenic-bearing phase. Cemented paste backfill, blast-furnace-slag binders, silica-gel encapsulation, red-mud-derived gels, and other alkaline matrices can reduce water access and immobilize arsenic, but the internal phase chemistry remains important. A matrix that achieves high compressive strength can still be unsuitable if carbonation, sulfate attack, cracking, or pore-water chemistry increases arsenic release (Jiang et al., 2024; Li et al., 2020b; Liang et al., 2022; Mohammadi et al., 2024; Quan et al., 2022; Wang et al., 2024; Ye et al., 2025; Zhao, Zhang, et al., 2024; Zhao et al., 2022).

Vitrification sits at the high-energy end of the stabilization spectrum. Glass can provide strong chemical confinement and enable product routes such as basalt fiber, but the process must be evaluated for energy demand, volatilization control, off-gas capture, and final glass stability. Long-term testing of vitrified arsenic trioxide waste illustrates the importance of evaluating the actual glass product rather than assuming inertness from the process temperature alone (Liu et al., 2024; Wang, Ptacek, et al., 2025).

Table 2 compares the principal arsenic-bearing solid sinks and their corresponding stability controls.

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Table 2
Principal arsenic-bearing solid phases and stability controls

Solid-phase sink	How it forms	Main strength	Main vulnerability
Scorodite / scorodite-like $FeAsO_4 \cdot 2H_2O$	Oxidative Fe(III)–As(V) crystallization, often seeded	High As density; identifiable crystal host	Reductive dissolution, ligand-promoted weathering, off-window precipitation
Hydrous ferric arsenate / Fe–As coprecipitate	Fe hydrolysis and coprecipitation	Fast removal; broad operational applicability	Aging, phase transformation, high sludge volume, uncertain crystallinity
Calcium arsenates / As–Ca residues	Lime or Ca-bearing neutralization	Simple reagent system; rapid precipitation	pH/redox sensitivity; carbonate, sulfide, and weathering effects
Arsenic sulfide sludge	Sulfide precipitation under reducing conditions	High As capture at low redox potential	Oxidative weathering; sulfur transformations
Cementitious / encapsulated composite	Binder hydration, silica/resin encapsulation, paste backfill	Secondary containment and handling strength	Cracking, carbonation, pore-water evolution, matrix compatibility
Vitrified glass/fiber product	High-temperature melting and glass formation	Low permeability and durable mineral network	Energy/off-gas burden; product-specific durability must be proven

Note. Representative mineralogical and long-term evidence: (Abbasi et al., 2026; Bobos et al., 2026; Li, Yang, et al., 2021; Liang et al., 2022; Ma, Qi, et al., 2022; Wang, Ptacek, et al., 2025; Warchulski et al., 2025; Yuan et al., 2020; Zhao, Ma, et al., 2024; Zhou et al., 2022).

6. Environmental risk, leaching tests, and regulatory constraints

6.1 Why short-term extraction tests are insufficient

Leaching risk depends on both the test protocol and the state of the residue when tested. Single-batch extraction can be useful for classification, but it cannot reproduce years of dry–wet cycling, freeze–thaw exposure, reductive dissolution, root-exudate attack, sulfide oxidation, or mineral aging. Long-duration and weathering studies repeatedly show that arsenic release can change after the original treatment step as Fe, Ca, S, and amorphous phases

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reorganize (Abbasi et al., 2026; Li, Yang, et al., 2021; Ma et al., 2025; Warchulski et al., 2025; Yuan et al., 2020; Zhang et al., 2020; Zhang, Xia, et al., 2024; Zhao, Du, et al., 2025; Zhao, Wang, et al., 2025).

A robust test program should therefore combine compliance testing with mechanism-oriented tests. Useful elements include pH-dependent leaching, oxidizing and reducing scenarios, column/percolation tests where relevant, cyclic weathering, mineralogical examination before and after exposure, and mass-balance closure. For monolithic binders, diffusional release and physical integrity should be assessed in addition to crushed-sample leaching (Mohammadi et al., 2024; Quan et al., 2022; Wang, Ptacek, et al., 2025; Zhao, Zhang, et al., 2024; Zhao, Ma, et al., 2024).

6.2 Regulatory comparison and the problem of non-equivalent limits

Regulatory numbers should not be compared without the extraction method and regulatory purpose. In the United States, the RCRA toxicity characteristic uses TCLP and a 5.0 mg/L arsenic regulatory level for D004 (U.S. Environmental Protection Agency, n.d.). The European Union landfill acceptance framework reports arsenic limits as cumulative release at specified liquid-to-solid ratios and as a percolation-test concentration; for example, granular hazardous waste acceptable at hazardous-waste landfills has an arsenic limit of 25 mg/kg at L/S = 10 L/kg and 3 mg/L for C0 (Council of the European Union, 2003). China retains GB 5085.3-2007 as the current mandatory extraction-toxicity identification standard, with 5 mg/L for total arsenic (Ministry of Environmental Protection of the People's Republic of China, 2007). Brazil's CONAMA Resolution No. 430/2011 sets 0.5 mg/L total arsenic for effluent discharge (Ministério do Meio Ambiente, Conselho Nacional do Meio Ambiente, 2011). These values regulate different objects and cannot be treated as a single international 'arsenic limit'.

This non-equivalence has direct consequences for research claims. A stabilized residue that passes one extraction protocol should not be described as universally "safe". Authors should state the extraction fluid, particle size, liquid-to-solid ratio, duration, redox condition,

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measured fraction (total or dissolved), and the legal endpoint against which the result is being compared. Where reuse is proposed, product-specific exposure scenarios may be more relevant than hazardous-waste classification alone.

