

Germanium Processing from Primary and Secondary Resources: Occurrence, Extraction Technologies, and Circular Economy Perspectives

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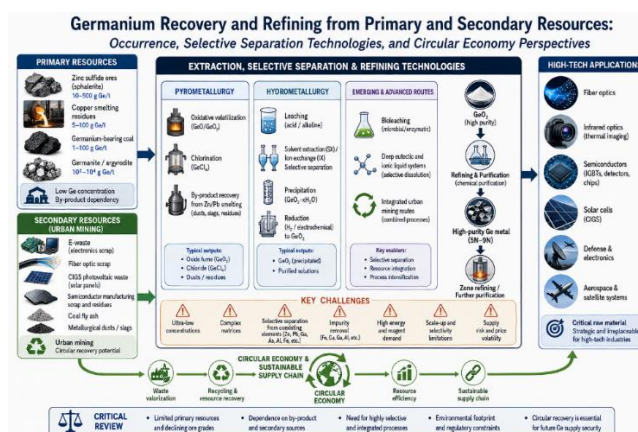
ABSTRACT: Germanium is a critical technology metal used in fiber optics, infrared optics, photovoltaics, semiconductors, and emerging energy systems. Despite its strategic importance, primary germanium resources are limited, and global production remains heavily dependent on by-product recovery from zinc processing, coal fly ash, and copper-related residues. This review critically examines the occurrence, mineralogy, and distribution of germanium in both primary and secondary resources, emphasizing the growing importance of urban mining and industrial waste valorization. Current recovery technologies are analyzed, including pyrometallurgical, hydrometallurgical, chlorination, volatilization, solvent extraction, ion exchange, and biohydrometallurgical routes. Particular attention is given to the efficiency of selective separation, impurity behavior, energy demand, environmental constraints, process integration, and scale-up limitations. The review highlights that germanium dissolution is often less challenging than downstream purification and selective recovery from chemically complex, highly dilute process streams. Major technological barriers include ultra-low Ge concentrations, impurity-rich matrices, solvent degradation, reagent consumption, and the limited industrial maturity of several emerging recovery technologies. Recent advances in secondary recovery from electronic waste, coal-derived residues, and metallurgical by-products are critically evaluated within the broader context of circular economy strategies and integrated multi-metal recovery systems. The analysis indicates that future germanium supply will depend less on primary mining expansion and more on the ability to selectively recover Ge from complex secondary resources through integrated, economically robust processing systems.

KEYWORDS: Circular economy, Critical metals, Germanium, Hydrometallurgy, Recycling, Secondary resources.

Highlights

- Germanium production remains strongly dependent on by-product recovery from zinc, coal, and copper processing streams.
- Secondary resources may become the dominant future source of recoverable germanium.
- Selective separation, rather than dissolution efficiency, remains the principal technological bottleneck in germanium recovery.
- Hydrometallurgical and chlorination-based systems offer high selectivity but still face major impurity control and scale-up limitations.
- Circular-economy strategies may redefine future germanium supply through integrated recovery from industrial residues, coal-derived materials, and electronic waste.

Graphical abstract





1. INTRODUCTION

Germanium (Ge) has become an essential technology metal because of its critical applications in semiconductors, fiber-optic communication, infrared optics, and high-efficiency photovoltaic systems. The rapid expansion of advanced electronics, renewable energy technologies, and photonic devices has significantly increased the industrial relevance of Ge, leading to its classification as a critical raw material (CRM) in several international assessments (Haghighi & Irannajad, 2022; Wong et al., 2025). However, despite its technological importance, global germanium supply remains structurally vulnerable because production is largely dependent on zinc refining and coal-related industrial systems.

The technological relevance of germanium is primarily associated with its favorable electronic and optical properties, including high carrier mobility, infrared transparency, and semiconductor compatibility. These characteristics make Ge particularly attractive for high-speed electronics, thermal imaging systems, photonic devices, infrared optics, and aerospace solar cells. Germanium dioxide (GeO₂) is widely used as a dopant in fiber-optic communication systems, while high-purity Ge substrates are essential for multi-junction photovoltaic applications and advanced semiconductor technologies (Wenlong & Bin, 2026; Yadav et al., 2026).

Unlike conventional industrial metals, germanium is rarely produced as a primary commodity. Most Ge is recovered as a by-product of zinc refining, coal fly ash, lignite, metallurgical slags, and industrial residues (Nguyen & Lee, 2021). Consequently, global Ge availability is strongly influenced by the production dynamics of the zinc and coal industries rather than by direct market demand for germanium. This indirect production route creates substantial supply risk and geopolitical vulnerability, particularly because extraction and refining capacity remains highly concentrated in a limited number of countries, especially China (Sverdrup & Haraldsson, 2024; Umbach, 2024).

Coal-derived materials, zinc smelting dusts, electronic waste, optical fibers, and combustion residues have therefore emerged as increasingly important alternative sources of germanium. The growing emphasis on urban mining, industrial waste valorization, and circular economy strategies has accelerated research on recovery technologies capable of processing low-grade and chemically heterogeneous materials (Alguacil & Robla, 2024; Meshram & Abhilash, 2022; Srivastava & Ilyas, 2025; Van Hoof et al., 2020). In many cases, secondary materials already contain significantly higher effective Ge concentrations than several primary ores, particularly after volatilization-condensation enrichment or metallurgical concentration stages.

Although high dissolution efficiencies are frequently achieved during leaching, the principal technological challenge in germanium metallurgy is not dissolution itself, but the selective recovery and purification of Ge from highly complex multicomponent systems. Germanium is commonly present at low concentrations in solutions containing substantially larger amounts of Zn, Fe, Si, As, Al, Ga, and In, making downstream purification particularly difficult (Aghazadeh et al., 2016). As a result, recent research has increasingly focused on advanced purification systems, including solvent extraction, quaternary ammonium extractants, ion-exchange resins, membrane-assisted separation, ionic liquids, and intensified hydrometallurgical processes (Fan et al., 2025; Peng et al., 2024; Vereycken et al., 2022a; Wu et al., 2025).

In parallel, sustainability concerns are increasingly reshaping germanium research and industrial development. Waste minimization, recycling efficiency, energy demand, carbon footprint reduction, and integrated multi-metal recovery are now viewed as central factors for long-term Ge supply stability (Tao et al., 2021; Yandem & Jabłońska-Czapla, 2024). Nevertheless, the current literature remains highly fragmented across zinc hydrometallurgy, coal processing, electronic waste recycling, semiconductor refining, and secondary metallurgy, with many studies focusing only on isolated process stages or simplified laboratory systems that do not adequately represent industrial process complexity (Huang et al., 2024).

Therefore, this review critically examines germanium occurrence, extraction technologies, purification systems, recycling strategies, and sustainability challenges associated with both primary and secondary resources. Particular emphasis is placed on the distinction between metal dissolution and selective recovery, highlighting that the main bottleneck in germanium metallurgy is the efficient separation of Ge from chemically complex and highly dilute industrial systems.

2. METHODOLOGY

This review was developed using a structured literature assessment approach based on the PRISMA 2020 framework for systematic reviews, adapted to the multidisciplinary characteristics of germanium processing research (Page et al., 2021). The methodology was modified to address the broad range of topics associated with germanium metallurgy, including mineralogy,



pyrometallurgy, hydrometallurgy, selective separation, recycling technologies, purification systems, and sustainability assessment. Similar adaptations have recently been applied in critical reviews involving strategic metals and hydrometallurgical processing systems (Haghighi & Irannajad, 2022; Meshram & Abhilash, 2022).

The literature survey was conducted using the Scopus, Web of Science, and ScienceDirect databases due to their broad coverage of publications in metallurgical, chemical engineering, mineral processing, and materials science. Complementary searches were also performed using Google Scholar to identify recent conference proceedings, industrial reports, and emerging technologies not yet fully indexed in conventional databases. Publications from 2020 to 2026 were considered to integrate both foundational studies and recent developments in ionic liquids, intensified extraction systems, selective leaching strategies, and recycling technologies.

The search strategy employed keyword combinations related to the occurrence, extraction, separation, purification, and recycling of germanium. Representative search terms included “germanium recovery,” “germanium extraction,” “germanium purification,” “selective leaching,” “solvent extraction,” “ionic liquids,” “coal fly ash,” “zinc residues,” “urban mining,” and “critical raw materials.” Boolean operators and database-specific filters were applied to improve search precision and reduce redundancy. Particular attention was given to studies involving zinc hydrometallurgy, coal-derived materials, industrial dusts, electronic waste, and advanced selective separation technologies.

The inclusion criteria prioritized studies containing quantitative experimental, pilot-scale, or industrial data relevant to germanium processing. Publications were selected when they reported at least one of the following parameters: germanium recovery efficiency, extraction selectivity, impurity removal behavior, process conditions, reagent consumption, energy demand, purification efficiency, thermodynamic analysis, or industrial scalability indicators. Studies involving technology readiness assessment, pilot-scale validation, or industrial integration were also prioritized, as laboratory-scale extraction efficiency alone is often insufficient to assess industrial feasibility (Nguyen & Lee, 2021).

Studies were excluded when they contained only qualitative discussions without experimental validation, lacked relevant process parameters, or presented insufficient analytical characterization. Purely theoretical investigations without practical relevance to extraction or purification were also excluded unless they contributed directly to the interpretation of thermodynamic behavior or selective separation mechanisms. Duplicated publications, non-peer-reviewed summaries, and studies with incomplete methodological descriptions were removed during the screening stage.

One important observation from the literature assessment was the pronounced methodological heterogeneity in research on germanium processing. Significant variations were observed in leaching conditions, solid-to-liquid ratios, pH control strategies, oxidizing systems, extraction reagents, residence times, and purification methodologies. Consequently, direct quantitative comparison of reported recovery efficiencies is often unreliable without accounting for impurity profiles, solution chemistry, and downstream purification requirements. In many cases, studies reporting high Ge recovery values employed substantially different experimental conditions, while selectivity, reagent consumption, energy demand, and final product purity were not consistently evaluated.

Another major limitation identified in the literature was the lack of standardization in the reporting of key performance indicators. Several studies reported only Ge extraction percentages without discussing impurity co-extraction, germanium concentration factors, downstream purification requirements, or final product quality. Similarly, energy consumption, environmental impact, solvent regeneration performance, and process integration were frequently absent, particularly in emerging extraction systems involving ionic liquids or intensified separation technologies. This lack of standardization complicates comparisons among hydrometallurgical, pyrometallurgical, and hybrid recovery routes and remains a major challenge for the critical evaluation of germanium processing technologies.

The overall literature selection workflow employed in this review is summarized in Figure 1.

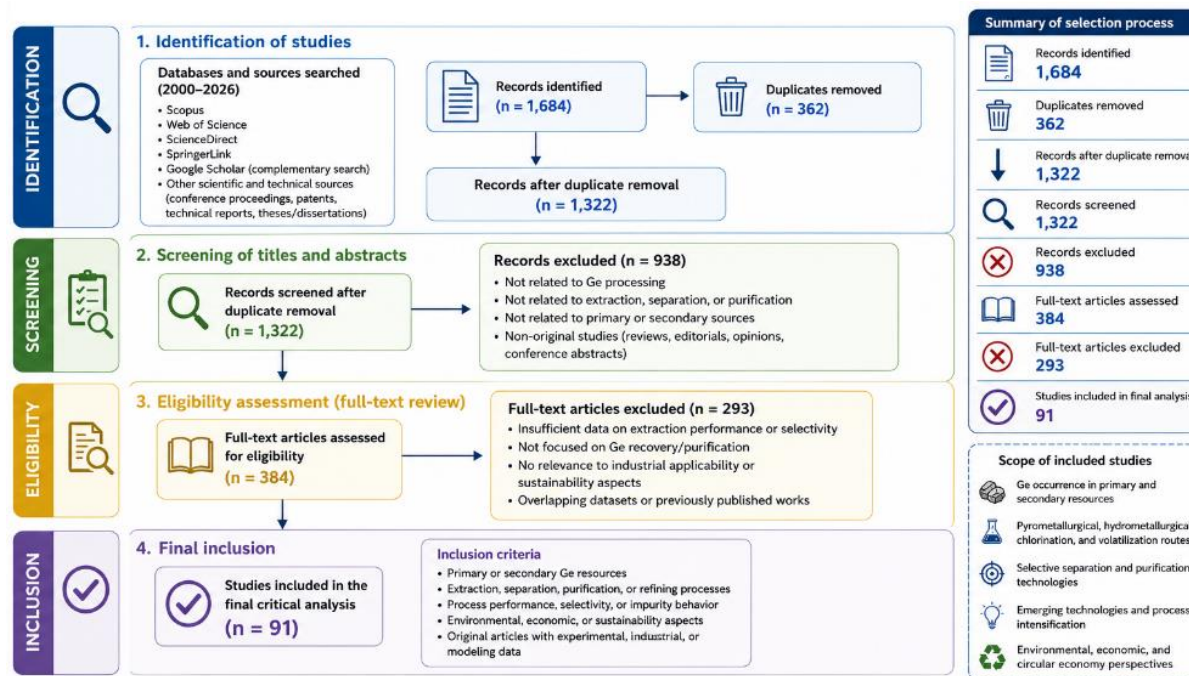


Figure 1. Adapted from the PRISMA 2020 statement (Page et al., 2021) and modified according to methodologies reported by Haghighi and Irannajad (2022), Meshram and Abhilash (2022), and Nguyen and Lee (2021)

Figure 1 illustrates the sequential stages used for identification, duplicate removal, screening, eligibility assessment, and final inclusion of studies relevant to germanium occurrence, extraction, purification, recycling, and sustainability. A total of 1,684 records were initially identified from scientific databases and complementary technical sources, including Scopus, Web of Science, ScienceDirect, SpringerLink, and Google Scholar. After duplicate removal and sequential screening stages, 91 studies were retained for the final critical analysis.

