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Recovery of Hafnium from Mineral and Secondary Resources: Separation Chemistry, Process Intensification, Electrochemical Routes, and Industrial Perspectives (2015–2026)

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Abstract

Hafnium is indispensable to nuclear reactor control systems, high-temperature alloys, advanced electronics, and high-k dielectric technologies, yet it is rarely produced from a stand-alone ore. Its supply is therefore structurally coupled to zirconium production, and its recovery depends on one of the most difficult neighboring-element separations in extractive metallurgy. This critical review synthesizes 108 cited sources (including one 2026 institutional report) from 2015 through September 2026 using a performance-first framework that links feed mineralogy and conditioning to Zr/Hf speciation, separation mechanisms, product purity, reagent regeneration, environmental burden, and industrial readiness. The evidence indicates that the central technical challenge is not simply hafnium dissolution, but deliberately amplifying small differences in hydrolysis, anion coordination, ligand exchange, aggregation, volatility, and redox behavior. Conventional solvent extraction remains the industrial benchmark because of its throughput and flowsheet flexibility, but requirements for acidity control, scrubbing and stripping, solvent management, and coextraction control constrain sustainability. Ion exchange, extraction chromatography, functionalized adsorbents, ion-imprinted membranes, MOF/COF-derived systems, and oxo-cluster precipitation broaden the selectivity toolbox, although most still lack long-term continuous validation with realistic feeds. Thermal-halide and molten-salt routes can integrate purification with metal production but impose more demanding materials-of-construction, energy, and corrosion-control requirements. Secondary streams are strategically important because they can partially decouple hafnium supply from primary zircon throughput. The review therefore proposes a chemistry-to-flowsheet decision framework and identifies the evidence required to translate high laboratory selectivity into industrially robust hafnium recovery.

Keywords: Hafnium; Zirconium–hafnium separation; Solvent extraction; Ion exchange; Molten salt electrolysis; Secondary resources

Highlights

- Hafnium recovery is governed by Zr/Hf speciation control rather than extraction percentage alone.
- Solvent extraction remains the industrial benchmark, while solid-phase and cluster-based routes expand the selectivity toolbox.
- Molten-salt and halide routes can couple separation with metal production but intensify energy, corrosion-control, and materials-of-construction demands.

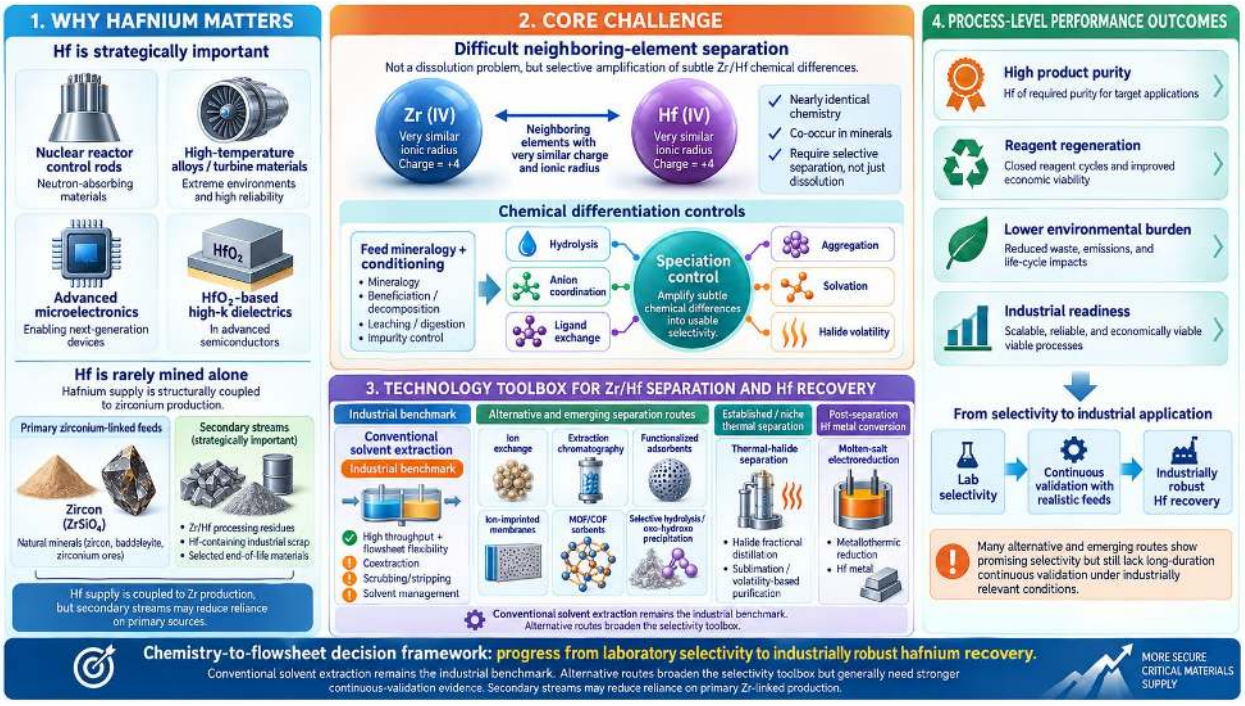
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- Secondary Zr-processing residues can become strategic hafnium feeds when impurity-control and reagent-recycle loops are closed.

Graphical abstract



1. Introduction

Hafnium occupies an unusual position among critical and strategic metals. It is technologically valuable because of its nuclear, high-temperature, corrosion-resistant, and electronic applications, but it remains geologically and metallurgically subordinate to zirconium. Zircon and related Zr-bearing minerals normally contain Hf as a coupled minor constituent, so commercial hafnium availability follows the throughput, purification strategy, and product specifications of zirconium supply chains rather than an independent mine-to-metal system. This co-production structure is strategically important: hafnium demand can increase without creating an immediate incentive for a dedicated Hf mine, while changes in the zirconium industry can alter Hf availability even when Hf demand remains unchanged (Harper et al., 2015; Jones et al., 2017; Torres de Matos et al., 2021).

The separation problem is equally distinctive. Zr(IV) and Hf(IV) have the same dominant oxidation state in conventional aqueous processing, similar ionic radii and hydrolysis behavior, and strong affinities for oxygen- and halide-containing ligands. Consequently, most

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recovery routes do not exploit a large intrinsic thermodynamic contrast. Instead, they amplify small differences through acid activity, counter-anion coordination, extractant structure, aggregation, interfacial transfer, solid-phase binding, volatility, or electrochemical behavior. Reviews of nuclear-grade zirconium production and Zr/Hf separation therefore consistently place separation chemistry, rather than primary dissolution, at the center of flowsheet design (Banda & Lee, 2015; de Oliveira Rodrigues, de Carvalho, et al., 2026; Wang & Lee, 2016b; Xu et al., 2015).

The 2015–2026 literature also marks a transition from empirical reagent screening toward mechanism-guided separation. Recent work has resolved nitrate- and sulfate-dependent extraction equilibria, identified oxo-cluster structures in thiocyanate media, coupled density-functional calculations with industrial liquors, and introduced selective membranes, porous adsorbents, and new phosphinic/phosphonic ligands. In parallel, electrochemical studies and process-design work on molten salts have progressed beyond proof-of-principle reduction toward questions of redox control, conductivity, deposition, distillation, and product formation (Dong et al., 2025; Ma et al., 2025; Roseborough et al., 2025; Sommers et al., 2022; Wei et al., 2024).

This review critically evaluates hafnium recovery from primary minerals and secondary resources from 2015 through September 2026. The objective is not to rank technologies by a single reported separation factor, but to connect molecular selectivity to the complete flowsheet: feed conditioning, speciation, separation stages, scrubbing and stripping, regeneration, product finishing, waste generation, energy demand, and scale-up. The central thesis is that the strongest future routes will preserve selectivity under realistic feed compositions, impurity loads, and recycle conditions rather than maximize selectivity only in simplified batch solutions.

This review differs from earlier Zr/Hf-focused reviews by integrating five levels of evidence usually treated separately: feed conditioning, solution speciation, separation mechanism, downstream regeneration and product finishing, and industrial-readiness constraints. Earlier syntheses established the fundamentals of solvent extraction, aqueous Zr/Hf chemistry, and nuclear-grade zirconium purification, while recent reviews have expanded the

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discussion toward solution chemistry and hydrometallurgical routes (Banda & Lee, 2015; de Oliveira Rodrigues, de Carvalho, et al., 2026; Dong et al., 2025; Pereira, 2026f; Wang & Lee, 2016b). Here, we extend those contributions by treating secondary resources, process intensification, reagent recycle, continuous-operation evidence, thermal and electrochemical integration, and whole-flowsheet burden as coequal criteria for technology assessment.

Table 1 compares this review's boundary with overlapping prior syntheses, clarifying where the contribution is integrative rather than a claim of newly discovered Zr/Hf chemistry.

Table 1. Novelty and scope relative to recent zirconium–hafnium reviews

Review	Principal emphasis	Distinctive boundary in the present review
Dong et al. (2025)	Solution speciation and ligand-mediated Zr/Hf separation	Adds secondary streams, regeneration, continuous performance, halide/electrochemical options, and system burdens
de Oliveira Rodrigues et al. (2026)	Hydrometallurgical decomposition, leaching, extraction, and exchange	Adds cross-platform readiness, membranes, advanced solids, thermal/electrochemical finishing, and circular flowsheets
Pereira (2026f)	Zirconium-centered purification and process integration	Shifts the endpoint to specification-defined Hf product recovery and distinct secondary Hf feed availability

Note. Scope-level synthesis of the cited reviews; the comparison is not a bibliometric novelty score. No text, tables, or figures are intentionally reproduced from these reviews; descriptions are newly authored. Claim of reuse or overlap requires a separate author-side originality check.

