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SELECTIVE THORIUM SEPARATION FROM RARE EARTH LEACH SOLUTIONS: HYDROMETALLURGICAL STRATEGIES, PROCESS LIMITATIONS, AND FUTURE PERSPECTIVES

Antonio Clareti Pereira
PhD in Chemical Engineering
São Paulo University - USP
Belo Horizonte – MG – Brazil
E-mail: claretipereira@gmail.com

https://orcid.org/0000-0001-8115-4279

Abstract

Thorium is a critical radioactive impurity in rare earth element (REE) processing and poses a major environmental, regulatory, and technological challenge to expanding sustainable REE supply chains. Selective removal of thorium from REE leach solutions is particularly difficult because efficient separation must be achieved while minimizing losses of valuable REE and maintaining process stability. This critical review analyzes recent advances (2020–2026) in thorium removal strategies for REE hydrometallurgical systems, including precipitation, solvent extraction, ion exchange, adsorption, membrane separation, and hybrid integrated processes. The fundamental chemical differences between Th(IV) and REE(III) species, including hydrolysis, complexation, and coordination behavior, are discussed to elucidate the mechanisms of separation selectivity. The review critically compares removal efficiency, REE losses, operational conditions, scalability, environmental impacts, and industrial feasibility across technologies. Particular attention is given to the limitations of laboratory-scale studies, the lack of pilot-scale validation, and challenges in radioactive residue management. Emerging trends involving functional materials, selective extractants, advanced membranes, and integrated flowsheets are also evaluated. The analysis demonstrates that future progress in REE processing depends on developing selective, scalable, and environmentally responsible strategies for thorium management compatible with industrial operations.

Keywords: Thorium removal; Rare earth elements ; Hydrometallurgy; Selective separation; Solvent extraction; Radioactive impurities

Highlights

- Selective thorium removal remains a major bottleneck in rare earth hydrometallurgy.
- High thorium removal efficiency frequently leads to undesirable rare earth losses.
- Hybrid separation flowsheets show greater industrial potential than isolated techniques.
- Pilot-scale validation and radioactive residue management remain critical research gaps.

Graphical abstract

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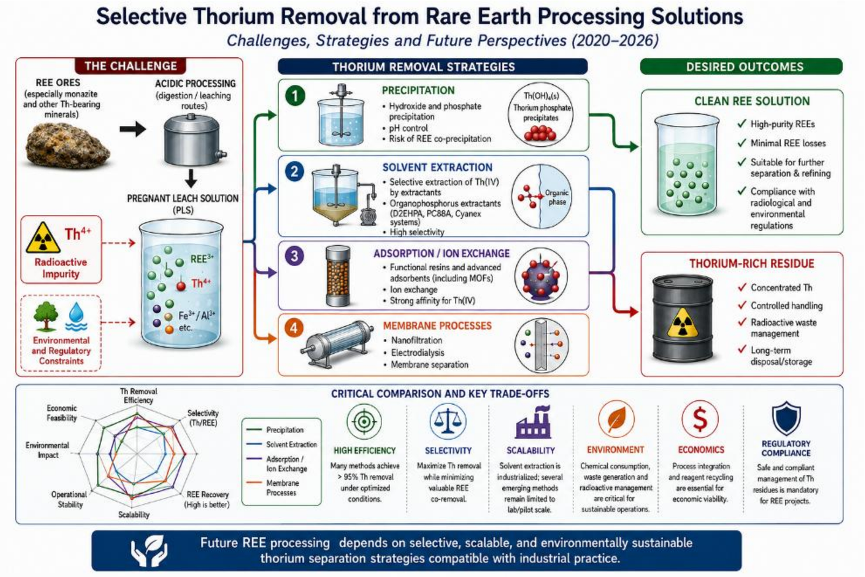

1. Introduction

Rare earth elements (REEs) are vital to technologies such as permanent magnets, electric vehicles, wind turbines, catalysts, electronics, and defense. The shift to renewable energy and digital infrastructure has boosted demand for critical REEs such as Nd, Pr, Dy, and Tb, raising concerns over supply security and sustainable processing (Vaughan et al., 2023; Rahman et al., 2025). Developing stable, eco-friendly, and geopolitically secure REE supply chains is now a key international goal.