The final dataset enabled comparative assessment of conventional and emerging germanium recovery technologies, including pyrometallurgical concentration, hydrometallurgical extraction, selective separation, process intensification, recycling systems, and circular-economy strategies. The methodology also supported the identification of current technological limitations, research gaps, and future directions associated with sustainable germanium supply chains and secondary-resource utilization.

3. OCCURRENCE AND DISTRIBUTION OF GERMANIUM

Germanium is a rare, dispersed element in Earth's crust, occurring at about 1–2 ppm. Unlike major industrial metals, Ge rarely forms primary deposits and is mostly found with sulfide minerals, coal, and industrial waste. Its geochemical behavior is driven by its chalcophile nature, which favors substitution in sulfides rather than the formation of germanium-rich minerals (Grigorieva et al., 2020). This leads to its occurrence and industrial use differing from those of typical base metals, complicating extraction and purification (Zhang et al., 2025).

Primary germanium mainly derives from zinc sulfide ores like sphalerite (ZnS), where Ge replaces Zn. Sphalerite is the main global source because zinc processing concentrates Ge in residues and streams (Hu et al., 2025). Ge in sphalerite ranges from tens to hundreds of ppm, depending on deposit origin, mineralogy, and hydrothermal conditions (Wenlong & Bin, 2026). Some deposits may locally exceed 1000 ppm.

Although relatively uncommon, specific germanium minerals such as germanite ($\text{Cu}_{13}\text{Fe}_2\text{Ge}_2\text{S}_{16}$) and argyrodite (Ag_8GeS_6) are direct Ge-bearing phases. These minerals are of mineralogical importance because they historically contributed to the discovery and early extraction of germanium. Nevertheless, their industrial relevance is currently limited by low global reserves and restricted geographic occurrence (Fleitlikh et al., 2021). Consequently, modern germanium production depends predominantly on recovering by-products from large-scale metallurgical systems rather than on the direct mining of Ge minerals.



Coal-derived materials and combustion residues have become increasingly important secondary sources of germanium. Some lignites and germanium-rich coals exhibit high Ge concentrations due to organic affinity and geochemistry. During combustion or gasification, germanium concentrates in coal fly ash via volatilization and condensation, often exceeding levels in primary ores (Mahandra et al., 2021). Studies report Ge concentrations in fly ash ranging from tens to hundreds ppm, with highly enriched ashes exceeding 1000 ppm under certain conditions (Pereira, 2025d).

Recent studies on coal fly ash and lignite highlight growing interest in alternative recovery methods, including selective leaching, chlorination, alkali treatment, and advanced extraction (Bo et al., 2024; Fan et al., 2025). In some lignite systems, germanium occurs as organometallic forms or mineral inclusions, complicating extraction. Mineral complexity leads to variability in extraction efficiency, reagent use, and impurity co-dissolution (Li et al., 2025). Additionally, silicon-rich matrices pose purification challenges due to the formation of silica gel, which disrupts downstream processes (Liu et al., 2024; Sujiang et al., 2025).

Secondary metallurgical residues, such as zinc refinery residues, copper smelting dusts, lead slags, and flue dusts, are key sources of germanium because high-temperature volatilization occurs during pyrometallurgical processing (Nakhaei et al., 2025; Vu et al., 2021). Germanium in these residues exists in oxides, glassy matrices, sulfates, or polymetallic forms with Zn, Pb, Fe, As, and Si. Zinc processing dusts are especially valuable since they can contain higher Ge levels than some ores and are partially processed for hydrometallurgy (He et al., 2026).

The mineralogical heterogeneity of metallurgical slags and dusts remains a major operational limitation for industrial Ge recovery. Slag cooling conditions, redox environment, furnace atmosphere, and feed composition strongly influence the distribution of Ge among metallic, oxide, and amorphous phases (Dzinomwa et al., 2023). As a consequence, extraction efficiency may vary significantly even within residues generated by similar industrial processes. This variability complicates process standardization and frequently limits the scalability of laboratory-developed extraction routes (Ettler et al., 2022).

Electronic waste and residues from advanced technology are promising sources of germanium recovery, including optical fibers, infrared optics, semiconductor scraps, photovoltaic materials, and electronic components, which contain high-purity Ge compounds (Kumar et al., 2025). These materials often have higher local germanium concentrations than natural ores, depending on the component type and degree of concentration (Srivastava & Ilyas, 2025). However, recovering Ge from e-waste presents challenges due to material complexity, polymeric encapsulation, hazardous additives, and separation selectivity (Robart et al., 2025).

The rising importance of secondary resources has shifted the global view on germanium supply. Industrial residues and electronic waste often have higher germanium levels than ores, making them economically appealing despite processing challenges. However, their extreme compositional variability remains a major obstacle, as extraction, impurity profiles, and purification needs differ widely across waste streams (Dhiman & Gupta, 2020). This underscores the need for highly selective separation systems for unstable, heterogeneous conditions.

The typical germanium concentrations observed in major primary and secondary resources are summarized in Table 1.

Table 1. Typical germanium concentrations in primary and secondary resources used for industrial recovery. Adapted from Nguyen and Lee (2021), Meshram and Abhilash (2022), Rudnik (2025), and Srivastava and Ilyas (2025).

Resource	Typical Ge Concentration	Main Associated Phases	Industrial Relevance
Sphalerite ores	10–500 ppm	Zn sulfides	Primary industrial source
Germanite	wt.% levels	Cu-Fe-Ge sulfides	Limited primary source
Argyrodite	wt.% levels	Ag-Ge sulfides	Rare mineral source
Coal fly ash	50–1500 ppm	Oxides, amorphous phases	Major secondary source
Lignite	10–500 ppm	Organic/mineral associations	Emerging source
Zinc refinery residues	100–5000 ppm	Oxides, sulfates	Highly relevant secondary source
Metallurgical flue dust	50–3000 ppm	Fine oxides and sulfates	Secondary industrial source
Copper slags	10–500 ppm	Silicate matrices	Potential secondary source
Optical fibers	0.1–5 wt.%	GeO ₂ -doped silica	Urban mining source
Semiconductor waste	wt.% levels	Metallic Ge and Ge compounds	High-value secondary source

Table 1 demonstrates that secondary resources may exhibit local germanium concentrations comparable to, or even higher than, those of conventional ores. Zinc residues, flue dusts, semiconductor wastes, and optical fibers are particularly attractive because of their relatively high Ge enrichment and increasing availability. However, the chemical and mineralogical variability of these materials significantly affects process stability and selectivity, making resource characterization a critical step in developing industrial routes for germanium recovery.

The global distribution pathways and major forms of occurrence of germanium in primary ores, coal-derived materials, metallurgical residues, and secondary resources are schematically illustrated in Figure 2.

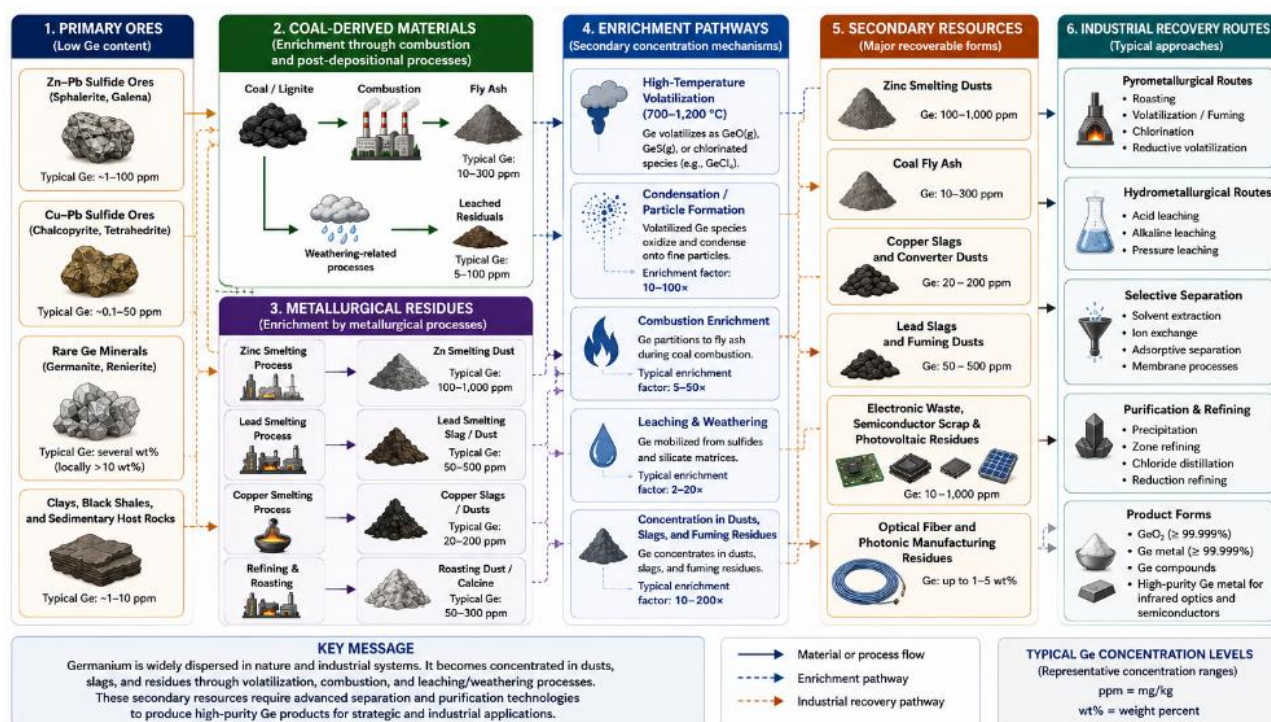


Figure 2. Schematic distribution of germanium in primary ores, coal-derived materials, metallurgical residues, and secondary resources, highlighting typical enrichment pathways and industrial recovery routes. Adapted from Nguyen and Lee (2021), Rudnik (2025), Srivastava and Ilyas (2025), and Teng et al. (2025).

Figure 2's framework shows germanium's dispersed nature in industry and its reliance on secondary concentration methods such as volatilization, condensation, combustion enrichment, and residue processing. It highlights the importance of selective separation technologies for processing chemically diverse secondary resources.

4. PYROMETALLURGICAL PROCESSING ROUTES

Pyrometallurgical processing is a key method for germanium recovery, especially in zinc smelting, coal combustion, and residue treatment. Its importance lies in the high volatility of germanium compounds at high temperatures, allowing Ge enrichment through volatilization and condensation. In practice, germanium is rarely recovered directly from ores; instead, it accumulates in residues like flue dusts, slags, and secondary streams during high-temperature processes (Jiang et al., 2021; Hu et al., 2025).

The pyrometallurgical behavior of germanium depends strongly on temperature, oxygen potential, sulfur activity, chlorination conditions, and slag chemistry. Under oxidizing conditions, it turns into volatile GeO₂ at high temperatures. In chlorination, GeCl₄, with a boiling point around 83 °C, forms, enabling efficient separation via gas-phase transport and condensation (Li et al., 2025). These traits have led to the use of volatilization and chlorination as key industrial methods for Ge recovery (Maubane & wa Kalenga, 2024).

Coal combustion and coal gasification systems represent classic examples of germanium enrichment through pyrometallurgical volatilization. During combustion, organically associated germanium and fine Ge-bearing mineral phases partially volatilize and subsequently condense onto fine ash particles during cooling. This process may substantially increase Ge concentration in fly ash relative to the original coal feed (Bo et al., 2024; You et al., 2025). In highly enriched coals and lignites, volatilization-condensation mechanisms may produce local enrichment sufficient for industrial recovery operations.

Recent studies on germanium-rich lignite and coal fly ash suggest the use of integrated pyrometallurgical-hydrometallurgical processes that combine oxidation, chlorination, alkali conversion, and selective condensation (Tang et al., 2025). Chlorinated distillation is promising because it increases Ge volatility and separation from silicate matrices. However, operational challenges arise from the volatilization of impurities such as arsenic, zinc, lead, and cadmium, which reduce purity and complicate separation (Rao et al., 2025).