2. Review Methodology and Critical-Assessment Framework

This work is a structured critical narrative review based on a bibliography initially comprising 107 distinct sources from 2015 through September 2026. The evidence set includes primary research, focused reviews, government and institutional reports, and process-oriented studies addressing zircon and alternative mineral feeds, decomposition and leaching, aqueous Zr/Hf chemistry, solvent extraction, ion exchange, adsorption, membranes, thermal-halide separation, molten salts, electrolysis, metal refining, secondary-resource recovery, and environmental or material-system analysis. Sources were retained when they contributed directly to separation mechanisms, process performance, real-feed behavior, regeneration, continuous operation, product quality, or scale-up interpretation.

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This review is not a formal systematic review or meta-analysis. The starting evidence set was a curated corpus rather than a raw database export with auditable identification and deduplication counts. Accordingly, the synthesis emphasizes transparent critical comparison rather than claims of exhaustive literature coverage. Each study was coded against five questions: (i) which feed and chemical medium were used; (ii) which Zr/Hf species or separation mechanism was targeted; (iii) which performance metric was reported; (iv) which downstream operations were required; and (v) what evidence was available for stripping or elution, recycle, continuous operation, real-feed tolerance, product quality, or industrial translation. This approach prevents high batch selectivity from being treated as equivalent to industrial readiness. The original reference list contains 107 distinct bibliographic entries; this revision adds one 2026 USGS institutional source, bringing the cited-source inventory to 108. The previously reported number of 102 cannot be independently reconstructed as a coded subset from the available records and is therefore withdrawn. No article-screening totals, formal exhaustive search, or retrospective coding of all 108 sources is claimed. The 108-item bibliography is a cited-source inventory, not a PRISMA-style screened sample. Search-platform logs, last-executed search date, language filters, and forward/backward citation-chaining records were not preserved; the literature coverage closes in September 2026 and should not be interpreted as exhaustive. English-language evidence predominates, but no retrospectively verifiable language-exclusion protocol is available. Government reports were retained for supply estimates and institutional context, not as experimental proof of selectivity. Duplicate bibliographic entries were checked by title and DOI where supplied; the original selection and exclusion history cannot be reconstructed.

The critical comparison uses a chemistry-to-flowsheet framework. At the chemistry level, acidity, free acidity, hydrolysis, counter-anion coordination, ligand donor atoms, aggregation, volatility, and redox state are treated as variables that change the identities and activities of the species entering a separation step. At the equipment level, the review considers phase disengagement, resin or sorbent regeneration, membrane stability, stage count, temperature, materials of construction, corrosion, off-gas treatment, and product finishing. At the system level, the review considers reagent recycle, secondary waste, solvent inventory, energy demand, and dependence on primary zircon throughput. This multiscale framing aligns

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with the need to distinguish pH from free acidity in concentrated hydrometallurgical liquors and to evaluate ion-exchange systems based on dynamic, regenerative performance rather than equilibrium selectivity alone (Pereira, 2026b, 2026c).

Evidence strength was interpreted in four classes: (a) direct Zr/Hf experiments performed with characterized feeds and measured product outcomes; (b) direct laboratory Zr/Hf experiments lacking industrial feed or regeneration; (c) chemically relevant analogues from other metal systems; and (d) conceptual hypotheses and engineering extrapolations. Class (c) sources, including generic acidity, precipitation, filtration, and electrochemical methodology papers, inform measurement or design principles only and do not establish Hf recovery performance. Statements of technology readiness preferentially rely on classes (a) and (b).

A limitation of the evidence base is the substantial heterogeneity of reported metrics. Many studies report equilibrium extraction or adsorption values without complete mass balances, stripping or elution data, cycle-life information, real-feed validation, or product-purity measurements. Direct numerical ranking across all technologies would therefore create false precision. Comparative judgments in this review are consequently qualitative unless the underlying studies provide directly comparable performance data.

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Figure 1 summarizes the evidence-synthesis workflow used to connect mechanistic evidence to flowsheet and sustainability interpretation.

2015–September 2026 literature scope → 108 cited sources (original 107 + 2026 USGS) → Evidence classification → Chemistry/mechanism → Flowsheet and product-quality assessment → Burden and industrial-readiness synthesis

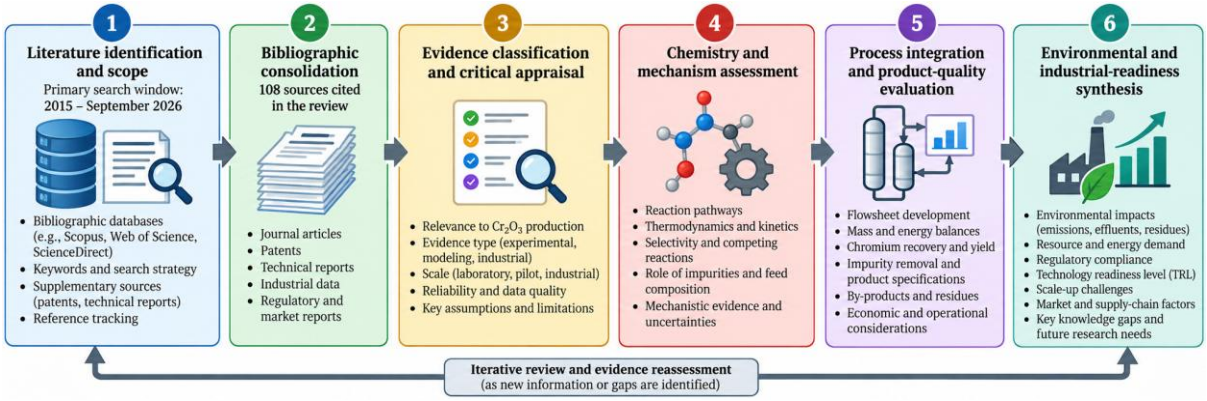


Figure 1. Evidence-synthesis workflow for the critical review
Note. Author-generated narrative evidence-synthesis workflow; 108 is the count of cited sources, not a retrospectively reconstructed screened corpus. No systematic identification counts are implied.

Analytical determination of free acidity requires particular attention in sulfate-rich circuits. Interfering dissolved ions may affect the Gran titration method, while oxalate-based determinations have a distinct applicability window and require validation against matrix composition. These techniques should therefore be treated as process-control methods that require feed-specific analytical verification, rather than assumed interchangeable with direct pH measurements (Pereira & Santos, 2025; Pereira et al., 2025).

The workflow deliberately places mechanism before technology ranking so that apparently strong batch results are interpreted in the chemical context that produced them.

3. Hafnium Supply, Occurrence, Feedstocks, and Feed Conditioning

The 2026 U.S. Geological Survey commodity assessment reports that world primary hafnium production data and quantitative estimates of hafnium reserves are unavailable; it estimates approximately 1.2 million metric tons of global zirconium mineral-concentrate production in 2025, a measure that must not be misrepresented as hafnium output (U.S.

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Geological Survey, 2026). Strategic or critical designation depends on jurisdiction and policy, not intrinsic classification of the element.

Hafnium is recovered mainly because it accompanies zirconium. Zircon mineral sands remain the dominant upstream context, with beneficiation and zircon-product quality determining the composition presented to chemical decomposition. Baddeleyite and more complex Zr-bearing minerals, including eudialyte, broaden the mineralogical envelope but introduce different gangue and impurity-control requirements. Mineral-sand processing studies show that upstream zircon liberation and concentration are mature compared with the subsequent chemical differentiation of Zr and Hf, while geological studies show that Zr–Hf fractionation can vary during magmatic evolution and mineral crystallization (Monnier et al., 2025; Pownceby et al., 2015).

Chemical opening of the mineral matrix is the first major process fork. Alkali fusion and sub-molten NaOH routes transform refractory zircon into soluble or leachable sodium zirconate/silicate-bearing products, while chlorination converts Zr–Hf values to volatile or salt-processable chlorides. The decomposition step is not chemically neutral: phase formation, temperature, silica behavior, and residual alkali determine the composition and downstream acidity demand. Control of Na_2ZrSiO_5 formation during alkali fusion, zircon decomposition kinetics in sub-molten NaOH, and baddeleyite chlorination behavior illustrate how feed conditioning affects both recovery and the impurity burden subsequently seen by the Zr/Hf separation circuit (Babintsev et al., 2024; J. C. Liu et al., 2016; Sun et al., 2019).

Alternative primary and intermediate feeds are increasingly important. Sulfuric-acid processing of eudialyte can recover Zr (+Hf) along with other value metals, but multicomponent chemistry complicates selectivity and residue management. Sulfuric dry digestion followed by water leaching has also mobilized Zr, Hf, and Nb from eudialyte residues. More recently, oxalic-acid leaching of underexplored tin-beneficiation residues has expanded the resource base to residues historically not treated as hafnium feedstocks (Balinski et al., 2019; de Oliveira Rodrigues, Pereira, et al., 2026; Ma et al., 2018).

Secondary resources alter the strategic logic of hafnium recovery because they can contain Zr and Hf already transferred from refractory mineral lattices into process residues,

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leach liquors, or metallic scrap. Petroleum ash liquor has been evaluated for recovery of U, Hf, and Zr; slurry waste from zirconium purification has been processed by solvent extraction; recovered hafnium from zirconium purification has been compositionally characterized; and technogenic hafnium has been examined under electron-beam refining (Abd El-Hamid et al., 2015; Joshi et al., 2021; Pandey et al., 2016; Vutova et al., 2022). These streams can reduce the need for primary mineral decomposition, but they usually increase variability in impurity chemistry.