Table 3 compares selected regulatory and leaching frameworks while preserving their distinct purposes and metrics.

Table 3
Selected arsenic leaching and regulatory frameworks: purpose, metric, and comparability

Framework	Object/purpose	Arsenic metric	Critical interpretation
U.S. RCRA TCLP / D004	Hazardous-waste toxicity characteristic	5.0 mg/L As in TCLP extract	Classification threshold tied to a specific extraction procedure; not a general environmental-quality limit.
EU Council Decision (2003)./33/EC	Waste acceptance at landfill classes	For hazardous-waste landfill: 25 mg/kg at L/S 10 and 3 mg/L C0 for As	Uses L/S-dependent release and percolation concepts; values are not numerically interchangeable with TCLP.
China GB 5085.3-2007	Hazardous-waste identification by extraction toxicity	5 mg/L total As	Current mandatory national standard; extraction method and scope must accompany the number.
Brazil CONAMA 430/2011	Effluent discharge	0.5 mg/L total As	Applies to liquid effluent discharge, not solid-waste acceptance or leaching classification.
Mechanism-oriented testing	Research/design validation	No single universal limit	Use pH, redox, aging, and column tests to understand release mechanisms before regulatory comparison.

Note. Regulatory status checked against official U.S., EU, Chinese, and Brazilian sources in September 2026. The table intentionally separates different regulatory purposes to prevent false numerical equivalence.

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7. Disposal and stabilization strategies

7.1 Controlled formation of scorodite and ferric arsenate phases

Controlled scorodite formation remains a benchmark route when the feed is acidic, oxidizing, and compatible with ferric chemistry. More informative studies go beyond reporting arsenic removal: they investigate iron source, Fe/As ratio, oxidation kinetics, seeding, sulfate incorporation, crystal evolution, and residue stability. Solid iron sources and staged gypsum–scorodite strategies can reduce soluble reagent demand, but they add kinetic constraints that must be addressed during scale-up (Jiang et al., 2022; Li, Qi, Shi, et al., 2022; Li, Cai, et al., 2021; Li et al., 2024; Ma, Su, et al., 2022; Pozo et al., 2020; Qi et al., 2020; Su et al., 2021; Tang et al., 2024a; Tang et al., 2024b; Tang et al., 2024c; Tang et al., 2024d).

7.2 Reconstruction of As–Ca and As–S residues

Legacy As–Ca and As–S residues often require reconstruction rather than simple encapsulation. $FeSO_4/H_2SO_4$ treatment, ferric or ferrous arsenate formation, magnetite-tailings-assisted conversion, hydrothermal calcination, alkaline oxidation, and other strategies aim to replace a reactive phase with a more stable host. These routes are attractive when the original sludge is already stockpiled, but their material efficiency depends on acid/base consumption, solid yield, wash-water demand, and the fate of Ca, S, and co-contaminants (Hu et al., 2024; Hu et al., 2026; Li, Yang, et al., 2021; Ma et al., 2025; Ma et al., 2020; Su et al., 2025; Sun et al., 2022; Wang, Xie, et al., 2025; Wang, Zhang, et al., 2023; Xu et al., 2020; Xu et al., 2022; Zhang, Lu, et al., 2021).

7.3 Solidification, encapsulation, backfill, and vitrification

Where chemical conversion alone is insufficient, a second barrier can be added. Slag-based binders, cemented paste backfill, resin or silica encapsulation, and red-mud-derived gels can lower hydraulic conductivity and physically isolate arsenic-bearing particles. The critical question is whether the matrix remains chemically compatible with the arsenic host over time.

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Mechanical strength, arsenic leaching, pore-water evolution, and phase transformation should therefore be reported together (Jiang et al., 2024; Li et al., 2020b; Liang et al., 2022; Mohammadi et al., 2024; Quan et al., 2022; Wang et al., 2024; Ye et al., 2025; Zhao, Zhang, et al., 2024; Zhao et al., 2022).

Vitrification can achieve a different level of immobilization by incorporating arsenic into a glassy network or producing a controlled glass-ceramic product. This is especially relevant for arsenic trioxide or high-risk legacy wastes, but it shifts some of the environmental burden to energy use and gas-cleaning systems. More defensible applications integrate off-gas capture, and the final glass has demonstrated geochemical durability (Liu et al., 2024; Wang, Ptacek, et al., 2025).

7.4 Disposal engineering and verification

Even a chemically stable phase requires engineered storage. Dewatering, filterability, dust control, drainage, liner compatibility, water balance, and segregation from reducing organic materials can determine field performance. Pilot biofilters and long-term weathering studies show that environmental context can dominate laboratory expectations; consequently, residue acceptance should be coupled to a monitoring plan that can detect changing arsenic release before it becomes a compliance failure (Thevenot et al., 2025; Warchulski et al., 2025).

Figure 3 summarizes the mechanism-based hierarchy from chemical conditioning to long-term verification.