In zinc metallurgy, germanium's behavior closely relates to zinc's thermochemical changes during roasting, reduction, and smelting. Germanium generally follows zinc because both volatilize similarly under industrial conditions. Consequently, Ge can be found in calcines, slags, flue dusts, condenser residues, and leach streams, depending on the furnace atmosphere and temperature. This causes operational challenges, as uncontrolled volatilization can lead to Ge losses or environmental emissions.

Hard zinc slags from zinc pyrometallurgy often contain high levels of germanium due to repeated volatilization-condensation cycles. Studies show germanium may accumulate in oxidized slags, dusts, and deposits in furnace systems (Zhou et al., 2025). However, Ge distribution depends on local oxygen potential and slag chemistry. Silicon-rich slags are especially problematic because germanium can form stable silicate phases, reducing volatilization efficiency and complicating extraction (Zhang et al., 2024).

The thermodynamic behavior of germanium in pyrometallurgy is complex, as Ge exists in metallic, oxide, sulfide, chloride, and amorphous silicate forms. The dominant form depends on temperature and gas composition. Under oxidizing conditions, GeO₂ forms, while reducing environments stabilize metallic Ge or sulfides. Chlorination favors volatile chlorides such as GeCl₄ (Liu et al., 2025; You et al., 2025), but selective chlorination is difficult because other metals also form volatile chlorides.

The key limitation of pyrometallurgical processing is its low industrial selectivity for germanium, which often necessitates secondary concentration stages rather than direct extraction. It is mainly used for enrichment, followed by hydrometallurgical purification. In many industrial systems, pyrometallurgical processing serves primarily as a concentration stage rather than a complete recovery route because downstream hydrometallurgical purification remains necessary.

The behavior of germanium in slags and dusts is a key operational issue. Factors such as slag viscosity, cooling rate, and the activities of iron and silica influence Ge partitioning. Fast cooling traps Ge in amorphous matrices, reducing recovery; slow cooling encourages redistribution into oxides. In flue dust, Ge enrichment is associated with ultrafine vapor-condensed particles, which aid hydrometallurgy but complicate dust handling.

The typical operating conditions and main characteristics of pyrometallurgical germanium recovery routes are summarized in Table 2.

Table 2. Main pyrometallurgical routes for germanium recovery and their typical operating characteristics. Adapted from Bo et al. (2024), Li et al. (2025), Tang et al. (2025), and Zhou et al. (2025).

Process Route	Main Mechanism	Typical Temperature Range	Main Ge Species	Main Limitations
Coal combustion-enrichment	Volatilization-condensation	800–1400 °C	GeO ₂	Low selectivity
Chlorinated distillation	Chlorination-volatilization	300–1000 °C	GeCl ₄	Co-volatilization of impurities
Zinc roasting/smelting	Oxidation-volatilization	900–1300 °C	GeO ₂	Ge follows Zn flow
Slag fuming	Vapor-phase enrichment	1100–1400 °C	Ge oxides/chlorides	Dust handling complexity
Alkali thermal treatment	Phase transformation	400–900 °C	Germanates	High reagent consumption

Table 2 demonstrates that pyrometallurgical routes are highly effective for germanium enrichment and concentration but generally exhibit limited selectivity. In most industrial operations, pyrometallurgy serves primarily as a pre-concentration stage, transferring germanium into secondary residues or volatile fractions prior to selective hydrometallurgical recovery.

The main pyrometallurgical pathways involved in germanium volatilization, chlorination, slag enrichment, and integration with zinc smelting operations are schematically illustrated in Figure 3.

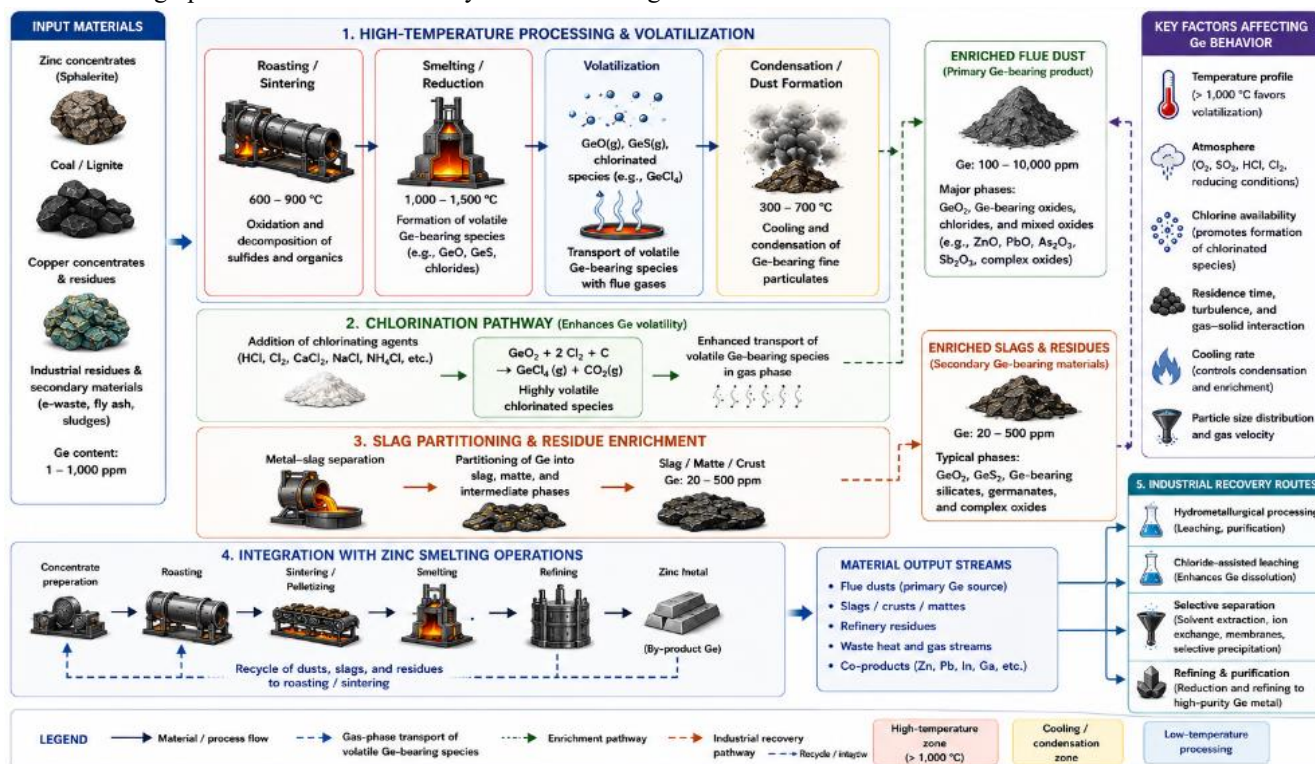


Figure 3. Main pyrometallurgical pathways for germanium recovery, showing volatilization, chlorination, slag partitioning, flue dust enrichment, and integration with zinc smelting operations. Adapted from Hu et al. (2025), Li et al. (2025), Tang et al. (2025), and Zhou et al. (2025).

Figure 3 highlights the strong coupling between germanium behavior and zinc pyrometallurgical systems. The schematic representation also illustrates the central role of volatilization-condensation mechanisms in Ge enrichment. It explains why uncontrolled furnace atmospheres or inadequate gas handling systems may result in substantial germanium losses during industrial operation.

5. HYDROMETALLURGICAL PROCESSING

Hydrometallurgical processing is now the main method for germanium recovery because it allows treatment of low-grade, complex materials under moderate conditions. Most industrial germanium feeds are secondary outputs from zinc processing, coal burning, or electronic waste recycling. These systems must handle highly heterogeneous feedstocks containing impurities such as Zn, Fe, As, Si, Al, and Pb. These impurities strongly affect selectivity and purification (Jiang et al., 2020; Meshram & Abhilash, 2022).

Acidic leaching systems remain the dominant industrial route for dissolving germanium from zinc residues, metallurgical slags, and secondary process materials due to their operational compatibility with conventional zinc hydrometallurgical circuits (Alonso et al., 2025; Bai et al., 2025). Sulfuric acid-based systems are particularly attractive since they enable the simultaneous dissolution of Ge and Zn from industrial residues while maintaining integration with existing refinery infrastructure. Typical operating conditions involve sulfuric acid concentrations between 50 and 250 g/L, temperatures ranging from 40 to 95°C, and

oxidation conditions controlled by mineralogical composition and impurity behavior. In recent years, oxygen pressure leaching has received increasing attention for treating refractory zinc dusts and slags because elevated oxygen availability enhances sulfide oxidation and promotes Ge liberation from iron-rich matrices (Lan et al., 2024).

Hydrochloric acid leaching is of interest because germanium forms stable chloro-complexes in chloride media, facilitating extraction and purification (Jiang et al., 2023). However, chloride media pose corrosion and waste-treatment issues, limiting industrial use in zinc plants (Alguacil et al., 2025).

Alkaline leaching is key for treating coal fly ash, lignite products, and silicate residues, in which germanium dissolves as a germanate in high-pH environments, with some impurities remaining insoluble (Wu et al., 2025). Typical conditions involve over 100 g/L sodium hydroxide and temperatures above 80 °C. However, silica dissolution often leads to gel formation, increases slurry viscosity, and hampers separation and purification.

Recent studies consistently demonstrate that the dissolution of germanium itself is not the primary technological limitation in hydrometallurgical processing. Under optimized conditions, Ge extraction efficiencies above 90% are frequently reported for both acidic and alkaline systems (Tang et al., 2025). The main industrial challenge emerges during downstream purification, where germanium must be selectively separated from chemically similar or co-dissolved elements.

Iron is a problematic impurity because ferric hydrolysis and precipitation can co-remove germanium from solution (Xu et al., 2022). Silicon causes operational instability through colloidal silica and silicate polymerization, reducing filtration and interfering with extraction. Arsenic remains a critical issue due to toxicity and complex chemistry. Therefore, selective separation from Zn, Fe, As, and Si is the main bottleneck in germanium hydrometallurgy, not initial leaching.

Purification strategies include precipitation, cementation, solvent extraction, ion exchange, and crystallization. Tannic acid's selective precipitation has been widely studied for the recovery of germanium from impurity metals (Aghazadeh et al., 2016). Other research has focused on enhanced purification methods, such as ultrasonic cavitation, oxidation, and hybrid routes, to boost purity and impurity rejection (Di et al., 2024).

Cementation is primarily used as a pre-purification step to remove interfering metallic species prior to final Ge recovery. Crystallization processes are typically used in advanced purification stages or in GeO₂ production. However, both operations remain highly sensitive to solution composition, pH control, and impurity concentration (Zhu et al., 2021).

The principal hydrometallurgical routes reported for the recovery of germanium from zinc residues, fly ash, and secondary resources are summarized in Table 3.

Table 3. Main hydrometallurgical routes used for germanium recovery from primary and secondary resources. Adapted from Aghazadeh et al. (2016), Bai et al. (2025), Jiang et al. (2023), Lan et al. (2024), and Wu et al. (2025)

Route	Main Reagents	Typical Conditions	Main Advantages	Main Limitations
Sulfuric acid leaching	H ₂ SO ₄	50–250 g/L; 40–95 °C	Industrial integration with Zn circuits	Co-dissolution of Fe and Zn
Hydrochloric leaching	HCl	Acidic chloride medium	Favorable Ge complexation	Corrosion and chloride effluents
Alkaline leaching	NaOH	>100 g/L; >80 °C	Improved selectivity in silicate systems	Silica gel formation
Oxygen pressure leaching	H ₂ SO ₄ + O ₂	Elevated pressure and temperature	Enhanced Ge liberation	High operational cost
Selective precipitation	Tannic acid, NH ₄ OH	Controlled pH systems	Partial impurity rejection	Co-precipitation losses
Cementation	Metallic reductants	Ambient to moderate temperature	Removal of interfering metals	Limited selectivity
Crystallization/refining	Thermal and solution purification	Variable	High-purity production	GeO ₂ Multi-stage purification required

Table 3 demonstrates that hydrometallurgical processing offers high flexibility for germanium recovery but also reveals the strong dependence of process performance on impurity management and downstream purification efficiency.

Final recovery stages generally target either the production of germanium dioxide or of metallic germanium. GeO_2 is typically obtained through precipitation, hydrolysis, or controlled thermal conversion of purified germanium-bearing solutions. Metallic germanium production requires additional reduction and refining stages, often involving hydrogen reduction and zone refining operations to achieve semiconductor-grade purity (Huang et al., 2025). The removal of refractory impurities such as Al, Si, B, and P remains particularly difficult because several of these elements exhibit segregation coefficients close to unity during refining processes (Wu et al., 2024).