The strategic implication is that a "hafnium feed" should be defined by chemical state rather than origin. A high-grade primary zircon concentrate may require severe decomposition before separation, whereas a dilute process raffinate may already contain soluble Hf in a form compatible with solvent extraction or ion exchange. Consequently, feed selection should compare total process intensity rather than Hf concentration alone. Life-cycle work on zircon sand and material-system analysis for hafnium further support evaluation of embedded upstream burdens and co-product dependence (Gediga et al., 2019; Sohn, 2025; Torres de Matos et al., 2021).

Table 2 compares the principal feed classes and shows why feed chemistry, rather than origin alone, determines downstream separation intensity.

Table 2. Hafnium-bearing feed classes and their principal processing implications

Feed class	Representative forms	Main advantage	Principal constraint	Selected evidence
Primary zircon	$ZrSiO_4$ mineral sands	Established supply and beneficiation chain	Refractory lattice; Hf diluted in large Zr inventory	Pownceby et al., 2015; Jones et al., 2017
Baddeleyite	ZrO_2-rich concentrate	Lower silica burden than zircon	Variable chlorination/decomposition behavior	Babintsev et al., 2024
Complex Zr minerals	Eudialyte and polymetallic concentrates	Co-recovery of Zr(+Hf), REEs, Nb, and Mn	Multicomponent leach and purification burden	Balinski et al., 2019; Ma et al., 2018

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Feed class	Representative forms	Main advantage	Principal constraint	Selected evidence
Process residues	Zr-purification slurry/raffinate	Hf already chemically mobilized	Dilute streams, solids, and plant-specific impurities	Pandey et al., 2016; Joshi et al., 2021
Industrial/technogenic residues	Petroleum ash, tin-beneficiation residue, Hf scrap	Potential supply decoupling from primary zircon	Heterogeneous impurity suites and variable inventory	Abd El-Hamid et al., 2015; de Oliveira Rodrigues, Pereira, et al., 2026; Vutova et al., 2022

Note. Author synthesis from the cited literature. Feed attractiveness depends on chemical state, impurity routing, and total flowsheet intensity rather than hafnium grade alone.

The comparison highlights the strategic advantage of process-derived residues: they may be lower grade than mineral concentrates, yet they can avoid the most severe mineral-decomposition step and integrate with existing Zr purification infrastructure.

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Figure 2 places these feed classes in a common resource-to-product chain and identifies the Zr/Hf separation node as the central bottleneck.

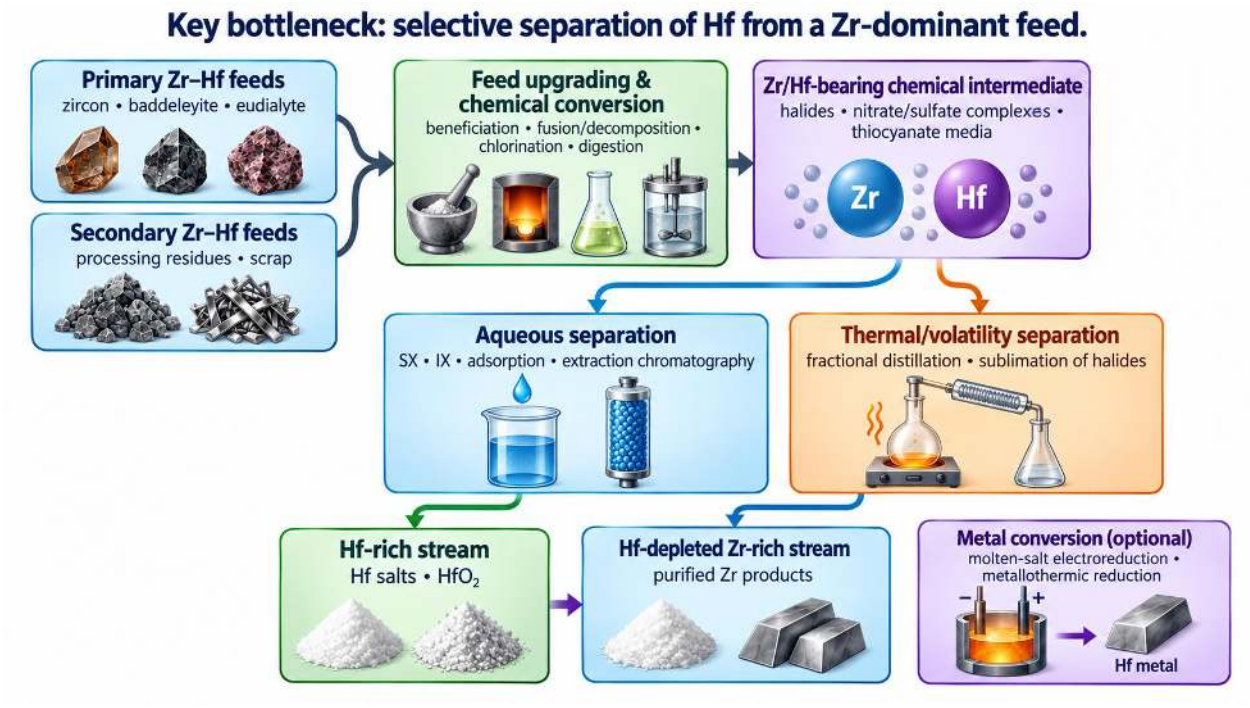


Figure 2. Resource-to-product chain for hafnium recovery
Note. Author-generated synthesis based on Jones et al. (2017), Xu et al. (2015), Pandey et al. (2016), Wei et al. (2024), and de Oliveira Rodrigues, de Carvalho, et al. (2026).

This integrated view avoids the common error of treating leaching recovery as equivalent to hafnium recovery: the metal is not recovered as a strategic product until it has been differentiated from zirconium and converted to the required chemical or metallic form.

3.1 Primary mineral feeds

Zircon, baddeleyite, and eudialyte represent distinct feed classes. Zircon combines high structural stability with established mineral-sand supply; baddeleyite can reduce silica-related processing but remains compositionally variable; and eudialyte links Hf recovery to polymetallic recovery of Zr, Nb, and rare-earth values. The practical question is therefore not which mineral contains hafnium, but which mineral-to-liquor route creates a composition compatible with selective Zr/Hf separation at acceptable reagent and residue cost.

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3.2 Secondary and process-derived feeds

Secondary and process-derived feeds include raffinate and slurry from Zr purification, residues from complex-ore processing, petroleum-derived ash liquors, and Hf-bearing metal scrap. From a feed-conditioning perspective, their principal advantage is that earlier industrial operations have already transferred part of the Hf inventory from refractory mineral lattices into chemically accessible phases. Their principal disadvantage is compositional variability in acidity, suspended solids, organics, and co-dissolved impurities. Section 8 evaluates the recovery, recycle, and circularity implications of these streams in greater detail.

4. Separation Chemistry: Speciation, Hydrolysis, Complexation, and the Origin of Selectivity

The near-identity of Zr(IV) and Hf(IV) does not mean that their solution chemistry is identical. Separation becomes possible because a chosen medium can amplify small differences in hydration, hydrolysis, ligand exchange, aggregation, and complex stability. The literature increasingly treats the aqueous phase as an active separation reagent rather than a passive carrier. Reviews of aqueous Zr/Hf chemistry and more recent solution-chemistry syntheses emphasize that extractant performance cannot be separated from the species distribution established by acid, anion, metal concentration, and aging history (Dong et al., 2025; Wang & Lee, 2016b).

Nitrate, sulfate, chloride, fluoride, and thiocyanate systems create different coordination environments. In nitric acid, TBP extraction responds strongly to acidity and nitrate-complex formation, and mechanistic work with Cyanex 572 indicates a cation-exchange route with nitrate participation in the extracted species. In sulfate systems, acidic organophosphorus extractants differentiate Hf from Zr through hydrolysis, sulfate coordination, and proton transfer. In fluoride-rich media, direct speciation measurements and calculations show multiple fluorinated species, while geological-fluid work reinforces the strong complexing role of fluoride for both high-field-strength elements (Amaral & Morais, 2020; Bertoli et al., 2021; He et al., 2021; Loges et al., 2024; Novaes et al., 2026).

Thiocyanate chemistry provides one of the clearest demonstrations that aggregation can generate separation. Molecular-scale work identified oxo-centered Zr/Hf tetramers in an

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industrially relevant SCN^- system and showed that Zr can access larger or more highly thiocyanate-coordinated species that are less favorable for transfer to the organic phase. Subsequent work on heterometal Zr/Hf oxo clusters showed selective precipitation of Hf-rich clusters and linked this behavior to differences in ligand lability and solubility. This reframes classical MIBK–HSCN extraction: selectivity does not arise simply from a stronger Hf–extractant bond, but from the combined effects of aqueous speciation, cluster size, charge, counterions, and interfacial partitioning (Roseborough et al., 2025; Sommers et al., 2022).

The operational consequence is that free acidity must be controlled as a thermodynamic variable. Two liquors with the same measured pH can exhibit different metal speciation if their acid inventory, ionic strength, sulfate or nitrate loading, and dissolved-metal concentrations differ. This is particularly relevant to aging effects and recycle loops, where hydrolyzed or polymerized species may evolve with residence time. A process optimized against pH alone can therefore drift when implemented with concentrated industrial feeds (Novaes et al., 2026; Pereira, 2026c).