A major challenge in REE hydrometallurgy is the presence of radioactive impurities such as thorium and uranium in the resources. Monazite, a primary mineral, often contains thorium. Others, such as bastnäsite, phosphogypsum, slags, coal refuse, and secondary residues, may also harbor radioactive elements, depending on mineralogy and processing (Fedorova et al., 2020; García et al., 2020). During acid digestion and purification, thorium can partially dissolve and spread through hydrometallurgical circuits, complicating processes and creating radioactive secondary residues.

Thorium separation from REE streams is difficult because thorium mainly exists as tetravalent Th(IV), while rare earth elements are primarily trivalent REE(III). This valence difference affects hydrolysis, complexation, ligand binding, adsorption, and precipitation, influencing separation selectivity (Teixeira et al., 2020; Gontijo et al., 2022). Therefore, thorium removal relies on subtle thermodynamic and kinetic differences rather than complete chemical dissimilarity.

Environmental and regulatory concerns over thorium residues have increased scrutiny of REE processing. Thorium wastes are classified as NORMs or TENORMs and require controlled handling, transportation, monitoring, stabilization, and containment (Aziman et al., 2021b; Atamanova et al., 2025). These steps heighten operational complexity, environmental liability, and costs. Recent life-cycle studies show that thorium stabilization and residue management can significantly impact the environmental footprint and sustainability of REE supply chains (Akhtar et al., 2025).

Selective thorium removal is a major challenge in REE hydrometallurgy. Though lab studies show 95–99% efficiency, high removal does not guarantee industrial viability. Poorly controlled separation can cause REE co-precipitation, higher reagent use, membrane fouling, faster extractant degradation, or unstable radioactive sludge. Many studies use synthetic solutions, short tests, or equilibrium conditions that do not reflect real industrial PLS, which often has high ionic strength, sulfate, solids, phosphates, and competing ions.

Over the last decade, research has focused on improving thorium selectivity using methods like precipitation, solvent extraction, ion exchange, functionalized adsorbents, membrane technologies, ionic liquids, deep eutectic solvents, and hybrid flowsheets (Chung et al., 2020a; Lv et al., 2022; Kanojia et al., 2025). Recent advances in covalent organic frameworks, selective adsorbents, and extraction systems show promising laboratory results (Liu et al., 2023; Zhong et al., 2024). However, the literature remains fragmented across hydrometallurgy, adsorption, membrane engineering, environmental remediation, and radiochemistry, complicating comparisons.

Another important limitation is the frequent extrapolation of laboratory-scale selectivity data to industrial systems without sufficient pilot-scale validation. Operational factors such as hydrodynamics, adsorption-site degradation, membrane fouling, reagent aging, residue stabilization, and long-term process robustness are still insufficiently investigated under realistic industrial conditions. Consequently, technologies that demonstrate excellent performance in simplified laboratory systems may exhibit substantially lower selectivity and stability in industrial operations.

This article was developed as a PRISMA-informed critical review rather than as a fully systematic review. The PRISMA 2020 framework was used to structure the identification, screening, eligibility assessment, and study selection, while the final synthesis was conducted

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as a critical, engineering-oriented analysis focused on selectivity, REE losses, scalability, environmental implications, radioactive residue management, and industrial feasibility (Page et al., 2021). The review critically evaluates recent advances (2020–2026) in thorium separation from REE hydrometallurgical systems, including precipitation, solvent extraction, adsorption, ion exchange, membrane separation, electrosorption, and hybrid integrated technologies. Particular emphasis is placed on the distinction between thorium removal and thorium management, as well as on the challenges of translating laboratory-scale separation technologies into robust industrial operations.

2. Methodology

The review methodology was structured according to the PRISMA 2020 framework (Page et al., 2021) to support a structured literature assessment focused on thorium separation from rare earth element (REE) process streams. The analysis emphasized the selectivity, REE losses, scalability, operational robustness, residue generation, environmental implications, and process applicability of thorium removal technologies.

The review focused on separation technologies applied to REE-bearing leach solutions, pregnant leach solutions (PLS), purification liquors, intermediate streams, and secondary residues generated during hydrometallurgical processing. Publications between January 2020 and March 2026 were prioritized to capture recent advances in thorium separation chemistry, functional materials, extraction systems, membrane technologies, and integrated purification flowsheets relevant to modern REE processing.

The literature survey was conducted using Scopus, Web of Science, ScienceDirect, and Google Scholar databases. Search strategies combined keywords related to thorium separation, REE purification, radioactive impurity management, and selective extraction technologies. The principal search terms included combinations of “thorium removal”, “selective thorium separation”, “rare earth purification”, “hydrometallurgy”, “solvent extraction”, “adsorption”, “ion exchange”, “membrane separation”, “pregnant leach solution”, “radioactive impurities”, and “REE processing”. Boolean operators and database-specific search combinations were used to improve specificity and reduce retrieval of unrelated reactor-engineering or nuclear-fuel-cycle studies.