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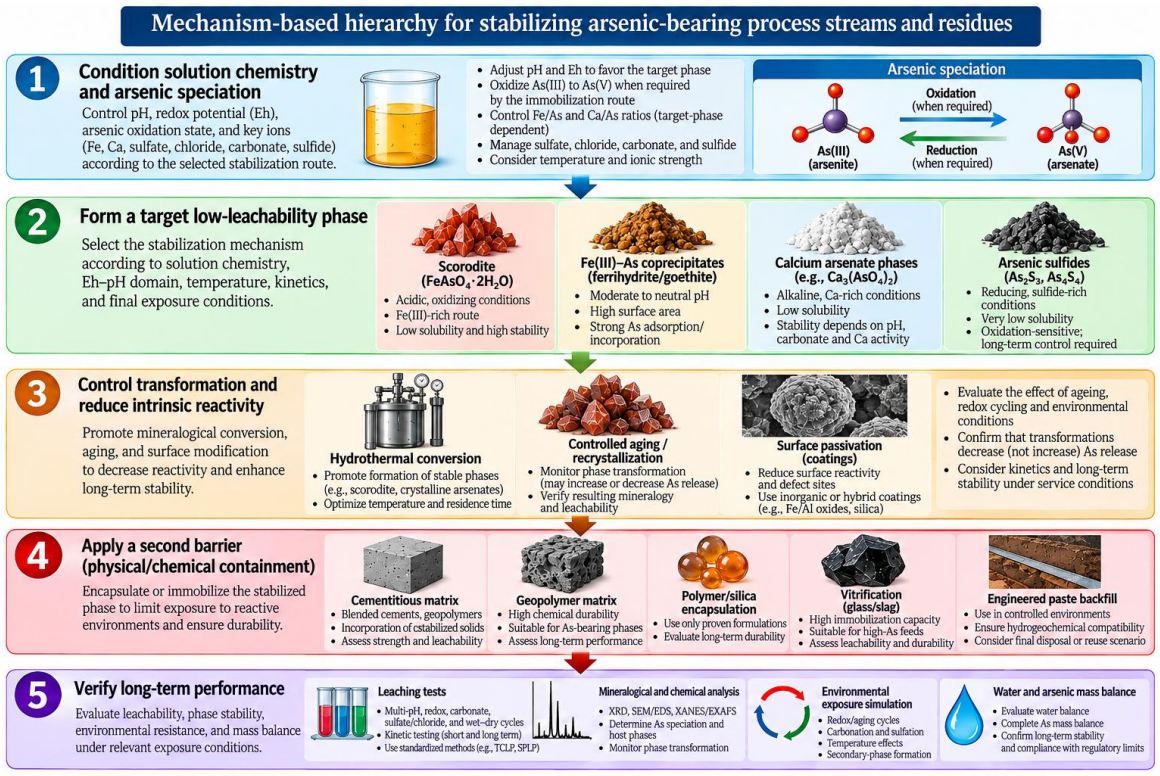

Figure 3. Mechanism-based hierarchy for chemical stabilization and engineered containment of arsenic-bearing residues.

Note. Original synthesis based on Hu et al. (2024), Li et al. (2024), Ma et al. (2020), Quan et al. (2022), Wang, Ptacek, et al. (2025), Xu et al. (2020), and Zhang, Lu, et al. (2021). Long-term verification is shown as a required final step rather than an optional characterization exercise.

Table 4 compares the stabilization and disposal routes discussed above.

Table 4
Comparison of arsenic stabilization and disposal routes

Route	Primary mechanism	Best-fit conditions	Critical limitation
Seeded scorodite crystallization	Convert As(V) into crystalline $FeAsO_4 \cdot 2H_2O$	Acidic Fe–As solutions with oxidation and residence-time control	Sensitive to solution chemistry; requires reliable oxidation, seeding, and solids handling.
Ferric coprecipitation / Fe-mineral conversion	Adsorption, coprecipitation, and Fe–As phase formation	Variable effluents and streams with available Fe sources	May create voluminous metastable solids; aging must be demonstrated.

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As–Ca reconstruction	Replace/react Ca–As phases with Fe-bearing or lower-mobility products	Legacy lime-neutralization residues	Acid/reagent demand and generation of secondary Ca/S-rich streams.
As–S hydrothermal/oxidative treatment	Transform sulfide sludge into more stable mineral or recoverable As form	Reducing precipitates and high-As sulfide residues	Oxidation state, sulfur balance, and gas/liquid secondary streams.
Cementitious solidification/backfill	Physical containment plus hydration/mineral reactions	Residues compatible with binder chemistry and mine backfill logistics	Durability can diverge from compressive strength; cracking/carbonation matter.
Vitrification/glass product	Incorporation into glass network	High-hazard, concentrated residues; legacy As2O3	High energy and off-gas control burden; product durability still requires testing.

Note. The comparison is qualitative and site-dependent; it is not a universal ranking. Evidence base: (Jiang et al., 2024; Li et al., 2024; Ma et al., 2020; Quan et al., 2022; Wang, Ptacek, et al., 2025; Wang, Zhang, et al., 2023; Xu et al., 2020; Zhao, Zhang, et al., 2024).

8. Conditional valorization and recovery pathways

8.1 Recover value before immobilizing arsenic

The most credible form of valorization is often selective recovery of valuable co-components before final arsenic stabilization. Copper, zinc, lead, sulfur, alkali, acid, and other process reagents can sometimes be recovered from dusts, slags, gypsum-rich wastes, or arsenic-rich liquors. This reduces the mass of material requiring high-grade containment and can improve the economics of the arsenic-control step (Che et al., 2022; Davoudi & Kamran Haghighi, 2026; Liu et al., 2021; Xu et al., 2023; Yong et al., 2022; Zeng et al., 2021; Zhang, Liu, et al., 2023; Zhang et al., 2025; Zhang, Han, et al., 2024; Zhang, Feng, et al., 2021).