The core separation metrics are the distribution ratio, $D_M = [M]_{org}/[M]_{aq}$, and the separation factor, $\beta_{Hf/Zr} = D_{Hf}/D_{Zr}$ (or its inverse when Zr is preferentially extracted). These metrics are necessary but insufficient. A high β can still produce an unattractive flowsheet if one metal is only weakly transferred, if stripping is difficult, if impurity rejection is poor, or if selectivity collapses at realistic metal loading. The correct unit of comparison is therefore a multidimensional set of selectivity, recovery, loading, stage count, scrubbing, stripping, recycle stability, and product specification.

Table 3 organizes the principal aqueous media by the chemical lever that creates useful Zr/Hf discrimination.

Table 3. Aqueous media and chemical levers used to differentiate Zr(IV) and Hf(IV)

Medium	Dominant separation lever	Typical route	Critical control variable	Selected evidence
HNO_3 / nitrate	Neutral nitrate complexation and cation exchange	TBP, Cyanex 572	Acidity and nitrate activity	Amaral & Morais, 2020; He et al., 2021

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Medium	Dominant separation lever	Typical route	Critical control variable	Selected evidence
H_2SO_4 / sulfate	Hydrolysis + sulfate coordination + proton exchange	D2EHPA, PC88A, phosphinic acids	Free acidity, sulfate loading, aging	Wang & Lee, 2016c; Novaes et al., 2026
HCl / chloride	Chloro-complexation and ligand selectivity	Amic acids, resins, β-diketones	Chloride activity and hydrolysis suppression	Ma et al., 2021; Nemati et al., 2022; Qi et al., 2026
F^--rich systems	Strong fluoro-complexation	Amine/organophosphorus extraction, halide routes	Fluoride speciation and corrosivity	Conradie et al., 2016, 2018; Bertoli et al., 2021
SCN^- / ketone systems	Oxo-cluster speciation, charge, and solvating extraction	MIBK/DIBK systems	SCN^-, modifier chemistry, cluster distribution	Sommers et al., 2022; Xiong et al., 2024; Chen et al., 2026

Note. The same extractant can behave differently when the aqueous species distribution changes; pH alone is not an adequate descriptor for concentrated acidic liquors.

The table shows that the extractant cannot be separated conceptually from the aqueous feed. The same donor group may behave differently when hydrolysis, sulfate binding, nitrate complexation, or oxo-cluster formation changes.

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Figure 3 summarizes this chemistry as a hierarchy from near-identical ions to controllable speciation differences and, finally, to process-level selectivity.

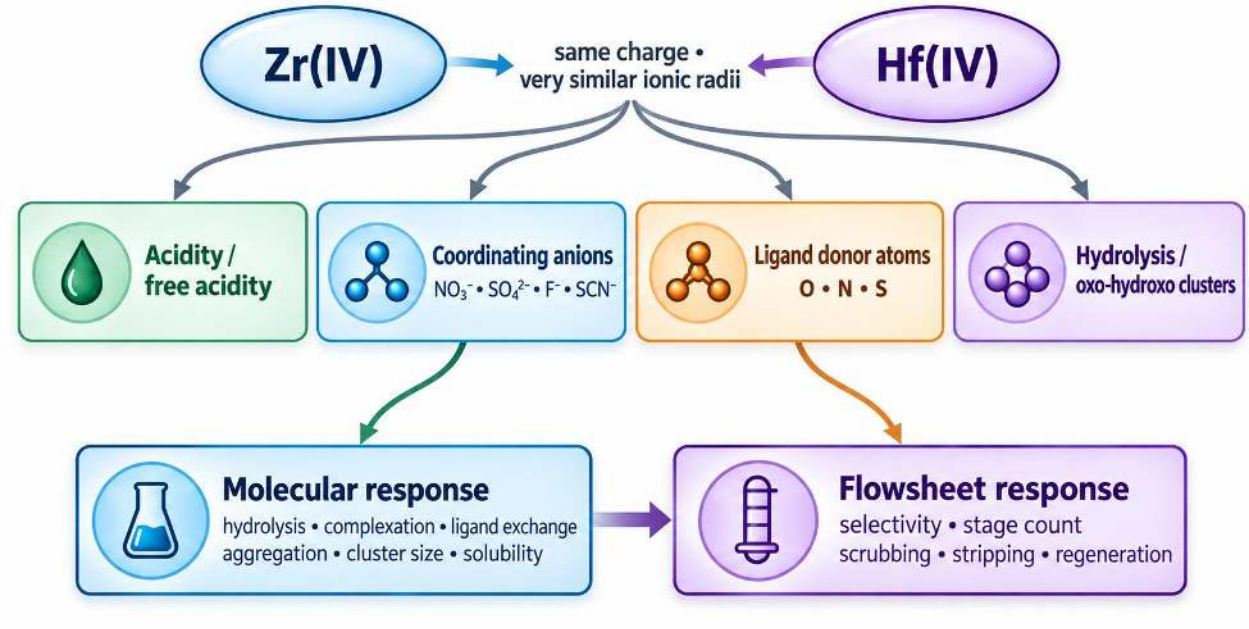


Figure 3. Chemical handles that generate practical Zr/Hf selectivity
Note. Author-generated conceptual synthesis based on Wang and Lee (2016b), Bertoli et al. (2021), Sommers et al. (2022), Roseborough et al. (2025), and Novaes et al. (2026).

Selective precipitation and solid–liquid separation must also be evaluated as part of the separation chemistry. Co-precipitation can entrain the nominally rejected element, especially when hydrolysis rates, local supersaturation, aging, and washing are poorly controlled. In sulfate circuits, the common-ion effect is relevant to precipitation and solubility equilibria but must not be invoked without identifying the controlling species and activity effects. These are general hydrometallurgical design principles requiring Zr/Hf-specific experimental validation (Pereira, 2026a, 2026g).

The most important design implication is that selectivity is an engineered system property rather than an immutable constant of the Zr/Hf pair.

For consistent comparison, the distribution ratio for each metal is $D_M = C_{M,org} / C_{M,aq}$ at a specified equilibrium condition; $\beta_{Hf/Zr} = D_{Hf} / D_{Zr}$, so $\beta_{Hf/Zr} > 1$ indicates preferential Hf partition to the organic phase, not greater recovery by itself. Report D_{Hf} and D_{Zr} alongside β and specify analytical basis, phase-volume ratio, metal loading, contact time,

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equilibration criterion, and temperature. Overall Hf recovery (%) = 100 × (mass of Hf in saleable product/mass of Hf in feed); product purity (%) = 100 × (mass of Hf or stated Hf compound in product / total corresponding product mass), with a stated elemental or compound basis. Zr loss (%) = 100 × (mass of Zr irreversibly diverted from the intended Zr stream / incoming Zr mass). Stripping recovery (%) = 100 × (Hf mass returned from loaded organic to the strip solution / Hf mass entering stripping in loaded organic). Scrubbing retention and transfer should likewise be defined on stage-inlet metal masses. Mass-balance closure (%) = 100 × (sum of quantified metal outputs plus inventory change/metal input). Values near 100% support accounting, but acceptance tolerances should reflect analytical uncertainty, not an arbitrary universal cutoff.

The reporting protocol must distinguish free acid concentration from measured pH and titratable total acidity; provide analytical validation in the actual chloride, nitrate, sulfate, or fluoride matrix, counter-anion concentrations, ionic-strength descriptors, total dissolved Zr and Hf, feed aging interval, phase-transfer kinetics, and equilibrium time. In continuous solvent extraction, publish mixer–settler or contactor stage counts, scrub and strip conditions, stagewise metal inventories, loading profiles, phase disengagement, organic entrainment, crud occurrence, solvent makeup and degradation, reagent consumption, and closed-loop regeneration efficiency. Values should be measured rather than inferred from a batch separation factor.

5. Solvent Extraction: Industrial Benchmark and Mechanistic Evolution

Solvent extraction (SX) remains the central benchmark for Zr/Hf separation because it can continuously process concentrated liquors, can be configured as extraction–scrub–strip cascades, and offers a broad ligand-design space. The literature from 2015 onward includes neutral solvating extractants, acidic organophosphorus reagents, amines, ketone–thiocyanate systems, synergistic mixtures, ionic liquids, and newly designed phosphinic or β-diketone ligands. The critical shift is from reporting extraction percentages to explaining which aqueous species transfer and how the mechanism changes with acidity and loading (Banda & Lee, 2015; de Oliveira Rodrigues, de Carvalho, et al., 2026).

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Foundational comparative studies across nitric, hydrochloric, and sulfuric media established how strongly Zr/Hf separation depends on the combined choice of aqueous medium and extractant class. Acidic, basic, neutral, amine, and alcohol-based systems repeatedly showed that a favorable ligand cannot be evaluated independently of acid concentration and anion chemistry (Amaral & Morais, 2016; Kabangu et al., 2019a, 2019b; Wang et al., 2015a, 2015b; Wang & Lee, 2015; Yang et al., 2019).

Neutral TBP systems illustrate the importance of medium design. Studies in nitric media have quantified extraction equilibria, evaluated the influence of acid and nitrate, and demonstrated liquid–liquid purification toward nuclear-grade zirconium products. Recent TBP work on zirconium oxychloride products shows that the reagent remains relevant because of its process familiarity, even as newer systems offer higher apparent selectivity (Amaral et al., 2020; Amaral & Morais, 2020; Rozana et al., 2025). Thermodynamic modeling of macroscale Zr/Hf reactive extraction also provides a basis for translating batch equilibrium into stagewise design (Kanth et al., 2020).