Initially, approximately 1,180 publications were identified. After removal of duplicates, inaccessible records, repeated conference papers, unrelated studies, and publications lacking relevant hydrometallurgical information, approximately 860 titles and abstracts were screened for relevance. The final reference database included 103 publications, comprising peer-reviewed journal articles, reviews, conference proceedings, theses, and selected technical studies that contain quantitative information on thorium separation performance.

The inclusion criteria prioritized studies that included experimental, operational, or comparative information on thorium removal efficiency, REE losses, acidity or pH, adsorption capacity, extractant concentration, membrane performance, selectivity, regeneration behavior, process stability, and continuous-operation performance. Studies focused exclusively on reactor engineering, thorium fuel cycles, radiopharmaceutical applications, or unrelated radiochemical systems were excluded unless directly connected to REE purification processes. Qualitative discussions lacking relevant process information were used only for contextual interpretation.

To improve analytical consistency, the selected studies were evaluated comparatively with respect to feed composition, thorium concentration, REE composition, acidity, competing ions, operational scale, regeneration behavior, residue generation, and technological maturity. The principal separation technologies identified in the literature included precipitation and co-precipitation, solvent extraction, adsorption, ion exchange, membrane separation, electrosorption, electrochemical purification, and hybrid integrated systems.

Because the reviewed studies exhibit substantial variability in feed composition, ionic strength, acidity, and operating conditions, direct quantitative comparison between technologies remains inherently limited. Consequently, the present review emphasizes critical comparative interpretation rather than strict statistical meta-analysis.

To improve the interpretation of the evidence, the reviewed studies were qualitatively classified according to their experimental representativeness and technological maturity. The evidence classification framework adopted in this review is summarized in Table 1.

Table 1. An evidence classification framework was adopted to categorize thorium separation studies according to experimental representativeness, operational scale, and technological maturity. Adapted from Page et al. (2021), Pereira (2026a), and the evidence-quality assessment criteria proposed in this review.

Evidence Level	Description
Level 1	Synthetic single-ion laboratory batch systems
Level 2	Multicomponent synthetic REE liquors
Level 3	Real PLS or industrial leachates
Level 4	Continuous-operation or pilot-scale systems

Level 5	Industrial demonstration or commercial operation

This classification was adopted to distinguish laboratory-scale selectivity from process performance obtained under more industrially representative conditions.

The literature selection and screening workflow adopted in this review is summarized in Figure 1.

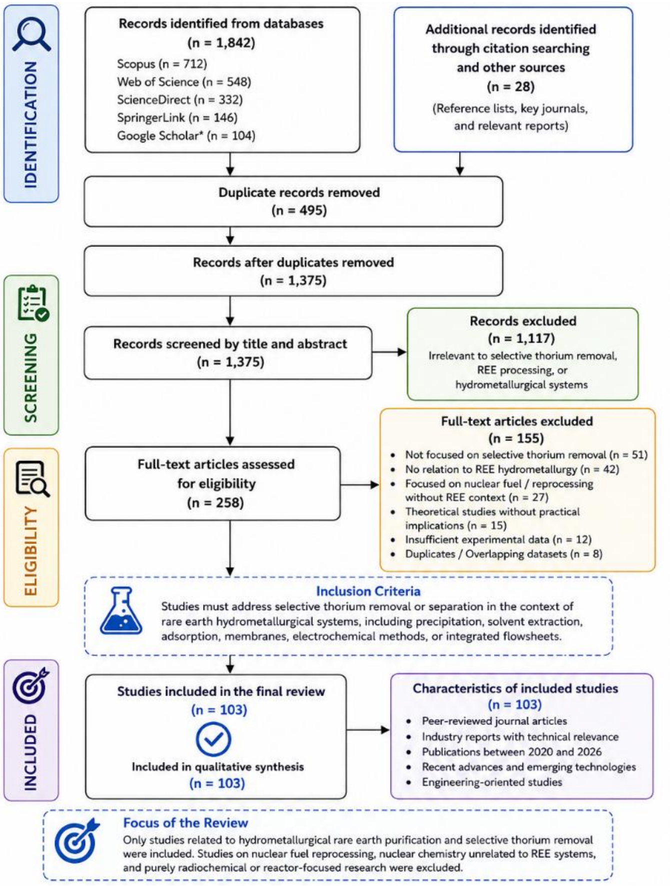

Figure 1. PRISMA-based workflow adopted for literature identification, screening, eligibility assessment, and final selection of studies related to selective thorium removal from rare earth hydrometallurgical systems between 2020 and 2026. Adapted from Page et al. (2021).