8.2 Recovery of arsenic compounds or elemental arsenic

Direct arsenic recovery is technically possible through oxidative leaching, hydrothermal reduction, or low-temperature reduction of sulfide residues. Recent studies on

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metallic As recovery and upcycling of As2O3 demonstrate that waste can be converted into a concentrated arsenic product. The constraint is not chemistry alone: a recovered arsenic product requires purity control, safe packaging, a legitimate market or controlled reuse route, and a contingency plan if demand disappears (Miao et al., 2025; Peng et al., 2025; Wang et al., 2026; Wang, Liu, et al., 2023).

Recovered arsenic is not equivalent to eliminated arsenic hazard. A defensible product route requires product purity and specification, stable market/offtake or a contingency destination, packaging and transport controls, occupational exposure management, traceable final use, and treatment of raffinate, wash liquors, and any off-gas or secondary residues. Direct recovery should therefore be compared with stabilization/disposal on a system basis rather than presumed environmentally superior.

8.3 Material reuse: only after exposure-pathway control

Material reuse can include basalt fiber, cementitious binders, paste backfill, or composite stabilization matrices. These approaches can be attractive when arsenic becomes structurally bound while the residue contributes silica, alumina, iron, calcium, or latent hydraulic phases. However, the product must be evaluated as a product, not merely as treated waste. Mechanical performance, leaching under realistic service conditions, end-of-life behavior, and possible grinding or demolition exposure are part of the environmental case (Liu et al., 2024; Mohammadi et al., 2024; Wang, Ptacek, et al., 2025; Ye et al., 2025; Zhao, Zhang, et al., 2024; Zhao et al., 2022).

Life-cycle analysis is especially valuable here because a route may lower landfill volume while increasing energy, reagent, or water consumption. The correct comparison is therefore system-wide: baseline stabilization and disposal versus recovery plus secondary treatment, not “recycling” versus “waste” as labels. A route that exports arsenic to another facility or creates a concentrated liquid requiring indefinite treatment has not necessarily improved circularity (Wan et al., 2025).

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LCA comparisons should state both the functional unit and system boundary. Useful functional units include per tonne of original residue treated, per kilogram of arsenic safely managed, and per kilogram of recovered metal or qualified product; each answers a different decision question. The boundary should include reagent manufacture, water and energy demand, solids/liquid separation, off-gas treatment, secondary residues and liquors, transport where material, final disposal or product use, and long-term monitoring when relevant.

The conditions required to support a defensible valorization claim are summarized in Table 5.

Table 5
Valorization pathways and the conditions required for a defensible claim

Valorization pathway	Potential benefit	Required evidence	Failure mode to avoid
Recover Cu/Zn/Pb or other co-metals	Revenue and smaller hazardous mass	Selectivity, product quality, As mass balance, raffinate treatment	Moving arsenic into a more dilute but larger liquid stream.
Recover alkali/acid / water	Reduced reagent demand and closed-loop operation	Impurity accumulation control, corrosion, purge strategy	Recycling arsenic back into the main circuit.
Recover elemental As / As compound	Converts waste into concentrated product	Purity, market/offtake, packaging, occupational controls	Producing an unsaleable toxic inventory with no final destination.
Basalt fiber/glass / ceramic product	Potential high-temperature immobilization and material value	Off-gas capture, product durability, end-of-life leaching	Assuming vitrification alone guarantees zero release.
Binder/paste backfill	Uses residue as construction/backfill feed	Strength + long-term leaching + site hydrogeochemistry	Using compressive strength as a proxy for chemical stability.

Note. Representative recovery and reuse evidence: (Liu et al., 2024; Miao et al., 2025; Peng et al., 2025; Wan et al., 2025; Wang et al., 2026; Wang, Liu, et al., 2023; Xu et al., 2023; Yong et al., 2022; Zhang, Han, et al., 2024; Zhao, Zhang, et al., 2024).

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9. Integrated hydrometallurgical–environmental flowsheets

9.1 Early arsenic separation and mass-balance closure

A robust flowsheet strategy is to decide early where arsenic should report. If arsenic is allowed to circulate through leaching, purification, solvent extraction, and recycle liquors, it can contaminate multiple products and create several secondary residues. Early oxidation-state control followed by a dedicated arsenic split can protect downstream operations and concentrate environmental controls in one manageable branch (Che et al., 2022; Chen et al., 2024; Du et al., 2024; Li, Qi, Li, et al., 2022; Mendes et al., 2021; Qi et al., 2020; Zeng et al., 2021).

An arsenic mass balance should include solids, pregnant leach solution, wash waters, bleed streams, filter cakes, off-gas scrubbers, and recycle liquors. This is particularly important in dust and secondary-residue processing, where the economic objective is often Cu/Zn/Pb recovery and arsenic appears as a penalty element. Selectivity should be reported as distribution of both valuable metals and arsenic across every product and residue (Davoudi & Kamran Haghighi, 2026; Zhang, Liu, et al., 2023; Zhang et al., 2025; Zhang, Guo, et al., 2021; Zhang, Liu, et al., 2024; Zhang, Xia, et al., 2023; Zhang, Che, et al., 2021; Zhang, Feng, et al., 2021).

Report mass-balance closure quantitatively as As closure (%) = [Σ As in quantified outlet streams / As in feed] × 100, along with analytical and flow-measurement uncertainty. No universal acceptance interval is proposed because uncertainty depends on matrix, scale, sampling frequency, and analytical method. Where valorization is claimed, equivalent distribution and closure should also be reported for the valuable metals or products. Normalize secondary streams to feed mass, residue mass, or arsenic treated so dilution or transfer is not mistaken for risk reduction.

9.2 Coupling recovery with stabilization

A practical integrated flowsheet can use three sequential decisions. First, determine whether you can separate valuable metals or reagents without increasing arsenic mobility.