The overall hydrometallurgical processing sequence for germanium recovery is illustrated in Figure 4.

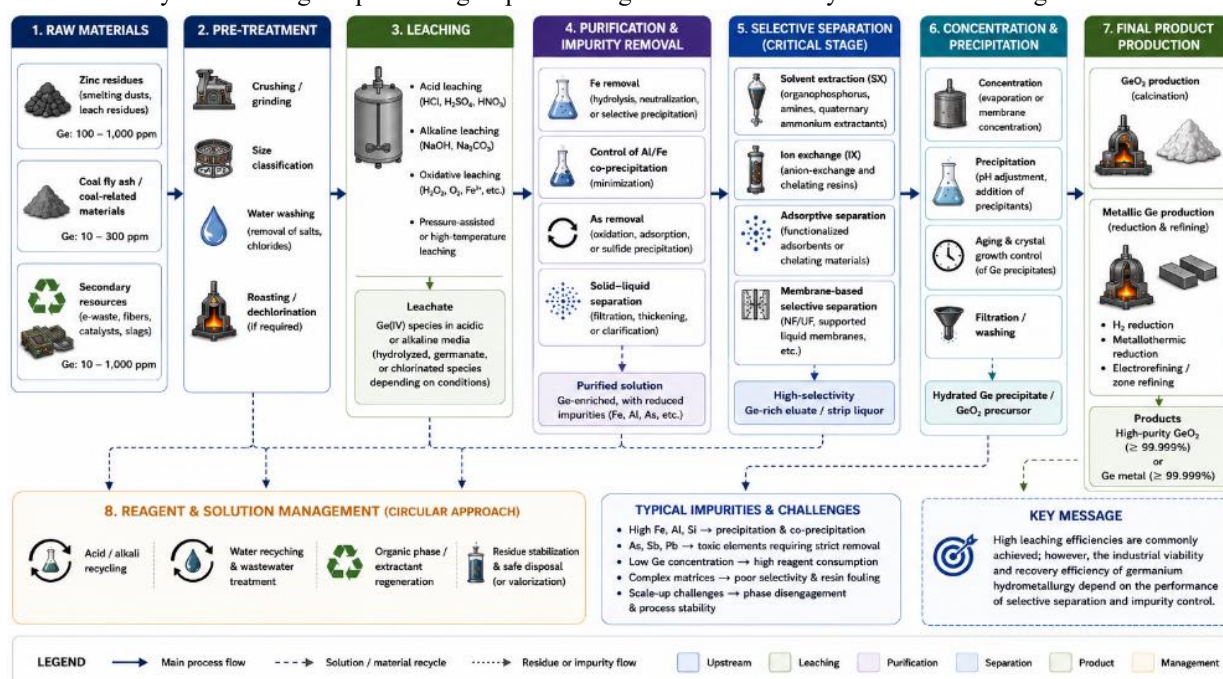


Figure 4. General hydrometallurgical processing flowsheet for germanium recovery from zinc residues, coal fly ash, and secondary resources, including leaching, purification, selective separation, and final GeO_2 /metallic Ge production stages. Adapted from Bai et al. (2025), Jiang et al. (2023), Lan et al. (2024), and Wu et al. (2025).

Figure 4 highlights that industrial germanium hydrometallurgy is fundamentally governed by the efficiency of selective separation rather than by dissolution performance alone. The flowsheet also illustrates the central role of impurity control in determining process complexity, reagent consumption, and final product purity.

The strong dependence of hydrometallurgical performance on impurity behavior explains why selective purification stages frequently dominate both operating cost and process complexity in industrial germanium recovery systems.

6. SELECTIVE SEPARATION TECHNOLOGIES

Selective separation is the main challenge in germanium processing because Ge is typically present at low concentrations in complex solutions containing large excesses of elements such as Zn, Fe, Si, Al, Pb, Cu, and As. In many industrial systems, germanium levels are measured in ppm, while impurity levels can be much higher. Therefore, separation technologies need high selectivity, chemical stability, robustness, and economic viability in aggressive conditions (Chen et al., 2025; Wei et al., 2024).

Unlike the initial dissolution stage, which frequently achieves extraction efficiencies above 90% under optimized conditions, downstream purification and selective recovery remain substantially more difficult. The industrial bottleneck is therefore not the leaching of germanium itself, but rather the selective separation of Ge from multicomponent process liquors generated during zinc metallurgy, coal fly ash processing, and secondary resource recycling (Aghazadeh et al., 2016).



Solvent extraction remains the most established industrial selective separation technology for germanium recovery. Chloride media are preferred because germanium forms stable chloro-complexes under acidic conditions, facilitating extraction into amine-based organic phases.

Industrial solvent extraction performance is strongly influenced by solution chemistry. Parameters such as acidity, chloride concentration, oxidation state, extractant loading, and impurity concentration directly affect extraction selectivity and stripping efficiency. In zinc hydrometallurgical liquors, Fe and Zn frequently compete with Ge for active extraction sites or modify aqueous speciation equilibria, thereby reducing separation efficiency (Peng et al., 2024). Silicon introduces additional operational instability because colloidal silica may stabilize emulsions, increase phase entrainment, and impair phase disengagement during continuous SX operation.

Under optimized conditions, conventional solvent extraction systems may achieve germanium extraction efficiencies exceeding 90%. Nevertheless, industrial operation remains constrained by organic degradation, extractant aging, entrainment losses, and stripping limitations (Drzazga et al., 2021). Furthermore, many laboratory-scale studies employ simplified synthetic solutions that do not adequately reproduce the impurity complexity observed in industrial zinc residues or coal-derived leachates.

Ion exchange technologies are mature options for selective germanium recovery, especially in dilute streams. Since the 1950s, studies have shown germanate species strongly adsorb on strongly basic anion-exchange resins (Everest & Salmon, 1954). Today, modern systems use chelating resins and functionalized sorbents to enhance selectivity amid complex hydrometallurgical conditions (Drzazga et al., 2024a).

Chelating resins have significant industrial potential as they work well in dilute systems where solvent extraction is less economical. They also offer lower solvent losses, reduced fire risk, and simpler operation than large-scale SX circuits. However, issues like resin fouling, competitive adsorption, capacity decline, and regeneration remain challenges, especially with liquors high in Fe, Si, or solids (Zhong et al., 2026).

Membrane-assisted separation systems and non-dispersive extraction technologies have also received increasing industrial attention. These systems are particularly attractive for low-concentration liquors because they may reduce solvent losses and improve mass transfer control compared with conventional extraction circuits. However, membrane fouling, long-term chemical stability, and operational durability under acidic chloride conditions remain significant industrial challenges (Zhou et al., 2025).

The comparative performance of the principal industrially mature selective separation technologies used for germanium recovery is summarized in Table 4.

Table 4. Comparative performance of selective separation technologies for germanium recovery and purification. Adapted from Everest and Salmon (1954), Jiang et al. (2023), Peng et al. (2024), Vereycken et al. (2022a), and Zhong et al. (2026).

Technology	Main Mechanism	Typical Ge Recovery	Main Advantages	Main Limitations	Industrial Potential
Solvent extraction	Organic phase transfer	80–98%	High extraction efficiency	Organic degradation and entrainment	High
Ion exchange	Selective adsorption	70–95%	Suitable for dilute solutions	Resin fouling and saturation	Very high
Chelating resins	Functional group complexation	80–97%	High selectivity in complex media	Regeneration requirements	Very high
Quaternary ammonium systems	Chloro-complex extraction	90–99%	Strong Ge affinity	Chloride dependence	High
Membrane extraction	Non-dispersive mass transfer	70–95%	Reduced solvent loss	Membrane fouling	Moderate

Table 4 demonstrates that no single technology simultaneously satisfies all industrial requirements related to selectivity, operational simplicity, reagent stability, impurity tolerance, and economic performance. In industrial practice, hybrid flowsheets combining multiple purification stages are often necessary to achieve high-purity GeO₂ or semiconductor-grade metallic germanium.

A schematic representation of the principal industrially mature selective separation technologies used in germanium hydrometallurgy is shown in Figure 5.

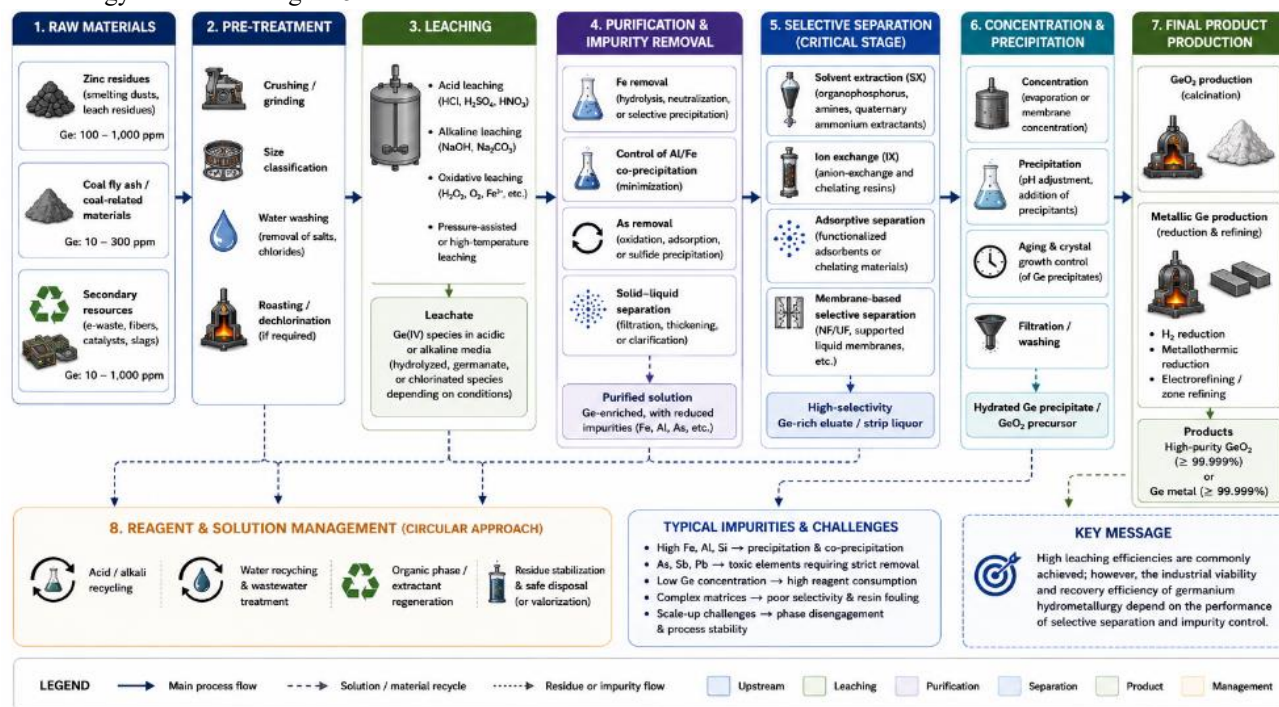


Figure 5. Main industrially mature selective separation technologies used in germanium recovery systems include solvent extraction, ion exchange, chelating resins, and membrane-assisted separation routes. Adapted from Jiang et al. (2023), Peng et al. (2024), Vereycken et al. (2022a), and Zhong et al. (2026).

The schematic presented in Figure 5 illustrates the strong dependence of industrial germanium recovery on downstream purification efficiency and impurity rejection. It also demonstrates that industrial advances in germanium metallurgy are currently driven more by improvements in selective separation performance than by increases in dissolution efficiency alone (Drzazga et al., 2024b).

Although solvent extraction, ion exchange, and chelating resins are the most mature for germanium recovery, recent research focuses on emerging systems to improve selectivity, reduce solvent losses, and treat heterogeneous secondary resources. These technologies are discussed next.

7. EMERGING AND ADVANCED TECHNOLOGIES

The rising importance of germanium drives the development of new recovery technologies that improve selectivity, reduce environmental impact, and enable the treatment of complex secondary resources. Most advanced systems are still in laboratory or pilot stages with low technology readiness levels (TRLs). While some show promising results in controlled experiments, industrial validation remains limited (Ingraham et al., 2026).

A major driving force behind the development of advanced technologies is the increasing difficulty associated with conventional germanium processing. Low Ge concentrations, extreme impurity complexity, silica-rich matrices, and highly diluted process streams continue to limit the efficiency of traditional solvent extraction and precipitation systems. Consequently, recent research has increasingly focused on intensified extraction systems, advanced solvents, electrochemical separation, engineered adsorbents, and data-driven process optimization strategies.

Ionic liquids (ILs) are widely studied for germanium separation due to their tunable properties, low vapor pressure, and affinity for metal chloro-complexes. Phosphonium and ammonium ILs show high efficiency in recovering germanium from zinc



liquors, coal fly ash, optical fibers, and e-waste (Fan et al., 2025; Vereycken et al., 2022a). Lab studies report Ge extraction above 95% under optimized chloride conditions.