Figure 1 summarizes the progressive reduction from the initial database to the final set of selected studies. The screening strategy intentionally excluded publications unrelated to REE purification, particularly studies focused exclusively on nuclear fuel processing or reactor applications, thereby maintaining the technological focus on thorium separation in REE hydrometallurgical processing.

Screening and classification of the literature were conducted by a single reviewer, a limitation of the present review that may introduce selection bias despite the structured PRISMA-informed workflow. Additional limitations include heterogeneity in reported operating conditions, inconsistent reporting of REE losses and residue stability, limited pilot-scale data, and reduced comparability across studies conducted under substantially different chemical environments.

The next section discusses the occurrence, aqueous chemistry, and behavior of thorium in REE process systems, emphasizing how hydrolysis, complexation, charge density, and coordination chemistry influence selective separation under acidic hydrometallurgical conditions.

3. Occurrence and Behavior of Thorium in REE Systems

Thorium, a radioactive impurity in REE resources, complicates extraction and purification, influenced by mineralogy, environment, and processing. Monazite, rich in LREEs and thorium, contains 2-12 wt.% ThO_2, though higher levels can occur (Fedorova et al., 2020; Chung et al., 2020a; Rahman et al., 2025). Bastnäsite, with lower thorium below 0.5 wt.% ThO_2, is more commercially attractive. Xenotime, apatite, and secondary phosphates may also contain thorium depending on crystal structure and geological history (Verbaan et al., 2022; Rahman et al., 2025).

Thorium's mineral distribution impacts hydrometallurgy. During sulfuric acid digestion of monazite, thorium dissolves with REEs at 200-250°C, producing sulfate liquors with radioactive impurities, phosphate, and metals. In alkaline cracking, some thorium stays in insoluble residues. Nitric acid systems, like for loparite, show different behavior due to nitrate complexes and hydrolysis.

Thorium is found in secondary REE resources like phosphogypsum, tailings, coal refuse, slags, red mud, and purification residues, not just primary REE ores. Recent studies show that the distribution of thorium in these residues is highly heterogeneous, complicating extraction and stabilization. In recycling flowsheets, thorium can accumulate in residues through recirculation, raising operational and radiological risks.

Before discussing thorium's aqueous chemistry, it is important to summarize the key REE minerals associated with thorium, as mineralogy affects impurity dissolution, radioactive residues, and purification in hydrometallurgy. Table 2 lists the main thorium-bearing REE minerals and their implications.

Table 2. Main REE-bearing minerals associated with thorium occurrence, typical thorium concentrations, and implications for hydrometallurgical processing and purification. Adapted from Fedorova et al. (2020), Chung et al. (2020a), Rahman et al. (2025), and Verbaan et al. (2022).

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Mineral	Main REEs	Typical Th content	Main processing route	Main hydrometallurgical implication
Monazite	LREEs	2–12 wt.% ThO_2	Acid digestion / alkaline cracking	High thorium dissolution and radioactive residues
Bastnäsite	LREEs	<0.5 wt.% ThO_2	Acid leaching / roasting	Lower radioactive burden
Xenotime	HREEs	Low to moderate	Acid digestion	Variable Th partitioning
Apatite	Mixed REEs	Trace to moderate	Sulfuric leaching	Thorium associated with phosphate phases
Phosphogypsum	Trace REEs	Variable	Secondary recovery	Heterogeneous Th distribution

Table 2 shows that monazite streams pose the biggest purification challenge due to the dissolution of REEs, thorium, phosphate, and other impurities under acidic conditions. Bastnäsite usually yields liquor with fewer radioactive impurities, but thorium management may still be needed based on recirculation and concentrate composition.

Thorium in REE minerals relates to substitution, with Th^{4+} replacing REE^{3+} in phosphate and silicate structures due to similar ionic radii. Charge imbalance from tetravalent substitution is balanced by coupled substitutions, vacancies, or distortion, thereby causing thorium and REEs to co-occur during processing steps such as crushing, flotation, roasting, and acid digestion (Teixeira et al., 2020; Gontijo et al., 2022). Hydrometallurgically, this complicates separation because thorium often solubilizes with REEs during leaching.