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Second, convert the remaining arsenic to a target mineral or concentrated recoverable product. Third, apply a secondary barrier only when mineral-phase stability alone is inadequate for the disposal or reuse scenario. This logic avoids unnecessary binder or glass production when a stable crystalline residue is already available, and it avoids premature "recycling" claims when arsenic remains poorly controlled (Liu et al., 2021; Ma, Su, et al., 2022; Peng et al., 2025; Su et al., 2025; Wang et al., 2024; Xu et al., 2023; Yong et al., 2022; Zhang, Han, et al., 2024; Zhang, Sun, et al., 2021).

The environmental branch should also be designed for water and reagent closure. Wash-water volumes, gypsum formation, sulfate/chloride accumulation, alkali recycle, and bleed treatment can dominate operating cost and environmental footprint. Integration therefore requires the same discipline used for metal recovery: stream-by-stream composition, flow rate, and recycle accumulation rather than isolated batch removal tests.

Figure 4 integrates value recovery, arsenic separation, stabilization, and closed-loop environmental controls within a single flowsheet.

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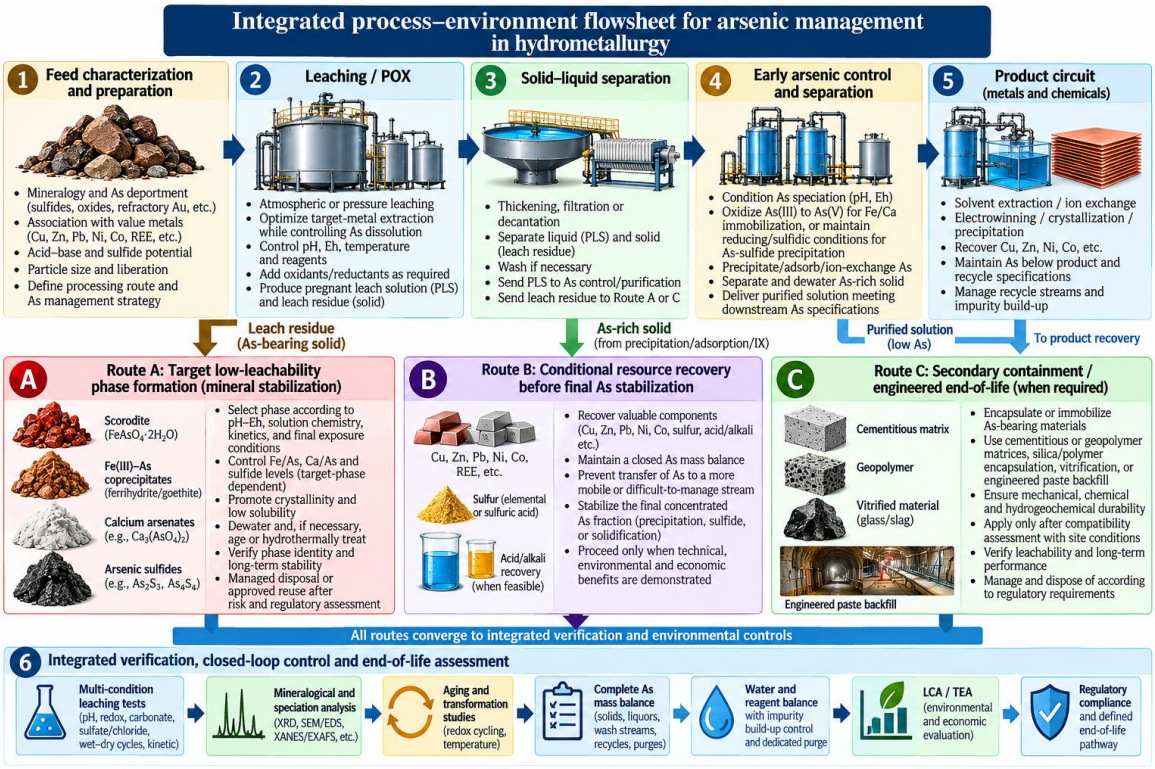

Figure 4. Integrated hydrometallurgical–environmental flowsheet for controlling arsenic while preserving value recovery.

Note. Original synthesis based on (Che et al., 2022; Davoudi & Kamran Haghighi, 2026; Du et al., 2024; Liu et al., 2021; Ma, Su, et al., 2022; Qi et al., 2020; Xu et al., 2023; Yong et al., 2022; Zhang, Liu, et al., 2023; Zhang, Han, et al., 2024). This is an author-developed conceptual integrated flowsheet synthesized from the reviewed evidence; it is not a single experimentally demonstrated or validated industrial campaign.

10. Emerging technologies, technology readiness, and sustainability

10.1 Biogenic and electrocrystallization routes

Biogenic scorodite and biologically assisted oxidation seek to lower chemical-oxidant demand and use controlled microbial or catalytic pathways to oxidize As(III) and form crystalline As(V)-bearing solids. Seed selection, particle size, iron source, residence time, and reactor robustness remain important for scale-up. Field-pilot biofiltration provides a useful counterpoint: biological systems can perform under realistic hydrological conditions, but their behavior depends strongly on temperature, substrate, and Fe supply (Kimura & Okibe, 2025;

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Okibe et al., 2020; Thevenot et al., 2025; Vega-Hernandez et al., 2021; Vega-Hernandez et al., 2020; Vera-Espíndola et al., 2024).