Despite these promising results, ionic liquid systems still face substantial industrial limitations. High viscosity may impair mixing efficiency and mass transfer kinetics, while solvent cost and long-term chemical stability remain major concerns. In addition, many experimental studies employ simplified synthetic solutions that do not adequately represent the impurity complexity of industrial leachates containing Fe, Zn, As, Al, and Si. As a result, the practical scalability of many IL-based systems remains uncertain (Zheng et al., 2023).

Deep eutectic solvents (DES) have emerged as lower-cost alternatives to conventional ionic liquids. DES systems generally exhibit lower toxicity, easier synthesis, and improved environmental compatibility while maintaining favorable extraction properties for strategic metals. Preliminary studies suggest that DES systems may improve the selectivity of Ge chloro-complex extraction while reducing organic solvent losses relative to conventional SX systems (Kumar et al., 2025). However, DES technologies remain in an early stage of development, and important operational issues involving viscosity, phase separation, solvent regeneration, and long-term stability remain unresolved (Hartzell & Moats, 2023).

One important limitation common to both ionic liquids and DES systems is the lack of a comprehensive techno-economic evaluation. Many studies emphasize extraction efficiency while neglecting solvent degradation, solvent recyclability, impurity accumulation, stripping behavior, and long-term operational stability. Consequently, reported laboratory-scale performance frequently overestimates industrial applicability (Pereira, 2026a).

Process intensification technologies have also received increasing attention in germanium hydrometallurgy. Ultrasound-assisted extraction systems are among the main intensified approaches investigated in recent years. Ultrasonic cavitation enhances local turbulence, particle fragmentation, and mass transfer, thereby accelerating dissolution kinetics and precipitation reactions (Di et al., 2024). Some studies involving ultrasound-enhanced extraction with N235 extractants and intensified tannin precipitation routes reported faster kinetics and improved Ge separation efficiency compared with conventional systems (Peng et al., 2024).

Combined ultrasonic-microwave systems have also been proposed for refractory Ge-bearing materials. These hybrid systems may improve dissolution efficiency through localized heating and intensified solid-liquid interaction. Nevertheless, scale-up remains highly uncertain because cavitation intensity distribution, energy efficiency, and reactor control become increasingly difficult in large industrial systems (Pereira, 2026b). In many cases, energy demand and equipment complexity may offset the kinetic advantages observed at the laboratory scale.

Electrochemical recovery technologies represent another promising direction for advanced germanium processing. Electrochemical systems may enable selective recovery under comparatively mild operating conditions while reducing reagent consumption and secondary waste generation. Recent investigations involving integrated electrochemical separation have demonstrated promising selectivity in the recovery of Ge from highly diluted secondary resources (Roy et al., 2025). However, current efficiency, electrode degradation, electrolyte management, and energy consumption remain important technical barriers to industrial deployment.

Advanced nanostructured sorbents are studied for germanium separation, with functional nanoparticles, hybrid oxides, and surface chemistries improving selectivity and transfer. However, regeneration, cost, durability, and resistance in industrial settings are unclear, so most systems are still not industry-ready despite promising lab results.

Artificial intelligence (AI) and data-driven optimization tools are also emerging in germanium recovery research. Machine learning models have been applied to optimize leaching conditions, predict extraction behavior, and identify key variables controlling selective recovery (Geng et al., 2025). These approaches may substantially reduce experimental workload and accelerate process optimization in highly multivariable systems. However, most currently available models are still based on limited laboratory datasets and remain poorly validated for industrial operation involving variable feed composition and complex impurity interactions.

Recent research explores hybrid systems that combine multiple technologies, such as electrochemical-assisted extraction, ultrasound-assisted ion exchange, membrane systems, and pyro-hydrometallurgical routes. While these can improve selectivity and reduce limitations, they often increase CAPEX and operational instability.

The principal emerging and advanced technologies currently investigated for germanium recovery are summarized in Table 5.

Table 5. Emerging and advanced technologies are being investigated for the recovery and purification of germanium. Adapted from Di et al. (2024), Fan et al. (2025), Kumar et al. (2025), Peng et al. (2024), Roy et al. (2025), and Vereycken et al. (2022a).

Technology	Main Principle	Typical Advantages	Main Limitations	Estimated TRL
Ionic liquids	Selective metal complex extraction	High selectivity and low volatility	High viscosity and cost	3–5
Deep eutectic solvents (DES)	Alternative selective solvent systems	Lower toxicity and cost	Stability and recycling issues	2–4
Ultrasound-assisted extraction	Cavitation-enhanced mass transfer	Faster kinetics	Scale-up uncertainty	3–5
Ultrasonic-microwave systems	Combined thermal and cavitation intensification	Enhanced dissolution efficiency	Energy demand and reactor complexity	2–4
Electrochemical recovery	Electrochemical deposition/separation	Reduced reagent consumption	Electrode stability and energy cost	3–5
Nanostructured adsorbents	High-surface-area adsorption	Improved adsorption capacity	Regeneration limitations	2–4
AI-assisted optimization	Data-driven process optimization	Reduced experimental workload	Limited industrial datasets	2–3

Table 5 shows that most advanced germanium recovery technologies are still at the lab or pilot scale. Despite high extraction efficiencies and promising selectivity, industrial use is limited by poor process integration, uncertain stability, limited data on continuous operation, and a lack of robust techno-economic assessments.

A comparative overview of the principal emerging technologies and their approximate technology readiness levels is illustrated in Figure 6.

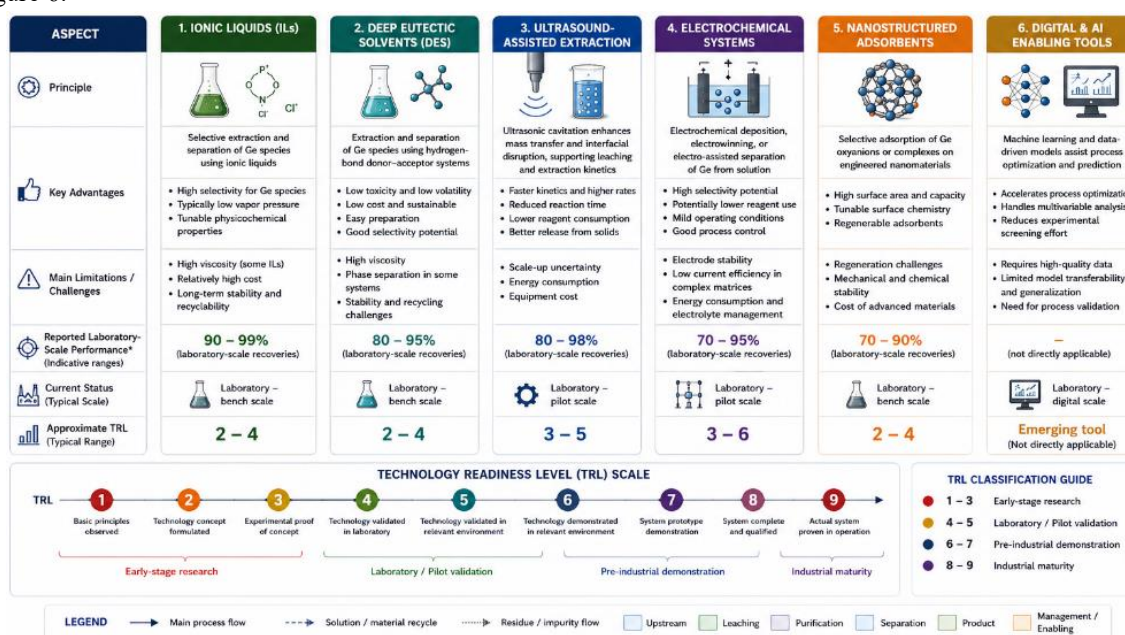


Figure 6. Comparative overview of emerging germanium recovery technologies, including ionic liquids, DES systems, ultrasound-assisted extraction, electrochemical recovery, nanostructured adsorbents, and AI-assisted optimization, with approximate technology readiness level (TRL) comparison. Adapted from Fan et al. (2025), Kumar et al. (2025), Peng et al. (2024), Roy et al. (2025), and Vereycken et al. (2022a).



The framework presented in Figure 6 highlights the substantial gap between laboratory-scale extraction performance and industrial implementation for most advanced germanium recovery technologies. It also demonstrates that future industrial adoption will depend not only on extraction selectivity but also on solvent recyclability, long-term stability, impurity tolerance, energy efficiency, and overall CAPEX/OPEX performance.

8. INTEGRATED PROCESSING FLOWSHEETS

The economic viability of germanium recovery is strongly dependent on process integration. Because Ge is rarely mined as a primary product and generally occurs at ppm to low wt.% levels, isolated recovery operations are seldom economically sustainable. Industrial germanium production, therefore, relies on integrated processing flowsheets that combine pyrometallurgical concentration, hydrometallurgical extraction, and multi-metal recovery strategies within larger metallurgical or recycling infrastructures (Meshram & Abhilash, 2022).

Most germanium recovery systems in industry are tied to zinc metallurgy, with Ge concentrating in residues, dusts, or process liquors from roasting, smelting, and refining. These recovery methods are usually auxiliary, integrated into zinc plants rather than standalone operations.

Integrated pyro-hydrometallurgical flowsheets are crucial for low-grade or refractory germanium materials. Pyrometallurgical stages promote Ge enrichment via volatilization, chlorination, or phase transfer; downstream hydrometallurgy performs dissolution and purification (Li et al., 2025). This hybrid approach boosts efficiency by reducing bulk and concentrating germanium for selective treatment.

Coal fly ash and lignite resources have spurred the development of integrated processing routes. Germanium in coal may become concentrated during combustion or gasification, producing residues with much higher Ge levels than the original material (Rudnik, 2025). Integrated processes that use thermal enrichment, leaching, extraction, and purification are promising approaches for unconventional germanium sources.

Recent studies highlight the importance of multi-metal recovery. Germanium materials often contain gallium, indium, zinc, scandium, and rare earth metals, which can boost process economics if recovered together (Roy et al., 2025). Therefore, modern flowsheets focus on combined recovery systems over isolated germanium extraction.

In zinc residues and metallurgical slags, for example, the economic value of Zn recovery may exceed the value associated with germanium itself. Similarly, electronic waste and urban mining residues often contain multiple strategic metals whose combined recovery is necessary to justify the costs of industrial processing (Pereira, 2026c). This multi-metal approach also improves material efficiency and supports circular economy strategies aimed at reducing waste generation and dependence on primary mineral extraction.

Germanium recovery in electronic waste recycling has grown, especially from optical fibers, infrared devices, semiconductors, and photovoltaic materials, which often have higher Ge concentrations than primary ores (Yadav et al., 2026). However, variability, low standardization, and impurities hinder large-scale use.

Circular industrial integration is a key goal for future germanium supply chains. Recycling systems that combine primary resources, residues, wastes, and electronic scrap can enhance supply security and reduce geopolitical risks associated with concentrated Ge production (Umbach, 2024). However, effective implementation requires strong links among metallurgical processes, waste management, and advanced separation technologies.

The principal integrated processing strategies currently investigated for germanium recovery are summarized in Table 6.

Table 6. Main integrated processing flowsheets for germanium recovery from primary and secondary resources. Adapted from Hu et al. (2025), Li et al. (2025), Roy et al. (2025), Teng et al. (2025), and Yadav et al. (2026).

Integrated Route	Main Feed Materials	Main Integration Strategy	Main Advantages	Main Limitations
Zn smelting + hydrometallurgy	Zinc concentrates, Zn residues	Pyro concentration + hydro purification	Existing industrial infrastructure	Ge recovery depends on Zn production
Coal combustion + Ge recovery	Coal fly ash, lignite residues	Thermal enrichment + selective extraction	Secondary resource valorization	Highly variable feed composition

Multi-metal recovery systems	Slags, dusts, polymetallic residues	Simultaneous recovery of Ge, Ga, In, Zn	Improved economics	Complex separation chemistry
E-waste recycling integration	Optical fibers, semiconductors	Urban mining + advanced purification	High local Ge concentration	Material heterogeneity
Circular recycling	Mixed industrial residues	Combined primary-secondary processing	Improved resource sustainability	High process integration complexity

Table 6 demonstrates that integrated processing significantly improves the economic feasibility of germanium recovery, as the value generated by associated metals and existing industrial infrastructure often exceeds that of Ge alone.

An integrated flowsheet illustrating the principal industrial pathways for germanium recovery from zinc plants, coal fly ash, and electronic waste is presented in Figure 7.