The aqueous chemistry of thorium differs substantially from that of trivalent rare earth. Under most hydrometallurgical conditions, thorium exists mainly as Th(IV), a strongly hydrolyzing tetravalent cation with high affinity for oxygen ligands. Hydrolysis may occur at low pH, forming species like $ThOH^{3+}$, $Th(OH)_2^{2+}$, and hydroxide complexes. Thorium often precipitates at lower pH than REE(III) species, enabling selective separation by pH control or reagents (Gontijo et al., 2022; Kornilov et al., 2025).

Thorium's stronger hydrolysis results from its higher ionic charge density compared to REE^{3+} ions. It more readily forms complexes with sulfate, phosphate, nitrate, carbonate, and organophosphorus ligands in hydrometallurgy. In sulfate media, stable thorium sulfate complexes form under highly acidic conditions, but at higher pH, hydrolysis and precipitation occur. In nitrate media, thorium complex stability influences extraction and distribution. Chloride media may also affect speciation and separation due to ionic strength and competing ions (Elatontsev & Mukhachev, 2021; Souza & Andrade Lima, 2024).

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Before discussing separation technologies, visualize differences in hydrolysis behavior and stability between Th(IV) and REE(III) under hydrometallurgical conditions. Figure 2 compares their stability and precipitation in sulfate, chloride, and nitrate systems.

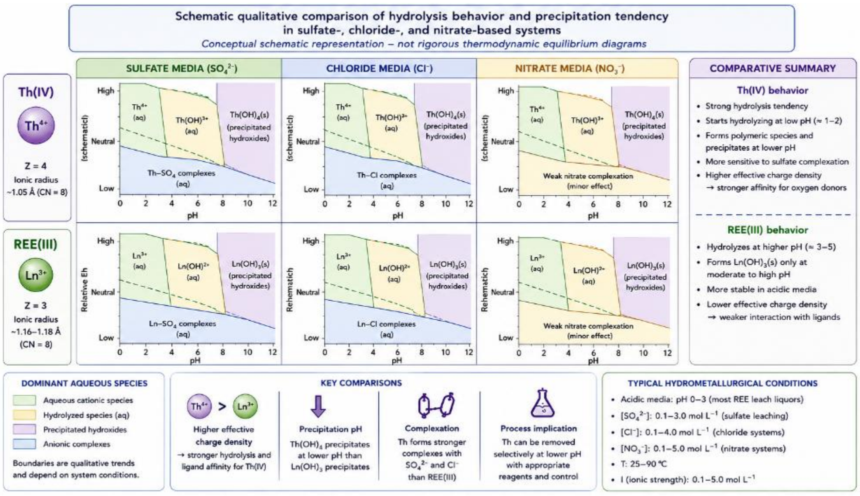

Figure 2. Schematic comparison of hydrolysis behavior, precipitation tendency, and stability domains of Th(IV) and REE(III) species in acidic hydrometallurgical systems containing sulfate, chloride, and nitrate media. Adapted from Gontijo et al. (2022), Teixeira et al. (2020), and Kornilov et al. (2025).

Figure 2 shows that Th(IV) hydrolyzes more strongly than REE(III), forming the basis for various separation methods. Real systems are affected by impurities such as Fe^{3+}, Al^{3+}, phosphate, silica, uranium, calcium, and magnesium, which influence thorium behavior, hydrolysis, and separation.

A common limitation in the literature is reliance on synthetic lab solutions that don't well mimic industrial pregnant leach liquors. Actual hydrometallurgical systems have high ionic strength, sulfate levels, residual organics, suspended solids, and complex interactions. As a result, thorium separation efficiencies in simplified lab studies may overstate industrial performance, especially in continuous, high-acidity conditions.

Thorium's occurrence and chemistry in REE systems relate to environmental risk, radioactive waste, and regulations. Understanding these is crucial since REE processing depends on the effective separation and safe handling of thorium residues. The next section reviews regulations, environmental limits, and radiological issues in thorium management.

4. Regulatory and Environmental Constraints

The environmental and regulatory issues of thorium management in REE processing are increasingly important due to rising demand and scrutiny of radioactive residues from

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hydrometallurgical operations. Thorium materials are classified as NORMs or TENORMs based on how processing alters radionuclide levels and exposure risks (Aziman et al., 2021b; Manchanda, 2023). The beneficiation, leaching, purification, and stabilization stages often concentrate thorium in waste streams, complicating environmental management and regulatory compliance.