Acidic organophosphorus extractants are particularly important in sulfate and chloride media. D2EHPA, PC88A, Cyanex-type reagents, Ionquest 801, and related phosphinic acids exploit proton exchange and metal–oxygen coordination. Studies across sulfuric-acid systems show that acid, metal, and reagent concentrations affect both extraction and selectivity, while mechanistic investigations show direct involvement of sulfate and ligand donor atoms. The 2026 DFT-supported study with industrial sulfate liquor is especially significant because it connects molecular thermodynamics to real-feed aging and sulfate coextraction, showing why batch optimization with freshly prepared synthetic feed can misrepresent industrial behavior (de Beer et al., 2016; Han et al., 2026; Lee et al., 2015; Min & Lee, 2015; Novaes et al., 2026; Vermaak et al., 2018; Wang, Liu, Xu, et al., 2023; Wang, Liu, Zhao, et al., 2023; Wang & Lee, 2016a, 2016c).

Mechanistic development within this family also includes BEAP in sulfate medium, phosphate-ester systems designed to favor Hf, diphosphonic extractants in hydrochloric media, and organic-acid-assisted D2EHPA complexation. Together, these studies reinforce that donor

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geometry and solution-side complex formation can be tuned deliberately rather than treated as empirical black boxes (Chen et al., 2017; Luo et al., 2024; Zhao et al., 2020; Zhao et al., 2019).

Nitrate and chloride media expand the ligand space. Cyanex 572 has shown selective Hf transfer from HNO_3; amic-acid extractants have been applied to chloride solutions; and newer aminomethyl phosphinic acids and dibenzoylmethane have been designed to better differentiate Zr and Hf. In the 2026 literature, this design philosophy is explicit: donor-atom architecture is tied to experimentally and theoretically resolved coordination, rather than optimized only by empirical concentration screening (He et al., 2021; Ma et al., 2021; Qi et al., 2026; Xie et al., 2026).

Thiocyanate–ketone systems remain a distinctive class because they use both aqueous complexation and organic solvation. DIBK or MIBK systems, P350-P204 synergy, TOPO–amine combinations, and the recent MIBK–HSCN–glycine design show that modifiers can improve separation by changing aqueous complexation without necessarily entering the organic phase. This is strategically attractive because it suggests that future selectivity gains may be obtained by "pre-organizing" the aqueous Zr/Hf species rather than continually increasing extractant complexity (Chen et al., 2026; Wu, Xu, Dong, et al., 2022; Wu et al., 2019; Xiong et al., 2024; Xu et al., 2016; H. Zhao et al., 2024).

Table 4 compares the main solvent-extraction families by chemical role, practical strength, and principal scale-up limitation.

Table 4. Representative solvent-extraction families for Zr/Hf separation

System	Medium	Preferential behavior / function	Strength	Key limitation
TBP	Nitric acid	Solvation of nitrate complexes; nuclear-Zr purification benchmark	Mature chemistry and stagewise design data	Sensitive to acidity and requires cascade control
D2EHPA / PC88A / phosphinic acids	Sulfuric acid	Proton-exchange extraction with sulfate participation	Broad ligand flexibility; good Hf/Zr discrimination in tuned media	Coextraction, aging effects, and stripping burden

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System	Medium	Preferential behavior / function	Strength	Key limitation
Cyanex 572	Nitric acid	Selective Hf extraction by cation-exchange mechanism	High reported selectivity in optimized nitrate medium	Performance depends on nitrate/acidity window
MIBK/DIBK–SCN systems	Thiocyanate	Selective transfer amplified by aqueous cluster chemistry	Mechanistically rich; amenable to modifiers and scrubbing	Organic solvent burden and SCN^- management
Ionic-liquid / synergistic systems	Variable	Alternative solvation and coupled extraction	Potentially lower volatility and tunable chemistry	Viscosity, stripping, cost, and long-term recycle
Designer phosphinic / β-diketone ligands	Nitrate or chloride	Molecularly tuned donor geometry	High selectivity potential with mechanism-guided design	Early-stage scale and reagent synthesis burden

Note. "Strength" and "limitation" are qualitative critical-review judgments, not a statistical ranking.

Across these families, the best-performing flowsheet should combine sufficient selectivity with high loading and easy regeneration; maximizing β at the expense of stripping or solvent stability is not an industrial optimum.

Ionic liquids and emulsion- or supported-liquid-phase systems seek to reduce volatile-solvent demand or intensify interfacial area. Task-specific ionic liquids and Aliquat 336 have shown useful Zr/Hf discrimination, and researchers have proposed green emulsion liquid membranes with environmentally benign diluents. However, these routes must still demonstrate low extractant loss, stable phase behavior, rapid stripping, and long-term recycle under impurity-bearing feeds (Ismail & Aly, 2020; Pathak et al., 2021; Wu, Dong, Wu, et al., 2022).

The major industrial weakness of SX is not insufficient selectivity, but the cost and complexity of maintaining selectivity across a complete extraction–scrub–strip cascade. Scrubbing is often required to recover coextracted Zr or reject impurities; stripping must release Hf without excessive reagent consumption; degradation and entrainment must be controlled; and solvent inventory creates safety and environmental burdens. Therefore, the most credible next-generation SX systems combine moderate-to-high separation factors with high loading, simple stripping, low phase-ratio demand, and tolerance to feed aging and recycle impurities.

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5.1 Nitrate and neutral-solvation systems

TBP-based systems remain useful reference cases because they clearly demonstrate how nitrate concentration and acidity alter metal speciation and neutral complex formation. Their value in a critical review is not that they are universally superior, but that they provide a mature benchmark against which novel ligands must be compared in stage count, loading, stripping, and solvent handling.

5.2 Sulfate media and acidic organophosphorus reagents

Sulfate systems are chemically demanding because sulfate can be both an aqueous complexant and part of the transferred neutral complex. The latest mechanistic evidence therefore supports direct control of sulfate activity, feed age, and proton exchange as process variables, not merely background composition.

5.3 Chloride, thiocyanate, synergistic, and designer systems

The fastest-evolving systems combine selective ligand architecture with deliberate aqueous speciation. This includes ketone–SCN systems modified by amino acids, synergistic organophosphorus mixtures, and donor sets designed using spectroscopy or DFT. Their industrial potential depends on whether the molecular advantage remains after scrubbing, stripping, recycling, and impurity accumulation.

6. Ion Exchange, Extraction Chromatography, Adsorption, and Membrane Separation

Solid-phase separation offers a different process logic from solvent extraction: the selective ligand is immobilized or structurally integrated into a resin, silica, carbon, membrane, or porous framework. This can reduce bulk organic-solvent circulation, but it transfers the engineering challenge to mass transfer, pressure drop, fouling, capacity, elution, and sorbent lifetime. Conventional ion exchange therefore remains an important baseline for emerging adsorbents (Felipe & Ladeira, 2018; Pereira, 2026b).

Anion-exchange systems exploit differences in the formation and retention of anionic Zr/Hf complexes in chloride or sulfate media. Work with strongly basic resins, real zircon leach solutions, eudialyte-derived sulfate liquors, and continuous annular chromatography shows that resin chemistry can be integrated into both batch and continuous process configurations.

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The strongest evidence comes from studies using real feeds or dynamic columns because equilibrium batch selectivity alone does not capture mass-transfer zones, regeneration, or bed productivity (Ismail et al., 2024; Ma et al., 2019; Nemati et al., 2022; Poernomo et al., 2026).

Extraction chromatography places an SX-like reagent on a solid support, potentially combining ligand selectivity with chromatographic staging. DMHMP Levextrel resin is an example of this hybrid logic. Chelating-resin stripping studies further show that elution chemistry is as important as adsorption: a sorbent that selectively loads Hf but cannot be stripped efficiently is not a viable separation medium (Fan et al., 2022; Jakóbik-Kolon & Bok-Badura, 2022).

Functionalized sorbents have become a major research frontier. Researchers have reported phosphoric-acid ligand-modified silica that differentiates Zr and Hf under relatively mild acidity; dialkylphosphinic-acid Merrifield resins tailored for adsorption and separation; P507-modified magnetic porous carbon derived from MOFs; phosphonate-functionalized COF-derived carbon aerogels providing high-area matrices; and SBA-15 silica recently demonstrated as an Hf-selective adsorbent. These materials show that donor chemistry, pore architecture, and local surface electronic structure can engineer selectivity (Das et al., 2020; Hu et al., 2025; Shu et al., 2026; Wan et al., 2026; Wang et al., 2025; F. Zhao et al., 2024).

MOF-based push–pull concepts add a second design variable: the solution-phase complexant can be selected to bias adsorption toward one metal while suppressing the other. The MIL-101-DGA/betaine hydrochloride system demonstrates this coupled-medium approach and is conceptually important because it attempts to replace the conventional MIBK–HSCN logic with a reusable solid phase. Industrial translation, however, requires evidence of shaping, mechanical stability, hydraulic performance, ligand retention, and many-cycle regeneration—not only powder-scale adsorption capacity (Yang et al., 2025).

Membranes offer a path toward shorter process trains by coupling selective recognition with transport. Ion-imprinted membranes have demonstrated strong Hf enrichment from zirconium oxychloride solutions, while hollow-fiber renewal liquid membranes intensify contact area and can combine extraction and stripping. Unresolved questions include

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membrane lifetime, carrier loss, fouling by silica or hydrolyzed species, and whether selectivity is maintained under high total Zr loading (Tang et al., 2023; Yadollahi et al., 2019).

Across solid-phase technologies, the decisive scale-up metric is dynamic productivity per unit sorbent or membrane area. Capacity, selectivity, and kinetics must therefore be reported together with breakthrough behavior, eluent consumption, regeneration efficiency, impurity tolerance, and structural stability. Without these data, highly selective materials should be considered promising molecular platforms rather than mature process alternatives.

Table 5 summarizes the shift from conventional ion exchange toward membranes and engineered porous materials.