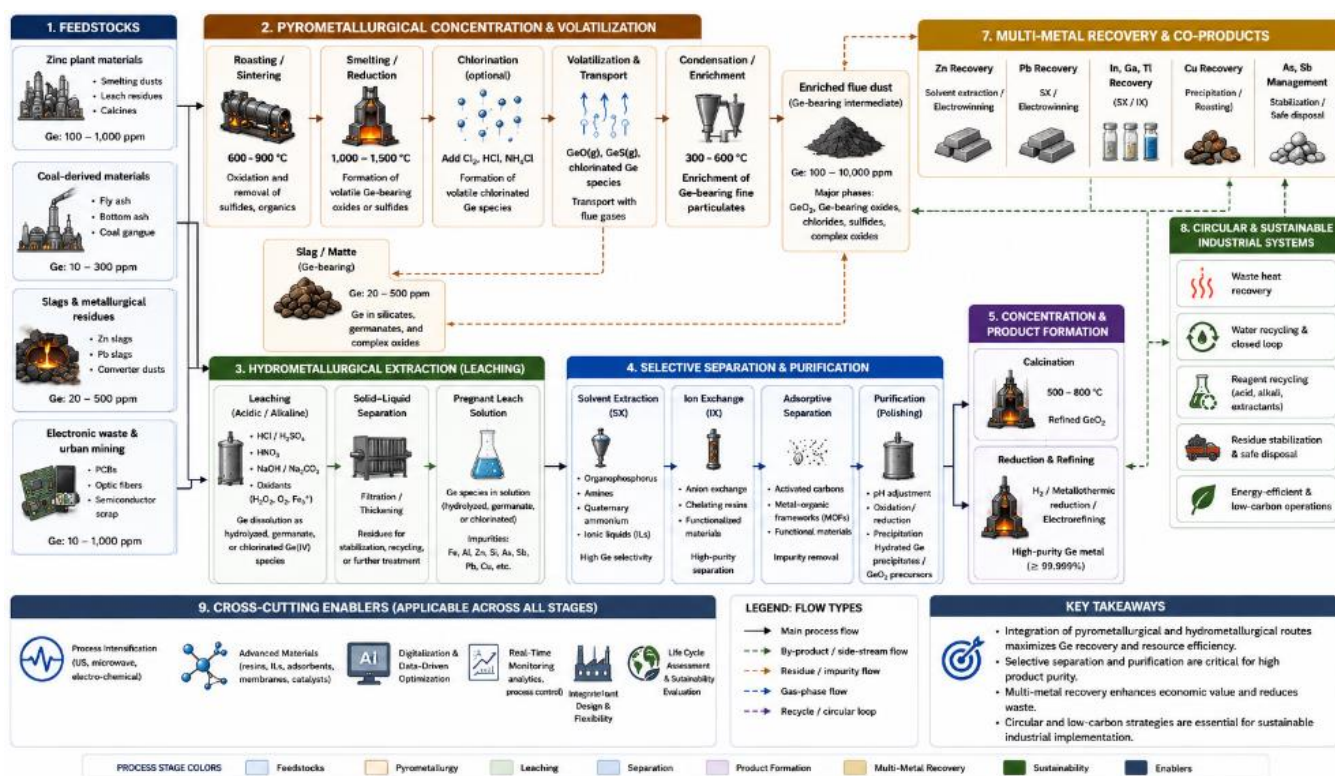


Figure 7. Integrated processing flowsheet for germanium recovery from primary and secondary resources, combining pyrometallurgical concentration, hydrometallurgical extraction, selective separation, and multi-metal recovery strategies. Adapted from Hu et al. (2025), Li et al. (2025), Roy et al. (2025), and Teng et al. (2025).

Figure 7 highlights the strong interdependence between germanium recovery and broader metallurgical processing chains. The figure also illustrates that future industrial viability will increasingly depend on hybrid flowsheets that integrate zinc metallurgy, coal-derived residues, electronic waste recycling, and multi-metal recovery within circular industrial systems.

9. KEY CONTROLLING FACTORS IN GERMANIUM RECOVERY

Germanium recovery is governed by a complex interaction between mineralogical occurrence, chemical speciation, impurity behavior, and process thermodynamics. Although the initial Ge concentration strongly influences process economics, recovery efficiency is frequently controlled more by solution chemistry and impurity interactions than by the original mineralogical



composition of the feed material (Jiang et al., 2023). This effect becomes particularly critical in low-grade systems where Ge concentrations are often below several hundred ppm.

The occurrence state of germanium varies substantially among ores, fly ash, slags, dusts, and secondary residues. In zinc-related materials, Ge is commonly associated with sphalerite and may substitute for Zn within sulfide structures. In coal and lignite-derived materials, germanium frequently occurs in dispersed forms associated with silicates, aluminosilicates, or organic matter (Bo et al., 2024). These differences strongly affect leaching behavior, volatilization efficiency, and downstream separation performance.

Mineralogy influences not only dissolution kinetics but also the distribution of germanium during thermal processing. Several studies have shown that Ge may partition into slags, flue dusts, condensed phases, or volatile streams depending on temperature, oxygen potential, sulfur activity, and chlorination conditions (Tang et al., 2025). Under oxidizing conditions, Ge may form GeO_2 , whereas chlorinating systems favor the formation of volatile GeCl_4 , which is significantly more volatile and easier to separate downstream.

Despite the importance of mineralogy, solution chemistry frequently becomes the dominant controlling factor during hydrometallurgical processing. Germanium exhibits complex aqueous speciation behavior that changes substantially with pH, redox conditions, chloride concentration, sulfate activity, and the presence of complexing agents (Everest & Salmon, 1954). These speciation changes directly affect solvent extraction efficiency, ion exchange selectivity, precipitation behavior, and adsorption performance.

The interference from iron and silicon is one of the most important industrial challenges in germanium hydrometallurgy. Silicon may form stable silicate or colloidal species that reduce germanium selectivity and complicate downstream purification operations (Bai et al., 2025). In highly acidic zinc leach solutions, silica gel formation may also increase solution viscosity and impair filtration and phase separation processes.

Iron introduces additional complications because Fe^{3+} hydrolysis may consume acid, promote coprecipitation, and alter the speciation of germanium. Furthermore, ferric iron may interfere with extraction equilibria in solvent extraction systems and reduce resin selectivity in ion exchange operations (Xu et al., 2024). The simultaneous presence of Fe, Zn, As, and Si therefore creates highly competitive chemical environments that significantly reduce the efficiency of selective Ge recovery.

Arsenic-containing systems present additional operational challenges due to toxicity, environmental restrictions, and complex precipitation behavior. Germanium may partially associate with arsenic-bearing phases during precipitation or thermal processing, reducing recovery efficiency and increasing purification requirements. Similar effects are observed in polymetallic zinc residues containing high concentrations of Pb, Cd, Cu, and Sb.

The influence of impurity concentration becomes particularly severe in dilute systems. In many industrial leachates, germanium concentrations are typically below 100–500 mg/L, while zinc and iron concentrations may exceed several tens of grams per liter (Jiang et al., 2023). Under these conditions, minor variations in pH, chloride concentration, extractant loading, or redox conditions may strongly affect Ge selectivity and process stability.

Thermodynamic control also plays a decisive role in pyrometallurgical and hybrid systems. Germanium volatilization depends strongly on temperature, gas composition, chlorination potential, and oxygen partial pressure (Liu et al., 2025). Insufficient control of these parameters may cause substantial Ge losses into slags or off-gas streams. Conversely, excessive volatilization may increase operational complexity and dust handling requirements.

In zinc hydrometallurgical circuits, Ge behavior is strongly tied to the operational conditions of the Zn process. Variations in acid concentration, oxidation conditions, neutralization stages, and residue recycling can alter germanium distribution throughout the circuit (Zhou et al., 2025). As a result, germanium recovery often becomes a secondary optimization problem within larger zinc production systems rather than an independent metallurgical objective.

The principal physicochemical factors controlling germanium recovery efficiency are summarized in Table 7.

Table 7. Main controlling factors affecting germanium recovery efficiency in pyrometallurgical and hydrometallurgical systems. Adapted from Bai et al. (2025), Everest and Salmon (1954), Jiang et al. (2023), Tang et al. (2025), and Xu et al. (2024).

Controlling Factor	Main Effect on Ge Recovery	Typical Industrial Impact
Initial Ge concentration	Controls economic viability	Low-grade systems require highly selective separation
Mineralogical occurrence	Influences dissolution and volatilization	Different behavior in sulfides, silicates, and fly ash
Solution pH	Alters Ge aqueous speciation	Affects extraction and precipitation efficiency
Chloride concentration	Promotes Ge complex formation	Enhances GeCl ₄ formation and SX performance
Iron concentration	Causes competitive reactions and coprecipitation	Reduces selectivity and increases reagent consumption
Silicon concentration	Forms colloidal species and silica gels	Impairs filtration and purification
Temperature	Controls dissolution and volatilization kinetics	Affects Ge partitioning between phases
Redox conditions	Alters oxidation state and phase stability	Influences extraction and precipitation behavior

Table 7 demonstrates that germanium recovery is controlled by strongly coupled physicochemical parameters rather than by a single dominant mechanism. In most industrial systems, the interaction between impurities and solution chemistry ultimately determines process selectivity and operational stability.

A schematic representation of the principal factors controlling germanium recovery efficiency is presented in Figure 8.

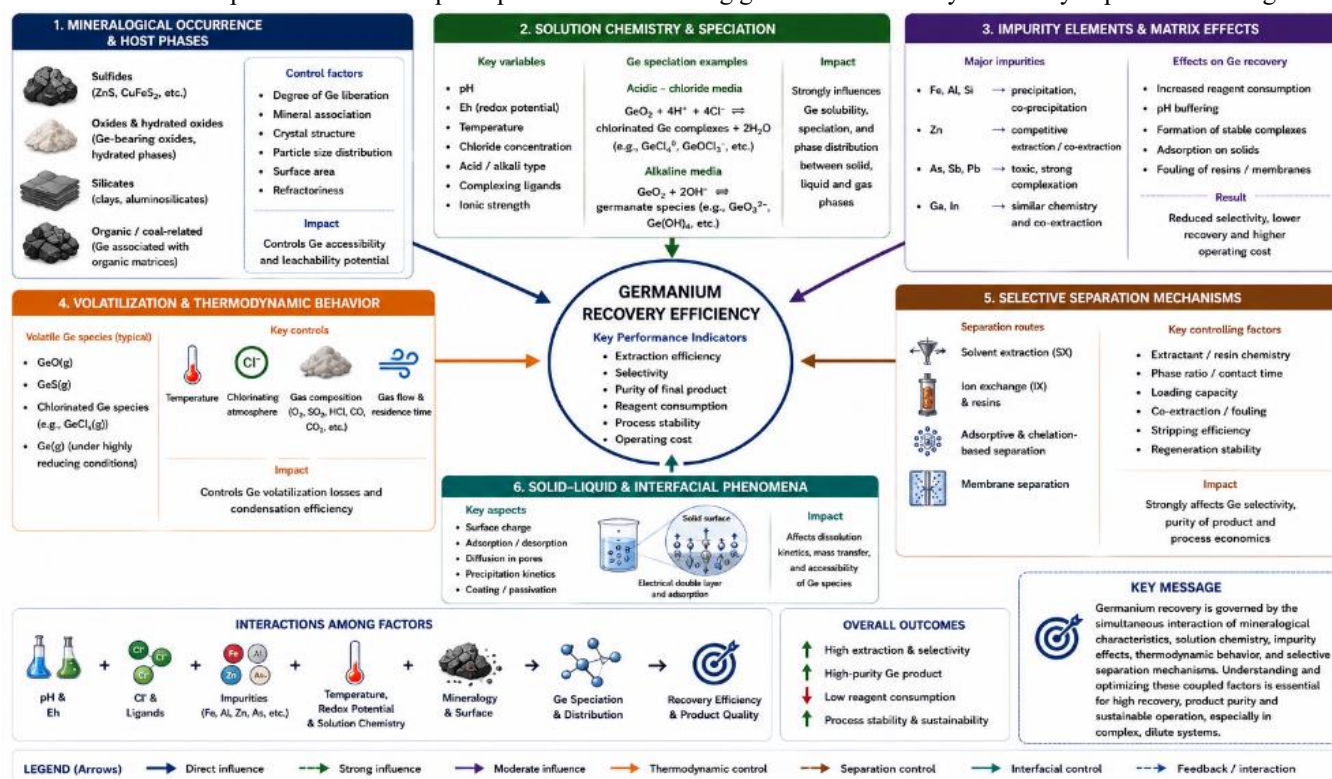


Figure 8. Main physicochemical factors controlling germanium recovery efficiency, including mineralogical occurrence, solution chemistry, impurity interactions, volatilization behavior, and selective separation mechanisms. Adapted from Bai et al. (2025), Jiang et al. (2023), Tang et al. (2025), and Xu et al. (2024).



Figure 8 shows that germanium recovery depends on thermodynamic, mineralogical, and hydrometallurgical factors. It also shows that solution chemistry often controls process performance more than Ge concentration or mineral source, especially in dilute industrial systems.