Unlike metallic impurities, thorium's radiological behavior creates long-term environmental liabilities, affecting project approval, social acceptance, and commercial viability due to the need for controlled storage, monitoring, and containment (Vaughan et al., 2023; Atamanova et al., 2025).

Regulatory limits for thorium residues differ across regions, mainly based on dose assessment and radionuclide activity. Many countries classify residues over ~1 Bq g^{-1} for alpha emitters as radioactive waste, but thresholds vary by law and use. Industrial REE residues from monazite often exceed these limits, especially after processing concentrates thorium into small streams (Aziman et al., 2021a). Consequently, storage often needs lined containment, groundwater monitoring, shielding, and long-term control.

Environmental risks of thorium residues depend on mineral stability, leaching, particle size, acidity, and climate. Poor storage can lead to thorium mobilization via acid drainage, colloids, particles, or groundwater. Fine hydrometallurgical sludges with high moisture, high sulfate content, and poor stability pose problems. Co-occurring uranium, radium, fluoride, phosphate, and heavy metals complicate disposal (Aziman et al., 2021b; García et al., 2020).

Before discussing industrial implications, it is important to summarize the main environmental and regulatory challenges of thorium-bearing residues from REE processing. The key constraints are summarized in Table 3.

Table 3. Principal regulatory, environmental, and operational challenges associated with thorium-bearing residues generated during rare earth hydrometallurgical processing. Adapted from Aziman et al. (2021b), García et al. (2020), Manchanda (2023), and Atamanova et al. (2025).

Constraint	Main concern	Industrial implication
NORM/TENORM classification	Radioactive activity concentration	Additional licensing and monitoring
Radioactive sludge generation	Long-term residue stability	Specialized disposal infrastructure
Groundwater contamination risk	Thorium mobilization	Environmental containment systems
Airborne particulate dispersion	Radiological exposure	Dust control and shielding
Long-term storage liability	Multi-decade management	Increased CAPEX and OPEX

Regulatory uncertainty	Country-dependent thresholds	Delays in project approval

Table 3 shows that thorium management involves more than impurity removal; it also includes environmental licensing, long-term monitoring, and radioactive residue stabilization, which can significantly affect the economics of REE projects, especially monazite-based ones.

Lynas Rare Earths in Malaysia exemplifies the management issues surrounding thorium. Its Lynas Advanced Materials Plant (LAMP) produced water-leach purification residues containing thorium and uranium from monazite processing, sparking regulatory and public debate over concerns about radioactive waste, storage, groundwater contamination, and exposure. This controversy highlights how radioactive residue management influences social acceptance, licenses, and supply chain stability (Courchesne, 2020).

The Lynas case highlights that selective thorium removal isn't enough; the remaining thorium must be stabilized, transported, monitored, and stored safely. Many lab studies report high removal efficiencies but overlook residue stability, disposal costs, and radiological risks. A process producing large amounts of unstable radioactive waste may be environmentally and economically unviable, despite good lab results.

Recent studies have explored improved residue stabilization, advanced adsorbents, membrane systems, and electrosorption to reduce secondary waste (Aziman et al., 2021a; Akhtar et al., 2025; Hassan et al., 2024). Most remain at the lab scale without proven long-term industrial robustness. Key issues such as adsorbent degradation, membrane fouling, regeneration, and residue behavior remain poorly understood.

The environmental aspect of thorium management is increasingly crucial in life cycle assessments (LCA). Recent studies indicate that the environmental impact of thorium stabilization, containment, and residue transport can significantly affect the sustainability of REE supply chains (Akhtar et al., 2025). Therefore, future REE processing should focus on enhanced separation and strategies to reduce radioactive residues and environmental risks.

Before exploring separation technologies, it is important to understand how thorium residues are produced and spread in typical REE hydrometallurgical flowsheets. Figure 3 schematically shows the main sources of thorium accumulation, residue points, and environmental management needs during REE processing.