Table 5. Solid-phase and membrane technologies for Zr/Hf separation

Technology	Selectivity basis	Process advantage	Scale-up evidence needed	Selected evidence
Strong-base anion exchange	Retention of anionic Zr/Hf complexes	Low bulk solvent inventory; column operation	Breakthrough, elution, resin lifetime	Nemati et al., 2022; Ismail et al., 2024
Extraction chromatography	Immobilized extractant on solid support	SX-like chemistry with chromatographic staging	Ligand bleed, loading, cycle life	Fan et al., 2022
Functionalized silica/resin	Surface phosphoric/phosphinic donor groups	Mild conditions and tailored binding	Pelletization, pressure drop, regeneration	Das et al., 2020; Hu et al., 2025; Wang et al., 2025
MOF/COF-derived adsorbents	Pore + donor-group recognition	High design flexibility and surface area	Shaping, attrition, impurity tolerance	Yang et al., 2025; Shu et al., 2026
SBA-15 silica	Intrinsic silanol binding preference	Simple inorganic adsorbent concept	Dynamic capacity and multi-cycle stability	Wan et al., 2026
Ion-imprinted / liquid membranes	Selective carrier recognition + transport	Short separation/enrichment path	Carrier loss, fouling, membrane lifetime	Tang et al., 2023; Yadollahi et al., 2019

Note. Industrial relevance requires dynamic productivity, regeneration, and impurity tolerance in addition to equilibrium selectivity.

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For precipitation-based polishing, high apparent selectivity does not establish product quality if colloidal solids remain difficult to filter or wash. Hydroxide particle morphology, agglomeration, cake permeability, and entrained mother liquor should be measured together with dissolved Zr/Hf concentrations. The literature on hydroxide filterability provides methodological support, rather than direct confirmation of industrial hafnium separations (Pereira, 2026d).

The comparison emphasizes a recurring translational gap: new materials are frequently evaluated by equilibrium capacity and selectivity, whereas industrial systems are constrained by dynamic capacity, pressure drop, eluent use, and cycle life.

For ion exchange, porous solids, and membranes, equilibrium selectivity cannot substitute for dynamic evidence. Minimum reporting includes breakthrough curves and working capacity (mass Hf recovered per mass or volume of conditioned sorbent before a specified breakthrough point), bed volumes treated, mass-transfer-zone progression, pressure drop, shaped-particle size and attrition, realistic Zr/Hf feed ratios, impurity tolerance, eluent consumption, regeneration efficiency per cycle, ligand bleed, and repeat-cycle lifetime. Membranes additionally require active area, permeate flux, permeability with driving-force basis, Hf/Zr transport selectivity, carrier loss, fouling rate, and membrane lifetime. For selective cluster precipitation, report separate Hf precipitation and Zr coprecipitation yields, washed-product assay, particle size, filter flux, cake resistance, moisture, wash water, and mother-liquor entrainment; no single batch selectivity result substitutes for this package.

7. Thermal Halide, Molten-Salt, and Electrochemical Routes

Thermal and electrochemical routes become attractive when separation integrates conversion to volatile halides, molten-salt intermediates, coatings, powder, or metallic hafnium. Their central advantage is flowsheet integration; their central penalty is the need to control high temperatures, corrosive salts or halides, moisture sensitivity, materials of construction, off-gas treatment, and electrical energy demand. The literature therefore spans both Zr/Hf separation and downstream preparation of Hf metal (Pereira, 2026e; Wei et al., 2024).

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Sublimation, distillation, and salt-mediated separation can exploit halide volatility. Theoretical and experimental work on ZrF_4/HfF_4 sublimation demonstrates that volatility differences can be amplified without an aqueous organic solvent, while extractive-distillation concepts for $ZrCl_4/HfCl_4$ and recent molten-salt distillation process design address the difficult nuclear-grade purification problem at the flowsheet level. The modest relative volatility in chloride systems means stage design, salt composition, and heat integration are critical, not optional details (Ma et al., 2025; Minh et al., 2015; Postma et al., 2015, 2017).

Molten salts also provide electrochemical windows unavailable in water. Studies of Hf(IV) reduction in NaCl–KCl–K_2HfCl_6, chloride-fluoride melts, and related systems describe stepwise electroreduction, electrodeposition, and the balance between cathodic and anodic processes. Electroforming work shows that the route can move from fundamental electrochemistry toward shaped Hf products, while conductivity data for $ZrCl_4$ and $HfCl_4$ in molten chloride media inform cell design (Kuznetsov, 2020, 2022, 2025; X. Liu et al., 2016; Salyulev & Potapov, 2022).

Direct electrochemical differentiation of Zr and Hf has also been explored. Redox behavior in LiCl–KCl has been examined alongside Zr/Hf separation, while molten-salt extraction in Sn–Cu–Zr–Hf and Cu–Zr–Hf alloy systems provides alternative partitioning mechanisms. Nonaqueous room-temperature electrochemistry in anhydrous n-butanol further expands the chemical space, although industrial metal production remains dominated by high-temperature approaches (Li et al., 2020; Wang et al., 2017; L. Xu et al., 2016).

Hafnium metal finishing adds further purification options. Electrolytic powder production, electron-beam processing of Hf ingots, and electron-beam refining of technogenic Hf demonstrate that the metal stage can remove or redistribute impurities and enable recycling. These operations should not be treated as substitutes for upstream Zr/Hf separation, but as complementary purification steps whose value depends on the final product's impurity specification (Mukhachov & Kharytonova, 2018, 2019; Vutova et al., 2022).

For industrial deployment, electrochemical routes require a full energy and materials balance. Faradaic efficiency, cell voltage, current density, salt make-up, moisture control, electrode life, corrosion, and anode-gas treatment determine economics and environmental

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performance. Reviews of nuclear-grade zirconium production via molten salts and Hf electrolysis reinforce the need to link electrochemical selectivity to cell-level productivity and product specifications, rather than using voltammetry alone to assess process readiness (Wei et al., 2024; Zhou et al., 2026).

Table 6 compares the main high-temperature separation and metal-production options.

Table 6. Thermal, halide, molten-salt, and electrochemical routes

Route	Primary driving force	Potential integration benefit	Main engineering penalty	Selected evidence
ZrF_4/HfF_4 sublimation	Volatility difference	Solvent-free halide separation	High-temperature corrosion and gas handling	Postma et al., 2015, 2017
$ZrCl_4/HfCl_4$ distillation	Relative volatility in molten-salt/halide system	Direct nuclear-grade halide purification	Low relative volatility; heat and stage demand	Minh et al., 2015; Ma et al., 2025
Molten-salt electroreduction	Redox-potential control	Direct Hf metal/coating production	Salt purity, corrosion, current efficiency	Kuznetsov, 2020, 2022, 2025
Molten-salt Zr/Hf electrochemistry	Differential redox/partitioning behavior	Potential separation + metal production	Narrow operating windows and materials constraints	Li et al., 2020; L. Xu et al., 2016
Electron-beam refining	Volatilization/segregation during high-vacuum melting	Metal purification and recycling	High energy and specialized equipment	Mukhachov & Kharytonova, 2019; Vutova et al., 2022

Note. These routes become most attractive when the separation step can be integrated with halide purification or final metal production.

These routes are strongest when they collapse two objectives—purification and metal production—into one high-temperature train; otherwise their energy and materials penalties can outweigh the solvent savings achieved by avoiding aqueous SX.

Thermal and electrochemical comparisons require a distinct material–energy balance for Zr/Hf separation and for subsequent Hf-metal production: define halide speciation, relative volatility, separation stages, operating temperature, moisture control, salt composition and purification, salt makeup and purge, cell voltage, current density, charge balance, Faradaic

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efficiency, electrode service life, Hf metal recovery and purity, specific thermal energy (MJ kg^{-1} specified product), specific electrical energy (kWh kg^{-1} specified product), corrosion rates or lifetime of wetted materials, and anode off-gas treatment. Demonstrating Hf electrodeposition does not, by itself, demonstrate selective separation from zirconium.

8. Secondary Resources, Recycling, and Circular Hafnium Recovery

Secondary recovery is strategically significant because primary hafnium supply is constrained by co-production with zirconium. A secondary feed does not need to rival zircon ore in total tonnage to matter; it can be valuable if Hf is already chemically concentrated, if disposal costs are high, or if recovery can be integrated into an existing Zr purification plant. The strongest examples therefore arise from residues that are already inside the zirconium value chain (Joshi et al., 2021; Pandey et al., 2016).

Purification-plant slurry and raffinate are particularly attractive because they contain dissolved or precipitated Zr/Hf values created by upstream chemical processing. Researchers have demonstrated solvent extraction with mixed alkyl phosphine oxide on slurry-derived streams, including countercurrent mixer–settler operation and reagent recycle concepts. Such work is more industrially informative than simple batch tests because it begins to quantify concentration build-up, phase conditioning, and recovery of both Zr and Hf values (Pandey et al., 2016).

Outside the conventional zirconium plant, petroleum ash, eudialyte residues, tin-beneficiation residues, and technogenic metals offer additional opportunities. Each requires a different impurity strategy: U and other metals in petroleum ash, Nb and REEs in eudialyte-derived material, complex gangue and organics in beneficiation residues, and metallic or interstitial impurities in recycled Hf. The correct objective is therefore selective recovery with impurity routing, not simply maximum dissolution (Abd El-Hamid et al., 2015; de Oliveira Rodrigues, Pereira, et al., 2026; Ma et al., 2018; Vutova et al., 2022).