10. ENVIRONMENTAL AND ECONOMIC ASSESSMENT

The environmental and economic performance of germanium recovery routes is vital due to Ge's role in semiconductors, photovoltaics, infrared, and optical uses. Though classified as critical raw material, recovery mainly relies on secondary extraction from zinc, coal residues, and metallurgical waste (Haghighi & Irannajad, 2022). Therefore, Ge's environmental footprint and cost-effectiveness depend more on large industrial systems than dedicated production facilities.

A key environmental issue in germanium recovery is the production of acidic, metal-rich effluents. Hydrometallurgical processes use sulfuric and hydrochloric acids, alkaline reagents, oxidants, and organic extractants, creating waste with Zn, Fe, As, Pb, Cd, and chlorides or sulfates (Rudnik, 2025). Treating these streams raises costs and environmental risks, especially in low-grade systems where large volumes are processed for small Ge quantities.

Arsenic management represents a particularly critical issue in zinc residues, flue dusts, and polymetallic secondary materials. In several zinc hydrometallurgical circuits, arsenic concentrations may reach levels that require stabilization before final disposal. The simultaneous presence of Ge and As often complicates purification operations because both elements may partially coprecipitate or behave similarly during solvent extraction and adsorption processes (Nakhaei et al., 2025). Consequently, selective separation stages become essential not only for metal recovery but also for environmental compliance.

Coal fly ash and lignite materials pose environmental challenges, containing sulfur, heavy metals, and particulates that need dust control and stabilization. Pyrometallurgical Ge enrichment produces secondary dusts and emissions with chlorides, sulfur, and metals (Rudnik, 2025). Without effective gas cleaning, Ge loss and environmental contamination are likely.

Energy consumption also constitutes a major operational concern. Pyrometallurgical routes involving chlorination, volatilization, or thermal upgrading frequently operate above 800–1100 °C, resulting in high energy demand and elevated CO₂ emissions. Although these routes may improve Ge concentration and facilitate downstream separation, their environmental performance depends strongly on energy source, process integration, and heat recovery efficiency (Van Hoof et al., 2020).

Hydrometallurgical systems usually use less direct energy than pyrometallurgical processes but often need more reagents and purification steps. Methods like solvent extraction, ion exchange, and crystallization can raise chemical use and wastewater. Their environmental benefit depends on reagent recycling and waste reduction, not just lower temperatures.

Despite numerous studies on Ge recovery, few include full techno-economic evaluations. Laboratory studies often report 90–95% extraction efficiency but omit key industrial factors like solvent degradation, extractant losses, impurities, energy use, residue management, and corrosion. This gap limits understanding of industrial feasibility.

The economic sustainability of germanium recovery is strongly influenced by its status as a by-product metal. In most industrial operations, Ge recovery is economically viable only when integrated with larger zinc, coal, or multi-metal processing facilities. Standalone germanium recovery plants are rare because Ge concentrations in primary or secondary resources are generally too low to support independent processing infrastructure (Robla et al., 2024).

Capital expenditure (CAPEX) often includes gas cleaning, residue treatment, solvent extraction, and purification. Operational expenditure (OPEX) mainly depends on reagent use, energy, wastewater treatment, and solvent replacement. Selective separation stages usually contribute most to operating costs, as Ge occurs in dilute solutions with excess Zn, Fe, and Si impurities.

Recent sustainability studies have demonstrated that secondary germanium production may significantly reduce environmental impacts compared with primary extraction routes. Life cycle assessment analyses indicate that Ge recovery from recycled materials and industrial residues may substantially reduce CO₂ emissions and resource depletion compared with coal-derived Ge production (Van Hoof et al., 2020). However, these benefits depend on collection efficiency, impurity management, and process integration within circular economy frameworks.

Urban mining and electronic waste recycling are increasingly considered strategic alternatives for future Ge supply. Nevertheless, the large compositional variability of electronic residues, combined with low Ge concentration and difficult liberation behavior, still limits industrial-scale implementation (Ondrák Fialová et al., 2023). Similar challenges are observed in photovoltaic waste recycling, where selective recovery of Ge from complex multilayer systems remains technologically demanding.

The principal environmental and economic characteristics of the main germanium recovery routes are summarized in Table 8.

Table 8. Environmental and economic comparison of major germanium recovery routes. Adapted from Haghghi and Irannajad (2022), Rudnik (2025), Srivastava and Ilyas (2025), Van Hoof et al. (2020), and Yadav et al. (2026).

Recovery Route	Main Feed Material	Main Environmental Concerns	Relative Energy Demand	Main Economic Limitation	General Industrial Viability
Zinc hydrometallurgy	Zinc leach residues and dusts	Acidic effluents, arsenic disposal	Moderate	Complex purification stages	High
Coal fly ash processing	Fly ash and lignite residues	Dust emissions, residue stabilization	High	Low Ge concentration	Moderate
Pyrometallurgical volatilization	Slags, dusts, lignite	Gas emissions, volatilization losses	High	Energy consumption	Moderate
E-waste recycling	Optical fibers, semiconductors	Complex multi-material residues	Moderate	Feed variability	Emerging
Ionic liquid systems	Secondary leachates	Solvent stability and disposal	Low–moderate	High solvent cost	Low–moderate
Integrated pyro–hydro routes	Mixed secondary resources	Multi-stream waste management	High	CAPEX complexity	High

Table 8 shows no recovery route achieves high selectivity, low environmental impact, and low cost simultaneously. Successful systems rely on process integration, multi-metal recovery, and infrastructure sharing with larger metallurgical operations.

Environmental and economic limits in current Ge recovery methods show literature inconsistency. Many studies focus on extraction efficiency but ignore energy balance, solvent recyclability, residue management, and purification costs. As a result, lab recoveries often overestimate industrial potential. Figure 9 presents a conceptual overview of how environmental burden, process complexity, and economic viability relate in germanium recovery systems.



Figure 9. Relationship between process complexity, environmental burden, selectivity, and economic viability in major germanium recovery routes. Adapted from Srivastava and Ilyas (2025), Van Hoof et al. (2020), Wong et al. (2025), and Yadav et al. (2026).



Figure 9 highlights that increasing recovery selectivity frequently requires additional purification stages, which simultaneously increase energy demand, reagent consumption, and waste generation. Consequently, the long-term sustainability of germanium production will likely depend on integrated flowsheets that combine selective recovery with effective waste minimization and circular-economy strategies.

11. CIRCULAR ECONOMY AND CRITICAL GAPS

The growing strategic importance of germanium has intensified interest in circular-economy approaches that reduce dependence on primary mining and improve long-term supply security. Because Ge is rarely mined as a primary commodity, its future availability will depend increasingly on the efficient recovery of secondary resources, including zinc residues, coal fly ash, metallurgical slags, optical fibers, photovoltaic waste, and electronic scrap (Srivastava & Ilyas, 2025). This transition is particularly important in the context of expanding semiconductor, infrared, fiber-optic, and renewable-energy industries, which continue to drive global Ge demand (Serpe et al., 2025).

Urban mining has emerged as one of the most promising alternatives for future Ge supply. Electronic waste frequently contains locally enriched germanium concentrations that may exceed those in many natural ores (Helbig et al., 2024). Optical fibers, infrared optics, semiconductor devices, and photovoltaic materials represent important secondary reservoirs of Ge, especially in highly industrialized economies with large electronic waste generation rates (Yandem & Jabłońska-Czapla, 2024).

Despite increasing interest in electronic waste recycling, industrial implementation remains limited. The complex composition of e-waste, low overall Ge concentration, heterogeneous material distribution, and difficult liberation behavior continue to hinder large-scale recovery. In many cases, germanium is present in multilayer assemblies or highly dispersed phases that require intensive pre-treatment before selective extraction becomes possible (Yadav et al., 2026).

Industrial integration is a key aspect of circular Ge recovery. It involves incorporating germanium recovery into existing zinc smelting, coal processing, or multi-metal plants rather than building new facilities. This lowers costs and enhances economic viability by sharing infrastructure like utilities, residue treatment, gas cleaning, and hydrometallurgical units (Umbach, 2024).

Integrated recovery systems also enable the simultaneous extraction of multiple critical metals, including Ga, In, Ge, REEs, and Zn. Multi-metal recovery strategies are increasingly important because isolating germanium alone is often economically insufficient to justify large-scale investment. Consequently, future Ge recovery systems will likely evolve toward complex, integrated metallurgical platforms rather than single-metal processes.

Despite progress in laboratory research, critical technological gaps remain, mainly due to the lack of reliable industrial data. Most studies are limited to controlled lab experiments with synthetic solutions or simplified feeds, leaving the practical behavior of many extraction systems in industrial settings uncertain.

Another major limitation is the lack of methodological standardization. Recovery efficiency, selectivity, purity, solvent stability, and energy consumption are often reported using different experimental conditions and inconsistent performance metrics. In many studies, extraction efficiency is emphasized without detailed analysis of impurity accumulation, solvent degradation, residue generation, or long-term operational stability.

The scarcity of complete mass and energy balances also represents a critical weakness in the literature. Numerous studies report high Ge extraction efficiencies while omitting essential industrial parameters such as reagent recycling, wastewater treatment, gas handling requirements, solvent losses, and purification costs. This omission frequently leads to unrealistic projections regarding industrial feasibility.

Pilot-scale validation remains particularly limited. Although several emerging technologies such as ionic liquids, deep eutectic solvents (DES), ultrasound-assisted extraction, electrochemical recovery, and advanced adsorbents demonstrate promising laboratory performance, very few studies evaluate process scalability, continuous operation, or long-term chemical stability. Consequently, the technology readiness level (TRL) of many advanced Ge recovery systems remains low despite impressive laboratory-scale recoveries.

A further challenge involves the disconnect between laboratory optimization and industrial operation. Many experimental systems are designed to maximize extraction efficiency under idealized conditions without considering industrial constraints such as slurry handling, corrosion, phase separation, reagent cost, solvent recyclability, or impurity accumulation. This disconnect partially explains why several technologies with excellent laboratory performance have not achieved industrial adoption.

The shift to circular economy frameworks brings geopolitical considerations. Countries aim to lessen reliance on imported raw materials by enhancing domestic recycling and urban mining (Wong et al., 2025). Germanium recycling is now seen as both environmentally essential and a strategic industrial goal.

The principal critical gaps identified in current germanium recovery technologies are summarized in Table 9.

Table 9. Main technological and industrial gaps identified in germanium recovery research and industrial implementation. Adapted from Meshram and Abhilash (2022), Srivastava and Ilyas (2025), Teng et al. (2025), Umbach (2024), and Yadav et al. (2026).

Critical Gap	Main Limitation	Industrial Consequence
Lack of industrial data	Most studies restricted to laboratory scale	Limited process validation
Poor methodological standardization	Different recovery and selectivity criteria	Difficult technology comparison
Scarcity of pilot-scale studies	Low TRL validation	Uncertain scalability
Limited mass and energy balances	Incomplete process evaluation	Overestimation of feasibility
Insufficient impurity management analysis	Simplified feed compositions	Reduced industrial applicability
Neglect of solvent recycling	Underestimated OPEX and environmental burden	Poor sustainability assessment
Weak integration with industrial systems	Isolated laboratory studies	Low implementation potential
Limited long-term operational studies	Short experimental durations	Unknown process stability

Table 9 demonstrates that the main barriers to industrial germanium recovery are no longer restricted to extraction efficiency itself. Instead, the major challenges involve process integration, scalability, operational stability, environmental management, and economic sustainability.

A framework for circular germanium recovery, including primary production, secondary resources, industrial recycling, and urban mining, is shown in Figure 10.