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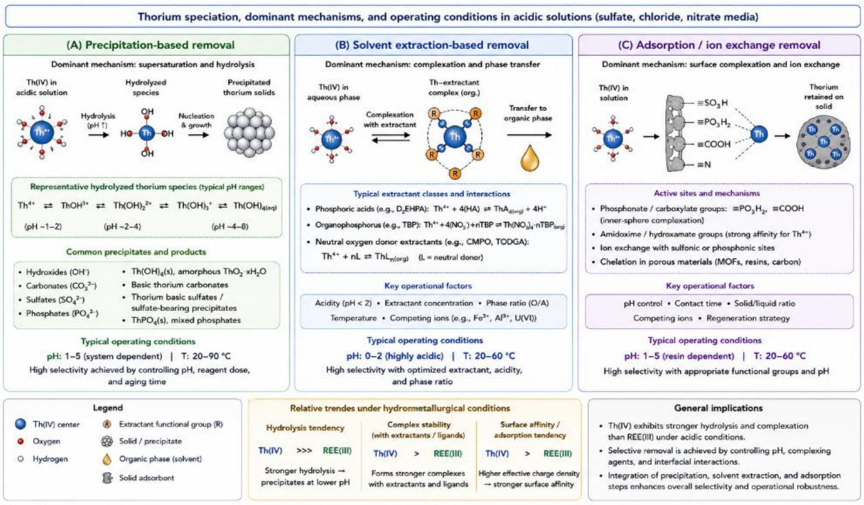

Figure 3. Simplified schematic representation of thorium distribution, radioactive residue generation, and environmental management stages during rare earth hydrometallurgical processing. Adapted from García et al. (2020), Vaughan et al. (2023), and Atamanova et al. (2025).

Figure 3 shows that thorium management encompasses the entire hydrometallurgical circuit, not just a single purification stage. Thorium can accumulate during leaching, precipitation, solvent extraction, filtration, and residue recirculation, necessitating multiple environmental and radiological controls. This holistic view is essential because environmental performance can't be judged by lab separation efficiencies alone.

The constraints indicate that thorium separation requires consideration of chemical, operational, environmental, and economic factors. Understanding the mechanisms of thorium selectivity is crucial for developing methods that minimize REE losses, radioactive residue, and environmental impact. The next section explains the principles behind selective thorium separation in hydrometallurgy.

5. Fundamentals of Selective Thorium Separation

Selective thorium separation from rare earth element (REE) process streams is fundamental. Separation relies on differences in charge density, hydrolysis behavior, complexation, coordination, and interfacial interactions between Th(IV) and REE(III). Although they coexist in hydrometallurgical liquors, their distinct aqueous chemistries allow selective separation through pH control, ligand design, adsorption, solvent extraction, or ionic transport (Othman et al., 2020; Lv et al., 2022).

Thorium primarily exists as Th^{4+}, while REEs are as REE^{3+}. Thorium's higher charge density leads to stronger interactions, increased hydrolysis, affinity for phosphate groups, and

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a greater tendency to polymerize and precipitate than REE^{3+} ions (Teixeira et al., 2020; Othman et al., 2020).

Thorium hydrolysis is key to selective separation, occurring at a lower pH than most REEs, especially in sulfate systems at pH 1–2. This difference enables pH-controlled separation, but industrial selectivity depends on factors like acidity, sulfate, phosphate, temperature, and competing ions, which can alter hydrolysis equilibria (Karmakar et al., 2021; Wang et al., 2023).

Complexation behavior also differs significantly between Th(IV) and REE(III) species. Thorium forms stronger complexes with phosphates, phosphonates, organophosphorus extractants, nitrate ligands, and oxygen-rich environments. Many solvent extraction systems use phosphorous-containing extractants designed to exploit Th^{4+}'s stronger affinity. Extractants such as D2EHPA, Cyanex derivatives, phosphoramidates, and ionic liquids bearing phosphonate or β-diketone groups often exhibit higher thorium distribution coefficients than those for REEs under controlled acidity (Saha et al., 2023; Dash et al., 2021; Li et al., 2025a).

Thorium's strong complexation is evident in adsorption and ion-exchange systems. Oxygen-rich groups such as phosphonate, carboxylate, amidoxime, and phosphate often prefer Th^{4+} due to its high Lewis acidity and hard-donor affinity. This is used in COFs, functionalized polymers, ion exchange resins, and adsorbents for thorium capture (Karmakar et al., 2021). However, selectivity observed in labs often drops in real liquors because other metals compete for active sites and alter local coordination.

Before discussing the thermodynamic and kinetic implications of selective thorium separation, it is important to compare the principal physicochemical properties that differentiate Th(IV) from REE(III) species under hydrometallurgical conditions. The main comparative characteristics governing selective separation are summarized in Table 4.