Gas-diffusion electrocrystallization is another example of moving from bulk precipitation to engineered nucleation and crystal growth. Its significance is conceptual as well as technological: it treats arsenic removal as a solids-quality problem, not only a dissolved-concentration problem. The scale-up challenge is to preserve mass transfer, energy efficiency, and crystal separability as reactor size increases (Pozo et al., 2020).

10.2 Advanced monitoring and mechanistic control

Direct quantification of As(III)/As(V) and mechanistic tracking of Fe–As transformations can reduce process uncertainty. Spectroscopic and in-line approaches are particularly valuable in high-ionic-strength liquors where conventional assumptions about pH and total arsenic are insufficient. The long-term trend is toward linking online aqueous measurements with solids characterization and predictive models of phase evolution (Yuan et al., 2026; Yang et al., 2026).

Species-resolved arsenic data also require analytical QA/QC because As(III)/As(V) can change during sampling, filtration, storage, preservation, and transport. Studies making speciation-dependent process claims should report sampling sequence, filtration conditions and timing, preservation chemistry and temperature, holding time, separation method, analytical technique, calibration/standards, detection limits, recovery or spike checks, and any oxidation-state stability checks performed before analysis.

10.3 Hydrothermal, vitrification, and high-selectivity recovery

Hydrothermal reconstruction of sulfide or calcium arsenic residues, selective recovery of arsenic metal, and vitrification represent higher-intensity routes that can be justified for concentrated, high-risk wastes. Their readiness depends less on whether the chemistry works at laboratory scale and more on continuous solids handling, corrosion, gas management, reagent recycle, product qualification, and the fate of secondary streams (Hu et al., 2024; Hu

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et al., 2026; Peng et al., 2025; Wang, Ptacek, et al., 2025; Wang et al., 2026; Xu et al., 2020; Xu et al., 2022; Zhang, Lu, et al., 2021).

10.4 LCA, TEA, and the evidence required for scale-up

Technology readiness should be coupled to life-cycle and techno-economic evidence. A process can achieve excellent arsenic removal and still be unattractive if it consumes excessive oxidant, produces large gypsum or iron-rich solids, requires high-temperature treatment, or creates a dilute wastewater burden. Conversely, recovery of co-metals or reagents can offset treatment costs if selectivity is high and the arsenic endpoint remains secure (Wan et al., 2025).

For publication-quality and scale-up-oriented reporting, technology-readiness claims should include arsenic and valuable-metal balances; reagent, water, and energy demand; residence time and throughput; settling rate and particle-size distribution; filtration flux, cake moisture, wash efficiency, and solids yield; rheology and dusting potential where relevant; corrosion-resistant materials and pressure equipment when required; off-gas and scrubber management; product specifications and market/offtake assumptions; recycle buildup and bleed treatment; residual-disposal cost; and long-term monitoring. Without these data, technology comparisons remain predominantly qualitative.

TEA should be developed alongside LCA using explicit system boundaries. At minimum, it should account for reagents, water, energy, labor where relevant, pressure or thermal equipment, corrosion-resistant materials, thickening/filtration, gas cleaning, recycle and bleed treatment, residual disposal, product value and qualification, transport where material, and long-term monitoring or closure obligations.

Figure 5 relates practical maturity to the long-term evidence burden required before arsenic-management technologies can be considered ready for broader deployment.

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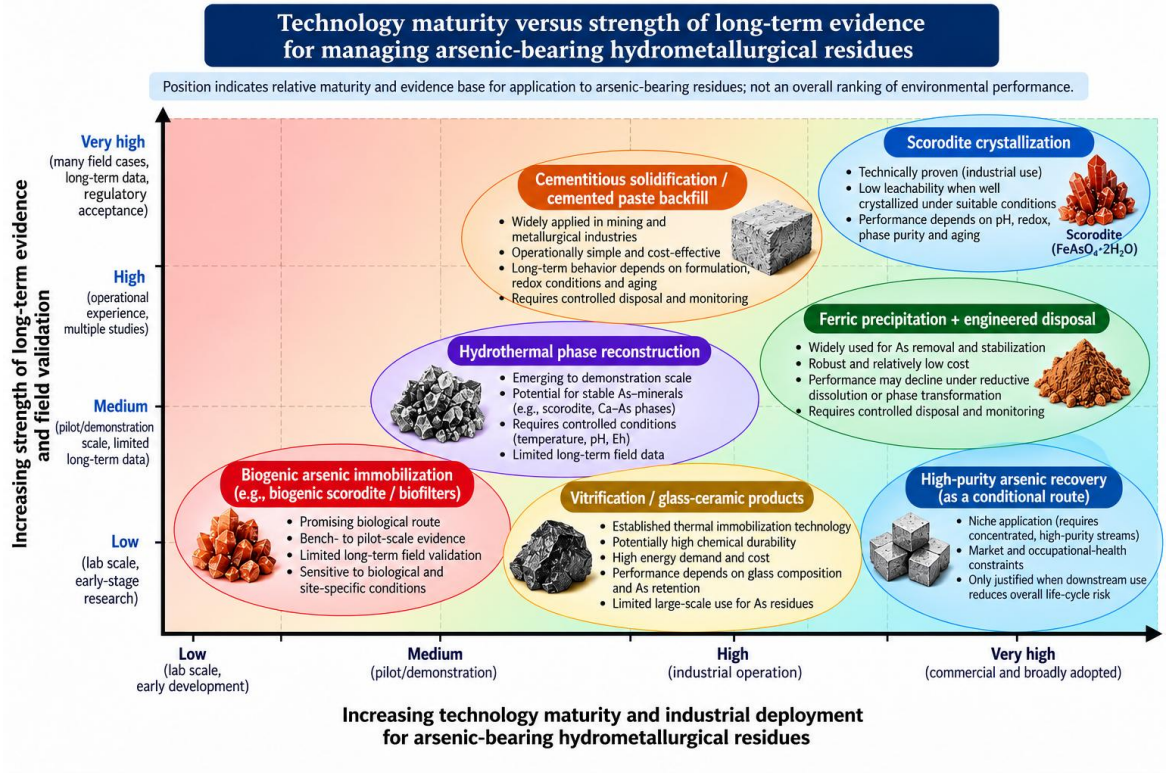

Figure 5. Qualitative relationship between practical maturity and the long-term evidence burden for arsenic-management technologies.