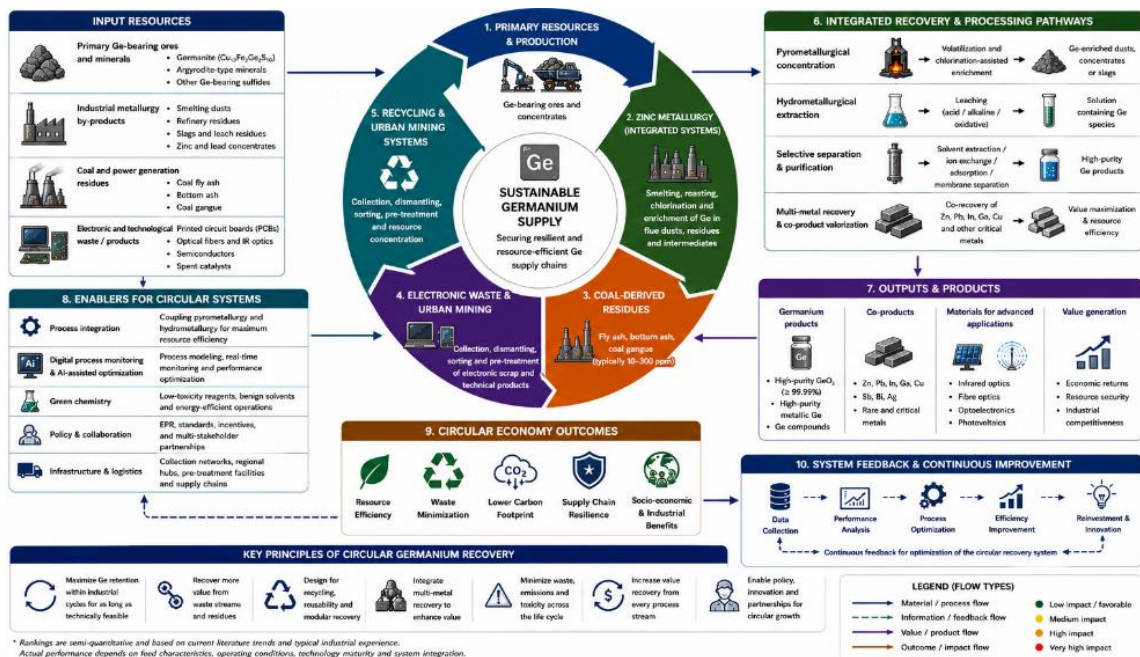


Figure 10. Circular framework for germanium recovery integrating primary resources, zinc metallurgy, coal-derived residues, electronic waste recycling, urban mining, and multi-metal recovery systems. Adapted from Srivastava and Ilyas (2025), Teng et al. (2025), Umbach (2024), and Yadav et al. (2026).



Figure 10 illustrates that future germanium supply will likely depend on interconnected industrial ecosystems combining primary extraction, secondary recovery, recycling, and waste valorization. The framework also emphasizes that the transition from laboratory-scale recovery toward industrial circular systems requires greater integration between metallurgy, environmental engineering, process intensification, and critical raw material policy strategies.

12. FUTURE PERSPECTIVES

The future development of germanium recovery technologies will depend on overcoming limitations in selective separation, impurity management, process integration, and industrial scalability. Although substantial progress has been achieved in hydrometallurgical extraction, solvent engineering, and recycling technologies, major technological and economic barriers remain unresolved. In particular, the increasing complexity of secondary resources and the declining availability of high-grade feed materials will require more integrated and selective processing strategies.

One of the most important future directions involves the integration of geometallurgical characterization with process design. Current recovery systems frequently treat germanium-bearing materials as chemically homogeneous feeds despite large variations in mineralogy, occurrence state, and impurity distribution. More advanced geometallurgical approaches combining mineralogical mapping, speciation analysis, and thermodynamic modeling may significantly improve process predictability and selective recovery performance.

Predictive modeling and AI are expected to play larger roles in future Ge recovery systems. Recent studies show machine learning models can identify relationships among leaching conditions, impurities, efficiency, and selectivity (Geng et al., 2025). These approaches can optimize complex systems where traditional methods are too time-consuming or costly.

Artificial intelligence could be crucial for managing complex secondary resources such as electronic waste, fly ash, and metallurgical residues, which exhibit nonlinear behavior due to mineralogical heterogeneity, impurities, and variable feed. Advanced models can enhance process control, reagent use, and recovery efficiency.

Selective solvent development remains another critical research direction. Current solvent extraction and ion exchange systems still exhibit important limitations regarding selectivity, solvent degradation, viscosity, phase disengagement, and chemical stability. Ionic liquids, deep eutectic solvents (DES), and advanced quaternary ammonium systems have demonstrated promising laboratory-scale performance; however, industrial implementation remains limited by solvent cost, recyclability, and long-term stability (Vereycken et al., 2022a).

Future solvent systems will likely require not only higher selectivity but also greater compatibility with industrial operating conditions. Parameters such as solvent regeneration efficiency, thermal stability, degradation resistance, phase separation kinetics, and environmental impact will become increasingly important as the field moves from laboratory experimentation toward continuous industrial operation.

Process intensification technologies, like ultrasound-assisted extraction, intensified solvent systems, membrane separations, and electrochemical methods, could improve Ge recovery efficiency by reducing mass-transfer issues and boosting extraction kinetics (Liu et al., 2026). However, their long-term industrial feasibility is uncertain due to limited pilot-scale validation and economic analysis.

Another important future trend involves the transition from isolated Ge recovery toward integrated multi-metal recovery platforms. Germanium rarely occurs alone in industrial residues and is commonly associated with Ga, In, Zn, Pb, REEs, and other critical elements. Consequently, future industrial flowsheets will likely prioritize the simultaneous recovery of multiple strategic metals rather than single-element extraction processes.

Integrated circular economy systems are expected to become increasingly important in future supply chains. Urban mining, electronic waste recycling, coal fly ash valorization, and metallurgical residue processing may collectively become major Ge sources over the next decades (Srivastava & Ilyas, 2025). In several regions, the availability of secondary germanium resources may eventually exceed the practical contribution from newly developed primary mining operations.

However, this transition will require substantial improvements in industrial infrastructure, feedstock collection, residue characterization, and recycling logistics. Current recycling systems still suffer from low collection efficiency, inconsistent feed quality, and incomplete material traceability. Without better integration of waste-generation and metallurgical-recovery systems, the full circular-economy potential of Ge recovery may remain unrealized.

Long-term sustainability studies also indicate that future Ge supply will be increasingly influenced by geopolitical and strategic factors rather than purely geological availability (Sverdrup & Haraldsson, 2024). Because germanium production remains highly concentrated in a few industrial regions and supply chains, disruptions in zinc metallurgy, coal utilization, or semiconductor manufacturing may directly affect global Ge availability and price stability.

Future industrial growth will likely focus on diversifying supply, developing recycling infrastructure, and improving recovery efficiency from secondary resources. Ge's importance for advanced electronics, infrared systems, renewable energy, and fiber optics will drive investment in selective separation and integrated metallurgical processes.

The principal future technological directions for germanium recovery are summarized in Table 10.

Table 10. Main future technological directions and research priorities in germanium recovery systems. Adapted from Geng et al. (2025), Meshram and Abhilash (2022), Rudnik (2025), Srivastava and Ilyas (2025), Vereycken et al. (2022a), and Yadav et al. (2026).

Future Direction	Main Objective	Expected Industrial Impact
AI-assisted process optimization	Improve selectivity and process control	Higher recovery efficiency
Advanced selective solvents	Increase Ge separation performance	Lower purification cost
Integrated multi-metal recovery	Simultaneous recovery of critical metals	Improved economic viability
Circular economy integration	Expand urban mining and recycling	Reduced supply dependence
Geometallurgical modeling	Improve feed characterization	Better process predictability
Process intensification	Enhance kinetics and mass transfer	Reduced equipment footprint
Pilot-scale validation	Improve industrial scalability	Higher TRL development
Sustainable solvent recycling	Reduce environmental burden	Lower OPEX and waste generation

Table 10 demonstrates that future progress in germanium recovery will depend on interdisciplinary integration among hydrometallurgy, process engineering, materials science, environmental management, and digital process optimization.

A conceptual framework illustrating the future evolution of germanium recovery technologies is presented in Figure 11.

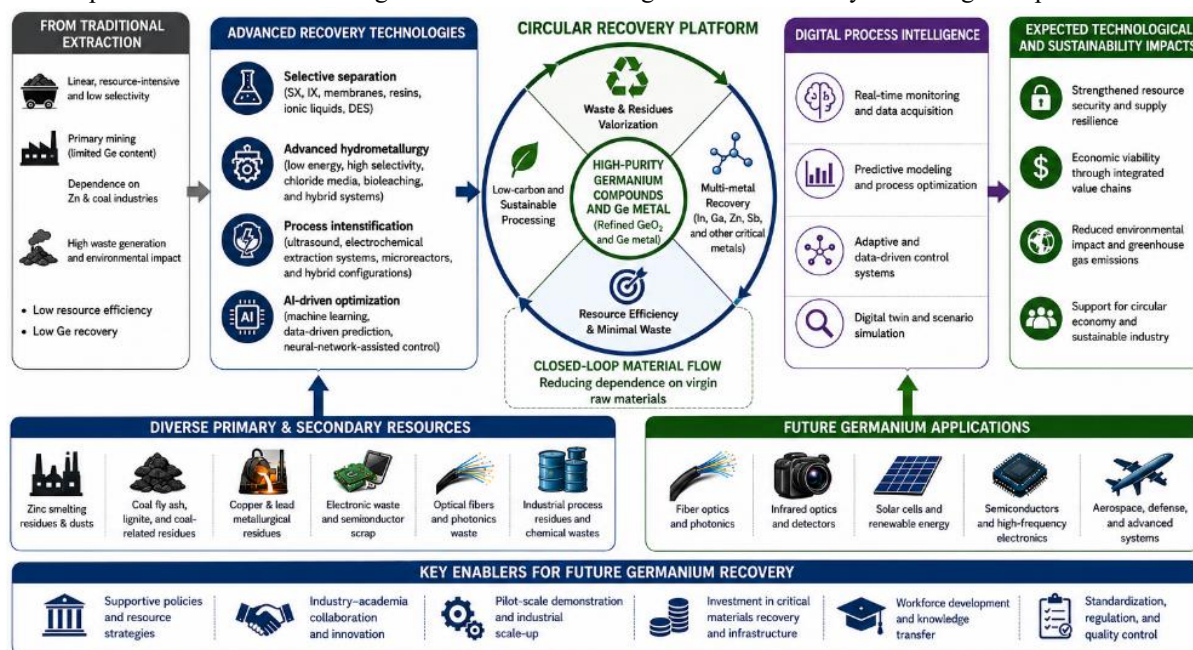


Figure 11. Future technological directions for germanium recovery: integrating selective separation, artificial intelligence, circular-economy systems, multi-metal recovery, and advanced hydrometallurgical processing. Adapted from Geng et al. (2025), Srivastava and Ilyas (2025), Vereycken et al. (2022a), and Yadav et al. (2026).



Figure 11 illustrates the shift from traditional extraction to integrated circular recovery platforms that leverage advanced separation, predictive control, and waste valorization. It also highlights that future competitiveness in the germanium supply chain will rely less on abundance and more on the ability to recover Ge from complex, dilute industrial systems.

13. CONCLUSIONS

Germanium is a crucial raw material for semiconductors, optics, solar cells, and electronics. Unlike major metals, Ge is rarely mined directly; it is derived from zinc, coal, and secondary recovery. This indirect supply limits availability, controlled more by related industries than direct demand.

This review demonstrated that the technological bottleneck in germanium production is not the dissolution of Ge-bearing materials but rather the selective separation and purification of germanium from highly complex and dilute systems. Although pyrometallurgical and hydrometallurgical routes can achieve high extraction efficiencies, the simultaneous presence of impurities such as Fe, Zn, Si, As, and Al continues to limit downstream purification and selective recovery performance.

Hydrometallurgical processing dominates germanium purification due to its operational flexibility and selectivity over pyrometallurgical methods. Acidic and alkaline leaching can dissolve Ge from zinc residues, fly ash, slags, and secondary materials. However, purification stages such as solvent extraction, ion exchange, precipitation, adsorption, and crystallization are the most technically sensitive and costly.

The review shows secondary resources are becoming increasingly important for germanium supply. Items such as coal fly ash, dusts, residues, e-waste, and fibers often contain high Ge levels, sometimes exceeding those of primary sources. Therefore, urban mining and industrial waste recovery are expected to play an increasingly important role in the global Ge supply chain.

Emerging technologies like ionic liquids, deep eutectic solvents, ultrasound extraction, electrochemical recovery, and AI optimization show promise in labs but remain at low industrial readiness due to limited pilot validation, solvent stability analysis, long-term operation, and economic assessments.

A major gap in the literature is the disconnect between lab studies and industrial use. Many reports high extraction efficiencies but neglect key industrial factors such as energy use, solvent recyclability, residue management, corrosion, impurity buildup, and process integration. This often leads to overestimating industrial feasibility and underestimating Operational complexity. Future industrial development will likely be dominated by integrated processing systems combining pyrometallurgical upgrading, hydrometallurgical purification, and multi-metal recovery. Ge recovery, often not economically sustainable on its own, will increasingly depend on integration with zinc metallurgy, electronic waste recycling, coal fly ash valorization, and circular economy platforms.

The long-term sustainability of the germanium supply depends more on the ability to recover Ge from complex secondary systems than on geological availability. Advances in separation technologies, industrial flowsheets, and circular economy strategies will shape the future competitiveness and resilience of global germanium production.

Future competitiveness in germanium metallurgy will likely depend less on geological abundance and more on the ability to selectively recover Ge from chemically complex secondary resources through integrated and sustainable metallurgical systems.

DECLARATIONS

Author Contributions

Antonio Clareti Pereira conceptualized the study, conducted the literature review, analyzed the data, developed the critical assessment, and wrote the manuscript.

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Conflicts of Interest

The author declares no conflict of interest.

Data Availability Statement

The datasets generated and analyzed during the current study are available from the corresponding author on reasonable request.

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