Circularity also changes how reagent use should be evaluated. If a secondary-recovery circuit returns Zr to the main plant, recycles extractant or acid, and reduces hazardous residue volume, its value can exceed the contained Hf revenue. Conversely, a route that produces a clean Hf product but creates a difficult fluoride-, chloride-, or organic-bearing waste can shift

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the environmental burden rather than solve it. For this reason, future techno-economic and environmental evaluations should link recycling studies, life-cycle analyses of zircon products, and material-system assessments (Gediga et al., 2019; Sohn, 2025; Torres de Matos et al., 2021).

9. Process Intensification and Emerging Separation Architectures

Process intensification in Zr/Hf separation is moving along three complementary directions: increasing interfacial transfer rates, immobilizing selective chemistry in structured media, and using speciation to create a new phase or transport pathway. Emulsion liquid membranes and hollow-fiber renewal systems represent the first direction; extraction chromatography, continuous annular chromatography, ion-imprinted membranes, and porous adsorbents represent the second; and oxo-cluster precipitation represents the third (Ismail & Aly, 2020; Poernomo et al., 2026; Roseborough et al., 2025; Yadollahi et al., 2019).

Intensified contactors appeal because they reduce inventory and stage count, but hydrodynamic performance must remain stable. A hollow-fiber or emulsion system can deliver high apparent mass-transfer rates yet remain industrially fragile if carrier loss, emulsion breakage, wetting changes, or fouling occur. Scale-up studies should therefore report interfacial area, flux, solvent or carrier loss, pressure drop, and stability as rigorously as chemical selectivity.

Advanced porous solids are evolving from generic ion exchange toward chemically programmed recognition. Functionalized silica, phosphinic resins, magnetic porous carbon, COF-derived aerogels, SBA-15, and MOF-based systems collectively show that the Zr/Hf problem can be attacked by tuning donor geometry, surface acidity, pore environment, and solution complexation (Das et al., 2020; Hu et al., 2025; Shu et al., 2026; Wan et al., 2026; Yang et al., 2025; F. Zhao et al., 2024). Their next development stage should prioritize pelletization, attrition resistance, regeneration, and continuous-flow testing.

Oxo-cluster chemistry offers a qualitatively different route because it separates via differential assembly, ligand lability, and solubility rather than an organic extractant. Hf-rich oxo clusters can selectively precipitate from mixed Zr/Hf systems under controlled conditions. The opportunity is substantial—a potential solvent-free separation step—but the industrial

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questions are equally clear: solids nucleation, filtration, washing, mother-liquor recycle, product redissolution, impurity incorporation, and cluster behavior at high metal concentration must be established (Roseborough et al., 2025; Sommers et al., 2022).

The critical lesson across intensified routes is that a "shorter flowsheet" is advantageous only when it also lowers total solvent, acid, energy, and waste demand. A one-step membrane or precipitation route that requires elaborate feed conditioning may simply relocate complexity upstream. Process intensification should therefore be judged by the total number and cumulative burden of integrated unit operations, not by the apparent simplicity of the separation device.

Secondary-feed opportunity should be assessed through annual stream tonnage, dry-basis Hf assay, recoverable Hf mass, achievable recovery, existing treatment route, Zr return to the parent circuit, and avoided disposal. Techno-economic and life-cycle comparisons must identify a functional unit explicitly (for example, 1 kg of specification-defined HfO_2 or Hf metal at plant gate), allocate shared upstream burdens transparently, and include mineral opening where applicable, reagents, neutralization, solvent and sorbent replacement, thermal and electrical energy, corrosion-resistant equipment, product finishing, and waste treatment. Residues are not automatically burden-free.

10. Comparative Performance, Sustainability, Economics, and Industrial Readiness

No single route dominates all criteria. Conventional SX performs strongly in throughput, controllability, and industrial precedent, but carries solvent-inventory, phase-separation, and scrubbing/stripping burdens. Ion exchange and extraction chromatography reduce bulk solvent use and can achieve high purity, but capacity and elution cycles limit productivity. Membranes and advanced sorbents may offer compact equipment and selective recognition, but evidence on lifetime and continuous real-feed operation remains limited. Thermal-halide and electrochemical routes can integrate purification and metal formation but require energy-intensive, corrosion-resistant high-temperature systems.

The most useful comparative concept is therefore "separation service delivered per unit burden." For an aqueous route, relevant denominators include kilograms of acid, extractant, scrubbing reagent, stripping reagent, and neutralization products per kilogram of Hf or nuclear-

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grade Zr produced. For a solid sorbent, they include dynamic capacity, eluent volume, cycle life, and sorbent replacement. For a molten-salt route, they include electrical and thermal energy, salt inventory, cell materials, off-gas treatment, and metal yield. Without such denominators, reported separation factors cannot be translated into environmental or economic performance.

Real-feed evidence is a major maturity discriminator. Studies using industrially representative liquors, zircon leach solution, or continuous equipment benefit TBP, D2EHPA-class SX, anion exchange, and Zr purification circuits. By contrast, many MOF, COF, silica, and membrane studies are still at synthetic-feed or small-batch scale. This does not diminish their mechanistic value, but it means that their industrial readiness should not be inferred from adsorption capacity or selectivity alone (Amaral et al., 2020; Ismail et al., 2024; Novaes et al., 2026; Shu et al., 2026; Wan et al., 2026; Yang et al., 2025).

Environmental comparisons must also include the upstream source. Zircon mining and concentration carry impacts before the separation plant, while secondary residues may enter with a portion of that burden already allocated to the host product. Life-cycle analysis of zircon sand and material-system analysis for hafnium show the importance of system boundaries, and recent critical synthesis of zirconium recovery further shows that Zr/Hf separation must be embedded in the full resource-to-product chain. A credible future TEA/LCA should model co-product allocation, avoided waste treatment, reagent recovery, and the energy intensity of metal finishing (Gediga et al., 2019; Pereira, 2026f; Torres de Matos et al., 2021).

Based on the 2015–2026 evidence, the technology landscape can be interpreted in four readiness tiers. Mature-to-industrial technologies include conventional SX and established halide-purification logic. Demonstrated but feed-specific technologies include anion exchange, extraction chromatography, and some continuous chromatographic approaches. Pilot-relevant emerging technologies include ion-imprinted membranes and advanced contactors. Laboratory-emerging concepts include designer MOF/COF adsorbents and oxo-cluster precipitation. Molten-salt electrochemistry occupies an intermediate position because its unit operations are industrially familiar in other metals, but Hf-specific integrated flowsheets

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remain less widely demonstrated. This classification is qualitative and should be updated as continuous data become available (Pereira, 2026e; Wei et al., 2024; Zhou et al., 2026).

Qualitative readiness anchors used in this review are: High = established continuous commercial processing with real feed and specified product; Medium–high = integrated pilot or sustained continuous real-feed evidence with regeneration and quality data; Medium = process-relevant equipment demonstrated but no full integrated Hf product train; Low–medium = dynamic laboratory or early pilot results lacking long-duration and impurity-tolerant verification; Low = predominantly synthetic-feed, batch, powder-scale, or proof-of-concept evidence. These are evidence categories, not formal technology readiness levels (TRLs), and cannot be mapped to numerical TRLs without independent qualification.

Table 7 condenses the route-level trade-offs, while Figure 4 positions the main technologies qualitatively by selectivity potential and industrial readiness.

Table 7. Critical comparison of hafnium recovery and Zr/Hf separation platforms

Platform	Industrial readiness	Solvent/energy burden	Selectivity control	Best-fit application
Conventional SX	High	Moderate solvent + acid	Aqueous speciation + extractant + staging	High-throughput Zr/Hf liquor purification
Ion exchange / chromatography	Medium–high	Low bulk solvent; eluent demand	Complex charge + resin affinity	Polishing, high purity, structured continuous separation
Advanced adsorbents / MOFs / COFs	Low–medium	Potentially low solvent; sorbent manufacture	Engineered binding sites	Future selective capture and polishing
Membranes / liquid membranes	Low–medium	Low inventory but carrier/membrane replacement	Selective transport	Compact intensification and enrichment
Halide distillation/sublimation	Medium–high	High thermal duty	Volatility difference	Nuclear-grade halide purification
Molten-salt electrochemistry	Medium	High electrical/thermal duty	Redox potential and salt chemistry	Integrated Hf-metal production