Note. Original critical synthesis based on the technology families represented by (Kimura & Okibe, 2025; Li et al., 2024; Pozo et al., 2020; Thevenot et al., 2025; Wang, Ptacek, et al., 2025; Wang et al., 2026; Xu et al., 2020; Zhao, Zhang, et al., 2024). Placement is qualitative and does not constitute a formal TRL certification. Qualitative maturity rubric: low = laboratory proof-of-concept with limited integrated operation; medium = repeated bench/pilot evidence with some integrated solids/liquid handling; high = pilot or industrially analogous operation with credible engineering data; very high = established commercial practice or broadly transferable industrial evidence. Long-term-evidence strength is graded independently from maturity: low = short-duration laboratory data; medium = multi-condition or intermediate-duration evidence; strong = extended/field-relevant evidence; very high = long-duration, multi-condition, field or regulatory performance evidence. These axes must not be interpreted as environmental superiority.

Table 6 summarizes the maturity, opportunity, and unresolved scale-up issues for the emerging technology families discussed above.

Table 6
Emerging arsenic-management technologies: maturity, opportunity, and unresolved scale-up issue

Technology family	Current evidence profile	Main opportunity	Unresolved issue

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Biogenic scorodite/bio-oxidation	Bench to pilot evidence	Lower chemical oxidant demand; controlled crystal formation	Biological robustness, temperature sensitivity, solids recovery, continuous operation.
Electrocrystallization	Laboratory / reactor-development evidence	Engineered nucleation and compact crystalline product	Energy efficiency, electrode/reactor scale-up, fouling.
Hydrothermal phase reconstruction	Strong laboratory evidence; some field-oriented work	Converts reactive As–S or As–Ca residues to lower-mobility phases	Pressure equipment, corrosion, reagent recycle, continuous solids handling.
Metallic arsenic recovery	Emerging laboratory evidence	Creates concentrated product and may reduce waste mass	Product market, purity, occupational controls, long-term offtake.
Vitrification/fiber products	Bench-to-industrially familiar thermal platform, but residue-specific validation needed	Durable glass network and possible product value	Energy, volatilization/off-gas capture, product-specific durability.
Advanced speciation monitoring	Rapidly developing analytical capability	Better control of As(III)/As(V) and process transitions	Calibration in high-salt liquors and integration with control systems.

Note. The maturity descriptors are qualitative syntheses, not formal TRL scores. Representative evidence: (Hu et al., 2024; Kimura & Okibe, 2025; Peng et al., 2025; Pozo et al., 2020; Vega-Hernandez et al., 2021; Vera-Espíndola et al., 2024; Wang, Ptacek, et al., 2025; Wang et al., 2026; Xu et al., 2020; Yuan et al., 2026).

11. Critical assessment and research gaps

11.1 Long-term stability remains the dominant evidence gap

The literature is rich in removal efficiencies and short-duration leach tests but much thinner in multi-year transformation data. Yet available long-term studies show that Fe reduction, ligand attack, sulfate evolution, dry–wet cycling, freeze–thaw exposure, and anoxic or sulfidic conditions can substantially change arsenic release. Future work should treat aging as a designed experimental variable, not as an afterthought (Abbasi et al., 2026; Ma et al., 2025; Wang, Su, et al., 2025; Warchulski et al., 2025; Yuan et al., 2020; Zhang et al., 2020; Zhang,

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Xia, et al., 2024; Zhao, Du, et al., 2025; Zhao, Wang, et al., 2025; Zhou et al., 2022; Zhu et al., 2020).

A minimum exposure matrix should therefore include mechanisms relevant to the intended endpoint: acidic and near-neutral exposure; oxidizing and reducing conditions; carbonation; sulfide-bearing conditions; organic ligands or root exudates; and dry–wet or freeze–thaw cycling where climate justifies them. Not every test is required for every residue, but the chosen matrix should be justified by a plausible field or reuse scenario and followed by phase re-characterization and leaching.

11.2 Phase identity must be linked to process performance

A second gap is the tendency to infer stability from bulk arsenic removal without proving the host phase. This is particularly problematic for poorly crystalline ferric arsenates and calcium-rich sludges. XRD alone may miss amorphous or nanocrystalline components, so integrate spectroscopic and microscopic methods with selective extraction and leaching. For scorodite claims, crystal structure, substitutions, and precursor phases should be reported explicitly (Bobos et al., 2026; Ma, Qi, et al., 2022; Ma et al., 2024; Ma et al., 2021; Yang et al., 2026).

Phase claims should distinguish XRD-confirmed crystalline scorodite from scorodite-like material, hydrous ferric arsenate, poorly crystalline Fe–As phases, and surface-bound/coprecipitated arsenate. Where long-term behavior depends on a specific host, XRD should be complemented by orthogonal spectroscopy or microscopy that can constrain poorly crystalline phases, local coordination, substitutions, or surface association.

11.3 Scale-up data on solids handling are underreported

Third, laboratory reports often omit solids-handling data. Arsenic stabilization can generate fine, gelatinous, or high-moisture precipitates whose separation and transport determine plant viability. Scale-up studies should therefore report measurable variables such as settling rate, particle-size distribution, thickening behavior, filtration flux, cake moisture,

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wash efficiency, solids yield, rheology where relevant, and dusting or handling potential, alongside solution chemistry and phase identity. A process that forms a comparatively low-leachability phase but cannot produce a transportable and washable solid remains incomplete at industrial scale.

11.4 Valorization needs a stricter definition

Fourth, the term "valorization" is sometimes used when a waste is merely incorporated into another matrix. A more rigorous definition requires measurable resource recovery or functional material value, a lower total environmental burden than the disposal baseline, and a defined end-of-life pathway. Metallic arsenic recovery, co-metal recovery, binder production, and fiber production are fundamentally different propositions and should not be grouped under one circular-economy label (Liu et al., 2024; Peng et al., 2025; Wan et al., 2025; Wang et al., 2026; Wang, Liu, et al., 2023; Ye et al., 2025; Yong et al., 2022; Zhang, Han, et al., 2024; Zhao, Zhang, et al., 2024; Zhao et al., 2022).

11.5 Regulatory evidence must follow the exposure scenario

Fifth, regulatory compliance should be aligned with the actual exposure pathway. TCLP, EU landfill release criteria, Chinese extraction-toxicity standards, and Brazilian effluent limits address different matrices and purposes. Research papers should stop using a single favorable threshold as universal evidence of safety. For reuse, the relevant tests may include monolith diffusion, abrasion-generated fines, service-water exposure, carbonation, and end-of-life crushing, depending on the product.

For this revision, we rechecked the cited regulatory sources against official repositories in October 2026. The U.S. toxicity-characteristic listing retains arsenic D004 at 5.0 mg/L in TCLP extract; CONAMA Resolution 430/2011 retains 0.5 mg/L total arsenic for direct effluent discharge under Article 16; Council Decision 2003/33/EC remains the EU legal act establishing landfill waste-acceptance criteria; and the Chinese Ministry of Ecology and Environment continues to publish GB 5085.3-2007 as a compulsory extraction-toxicity identification

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standard. These values and frameworks apply to different regulatory objects and must not be collapsed into a generic arsenic "safe limit."

11.6 A proposed minimum reporting set

A minimum reporting set for future arsenic-management studies should include: feed and residue mineralogy; total and species-resolved arsenic with preservation/QA-QC details; Fe/As and Ca/As ratios where applicable; free acidity in addition to pH; sulfate, chloride, and major-metal concentrations; temperature and redox conditions; quantitative stream-by-stream arsenic mass balance and closure with analytical uncertainty; valuable-metal closure when valorization is claimed; wash water, recycle, bleed, and scrubber streams where relevant; solid yield, settling rate, particle-size distribution, filtration flux, cake moisture, wash efficiency, rheology and dusting potential where relevant; phase identification after treatment and after aging; at least one compliance leach test plus one mechanism-oriented test; a justified multi-condition exposure matrix; aged-residue retesting; explicit LCA functional unit/system boundary and TEA boundary when sustainability is claimed; and a transparent statement of the proposed regulatory endpoint and long-term monitoring requirement. This dataset would make cross-study comparison substantially more reliable (Pereira, 2026a; Pereira, 2026b; Yuan et al., 2026).

The field is moving from "remove arsenic from water" toward "engineer an arsenic endpoint". That shift matters because it forces hydrometallurgy, mineralogy, waste engineering, and regulation into the same design space. It also changes the meaning of process optimization: the optimum is no longer the lowest dissolved arsenic concentration at the reactor outlet, but the lowest system-level risk and cost across the residue's full life.

12. Conclusions and future perspectives

Arsenic-bearing wastes in hydrometallurgy should be managed as dynamic chemical systems rather than as static filter cakes. Arsenic is repeatedly transferred among aqueous species, ferric precipitates, calcium phases, sulfides, encapsulated solids, and glassy products.

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The decisive engineering question is whether the selected route creates a stable, verifiable final sink under the conditions the residue will actually experience.

A defensible general strategy is hierarchical. First, minimize arsenic circulation and establish a complete mass balance. Second, control oxidation state, acidity, and Fe/As or Ca/As chemistry so that arsenic forms a defined target phase. Third, use mineral reconstruction, encapsulation, solidification, or vitrification when the primary phase alone cannot meet the disposal or reuse requirement. Finally, verify stability after aging and under multiple leaching scenarios.

Scorodite remains an important benchmark, but it is not a universal solution. Calcium arsenates, arsenic sulfides, hydrous ferric arsenates, cementitious composites, hydrothermal products, and vitrified materials each occupy a different process and environmental niche. Their suitability must be determined from the complete residue chemistry, not from a single arsenic-removal percentage.

Valorization should remain conditional. Recovery of co-metals, reagents, or arsenic itself can improve resource efficiency, but only when it reduces the total inventory of mobile arsenic and leaves a credible destination for every secondary stream. Future progress will depend on coupling process chemistry with long-term mineralogical evidence, robust solids handling, scale-up data, life-cycle assessment, and regulation-specific validation.

Declarations

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Conflict of Interest

The author declares no conflict of interest.

Data Availability

No new experimental datasets were generated. All quantitative values discussed in the review are traceable to the cited literature.

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The author performed conceptualization, critical analysis, literature synthesis, visualization, and manuscript preparation.

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