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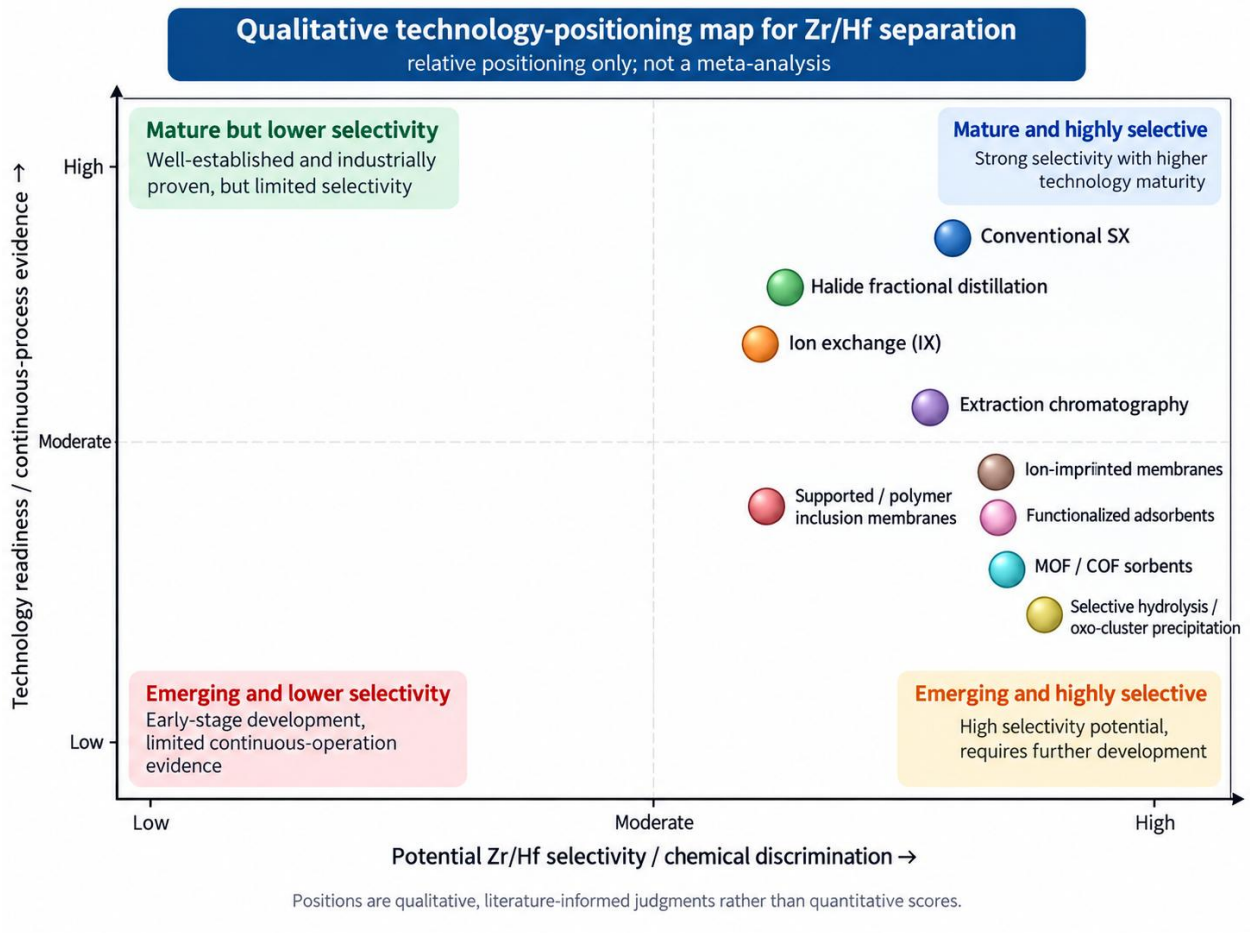
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Platform	Industrial readiness	Solvent/energy burden	Selectivity control	Best-fit application
Cluster-selective precipitation	Low	Potentially low organic-solvent burden	Aggregation, lability, solubility	Future organic-solvent-free aqueous separation

Note. Readiness is qualitative and reflects the evidence base through September 2026; it is not a formal TRL assignment.

Figure 4 qualitatively maps the principal separation platforms by selectivity potential and industrial-readiness evidence without implying a numerical technology score.



Qualitative literature-informed positioning — axis spacing is not quantitative.

Figure 4. Qualitative positioning of hafnium-separation technologies by selectivity potential and industrial readiness

Note. Author-generated qualitative synthesis based on the reviewed evidence. Positions are ordinal and interpretive; the figure deliberately omits numerical scoring because the underlying studies do not provide a common statistical basis for meta-analysis.

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An integrated flowsheet comparison should include an analytical control plan and a solid–liquid separation balance. For sulfate-bearing feeds this entails validated free-acidity measurement, mass-accounted precipitation and washing, and a documented interpretation of common-ion effects. Consequently, the operating window needs to be supported by matrix-appropriate analysis and by filtered-product recovery, not merely nominal pH or batch liquor composition (Pereira & Santos, 2025; Pereira et al., 2025; Pereira, 2026a, 2026d, 2026g).

The map highlights the central development challenge: the most novel molecular separation concepts tend to occupy the high-selectivity/low-readiness quadrant, whereas mature technologies occupy the high-readiness region with well-known reagent and equipment burdens.

11. Research Gaps and Future Directions

First, future studies should report the speciation state together with performance. Acidity, free acidity, metal loading, counter-anion concentration, aging time, temperature, and water activity should be treated as minimum descriptors. Mechanistic work has already shown that these variables can change hydrolysis, sulfate coordination, thiocyanate clustering, and extraction pathways; omitting them makes cross-study comparison unreliable (Bertoli et al., 2021; Novaes et al., 2026; Roseborough et al., 2025; Sommers et al., 2022).

Second, real-feed validation should become a publication standard for “promising” separation systems. At least one test should include industrially relevant Zr/Hf ratios and major impurities, followed by stripping or elution and recycle. Designer extractants, ion-imprinted membranes, MOFs, COF-derived sorbents, and silica adsorbents have advanced the molecular toolbox, but their comparative value will remain uncertain until durability, impurity tolerance, and product-quality data are reported (Shu et al., 2026; Tang et al., 2023; Wan et al., 2026; Xie et al., 2026; Yang et al., 2025).

Third, process intensification should target total flowsheet reduction. Continuous annular chromatography, extraction chromatography, hollow-fiber systems, and selective precipitation are particularly attractive because they may combine separation and enrichment, but they need direct comparison against a countercurrent SX baseline at equal product purity. Metrics should include residence time, stage equivalents, reagent inventory, metal holdup,

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wash demand, and recoverable off-spec material (Fan et al., 2022; Poernomo et al., 2026; Yadollahi et al., 2019).

Fourth, electrochemical research should progress from voltammetry to integrated material and energy balances. Hf deposition quality, faradaic efficiency, salt purification, anode reaction, cell corrosion, moisture sensitivity, and direct conversion of Hf-rich intermediates to metal should be quantified. The strongest research opportunity is an integrated hybrid route in which aqueous separation provides an Hf-rich feed suitable for a minimized high-temperature finishing stage (Kuznetsov, 2020, 2022, 2025; Wei et al., 2024).

Fifth, treat secondary-resource recovery as a supply-security strategy rather than a waste-treatment niche. Purification residues, tin-processing residues, eudialyte residues, and technogenic Hf should be inventoried by annual generation, chemical form, existing treatment, and recoverable Hf. The central question is how much Hf supply can be decoupled from primary zircon production while keeping marginal energy and reagent demand acceptable (de Oliveira Rodrigues, Pereira, et al., 2026; Ma et al., 2018; Pandey et al., 2016; Sohn, 2025).

Finally, the field needs a standardized benchmarking dataset. A minimum data package should include feed composition, Zr/Hf ratio, acid and anion concentrations, temperature, equilibrium time, D values for both metals, the definition of the separation factor, loading capacity, recovery after stripping or elution, impurity behavior, number of reuse cycles, and product purity. Continuous studies should additionally report throughput and residence time. Such standardization would enable meaningful meta-analysis and reduce the risk that apparent selectivity gains merely reflect incompatible test conditions rather than genuine process improvement.

Table 8 converts the recurring evidence gaps into a minimum research agenda for next-generation hafnium recovery.

Table 8. Priority research questions for next-generation hafnium recovery

Priority	Required evidence	Why it matters
Speciation-resolved testing	Free acidity, anion activity, aging, metal loading, and identified species	Makes studies comparable and prevents false selectivity attribution

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Priority	Required evidence	Why it matters
Real-feed validation	Industrial Zr/Hf ratio, key impurities, stripping/elution, and recycle	Tests whether molecular selectivity survives flowsheet complexity
Continuous operation	Breakthrough, stage equivalent, flux, residence time, and productivity	Links batch chemistry to equipment scale
Regeneration and lifetime	Multiple reuse cycles with mass balance and performance retention	Determines consumables cost and secondary waste
TEA/LCA integration	Reagent recycle, energy, co-product allocation, avoided waste treatment	Compares routes on whole-system burden
Secondary-resource inventory	Annual generation, Hf grade, chemistry, and host-plant integration	Quantifies supply-security contribution beyond primary zircon

Note. These priorities are derived from recurring evidence gaps across the reviewed technologies.

Adopting this minimum data package would make future studies more directly comparable and would enable meta-analysis of selectivity, recovery, reagent demand, and scale-up risk.

12. Conclusions

Hafnium recovery is best understood as a separation-intensive co-product system rather than a conventional stand-alone metal flowsheet. The central technical challenge is to create a controllable difference between Zr(IV) and Hf(IV) in a chemical environment in which their default behavior is nearly identical. Evidence from 2015–2026 shows that aqueous speciation, hydrolysis, counter-anion coordination, ligand design, aggregation, adsorption, volatility, and electrochemical response can amplify this difference.

Conventional solvent extraction remains the most mature and flexible route, but its future competitiveness depends on lowering solvent, scrubbing, stripping, and recycle burdens. Ion exchange, structured adsorbents, extraction chromatography, membranes, and cluster-based precipitation broaden the available selectivity mechanisms and may reduce solvent inventory, although most require stronger evidence from continuous operation and realistic feeds. Thermal-halide and molten-salt routes are particularly valuable when purification can be integrated with metal production, but energy demand, corrosion, moisture control, and salt management become dominant design constraints.

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Secondary streams deserve a larger role because they can recover hafnium that has already passed through energy- and reagent-intensive mineral-processing and decomposition steps. Their strategic value will be maximized when Hf recovery is integrated with Zr return, reagent recycle, and avoided waste treatment. Across all routes, the decisive research transition is from demonstrating selectivity to demonstrating a stable, regenerable, impurity-tolerant flowsheet. The most credible next-generation hafnium process will therefore preserve chemical discrimination while reducing total stages, reagent inventory, energy demand, and residual waste under realistic operating conditions.

Declarations

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Conflict of Interest

The author declares no conflict of interest.

Data Availability

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

Author Contributions

The author performed conceptualization, methodology, critical analysis, literature synthesis, visualization, original drafting, and review and editing.

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