Table 4. Comparative physicochemical properties governing selective separation behavior of Th(IV) and REE(III) species in hydrometallurgical systems. Adapted from Gontijo et al. (2022), Teixeira et al. (2020), Wang et al. (2023), and Karmakar et al. (2021).

Property	Th(IV)	REE(III)	Main separation implication
Oxidation state	+4	+3	Higher charge density for Th
Hydrolysis tendency	Very strong	Moderate	Earlier Th precipitation
Complexation strength	Strong	Moderate	Enhanced ligand selectivity
Affinity for phosphorous ligands	High	Moderate	Improved SX and adsorption selectivity
Polymerization tendency	Significant	Limited	Sludge formation and colloid generation

Solubility under acidic pH	Lower at moderate pH	Higher	Selective precipitation opportunity

Table 4 shows that thorium separation mainly depends on Th(IV)'s higher charge density and stronger coordination. These differences explain why strategies use preferential hydrolysis, selective ligand binding, or stronger adsorption to thorium species.

A key overlooked aspect is the difference between thermodynamic and kinetic selectivity. Many lab studies report equilibrium data after long residence times under controlled conditions. In contrast, industrial hydrometallurgical systems rarely reach equilibrium due to factors such as residence time, mixing, mass transfer, and hydrodynamics, affecting actual separation. In continuous solvent extraction, issues like incomplete phase separation, emulsion, and kinetic limits can reduce thorium selectivity despite good equilibrium data (Lv et al., 2022; Sert & Yusan, 2023).

The distinction between thermodynamic and kinetic control is crucial in adsorption and membrane systems. High-affinity adsorbents can exhibit slow diffusion under high ionic strength, and membrane systems may experience polarization and fouling, which affect selectivity over time. Many studies overestimate separation efficiency by focusing solely on equilibrium, ignoring operational factors.

Distribution coefficients are key to selective thorium separation. In solvent extraction, thorium's distribution coefficients are often much higher than those of REEs at moderate acidity because of stronger ligand interactions and lower hydration energy. However, higher acid levels can reduce selectivity by stabilizing thorium in water or by affecting extractant protonation. Similar trends occur in ionic liquids, where acidity, nitrate levels, and ligand structure influence extraction (Lv et al., 2022; Wang et al., 2024; Yu et al., 2025).

Before examining separation technologies, it is useful to visualize the main thermodynamic and coordination mechanisms governing thorium separation. Figure 4 schematically shows the primary selective interactions in modern hydrometallurgical purification.

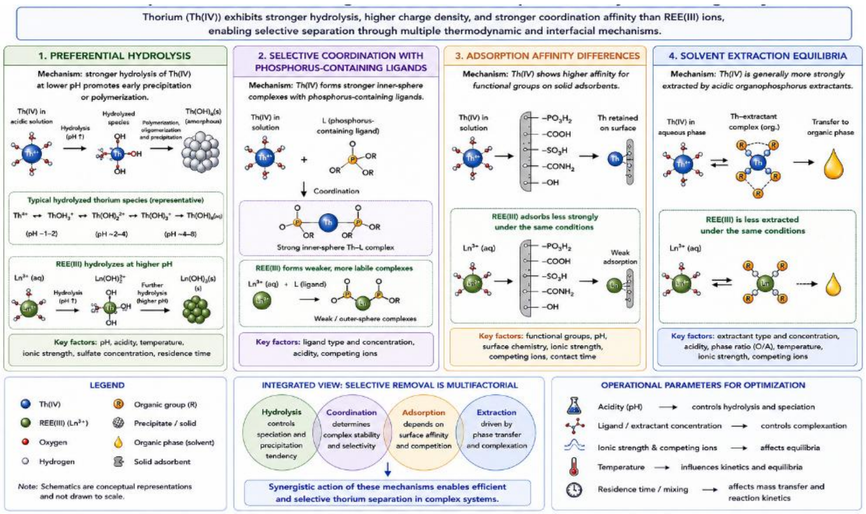

Figure 4. Schematic representation of the principal mechanisms governing selective thorium separation in hydrometallurgical systems, including preferential hydrolysis, selective coordination with phosphorous ligands, adsorption affinity differences, and solvent extraction equilibria. Adapted from Gontijo et al. (2022), Lv et al. (2022), Wang et al. (2024), and Li et al. (2025a).

Figure 4 shows that most thorium separation methods depend on multiple thermodynamic and interfacial processes, not just one. Techniques such as preferential hydrolysis, ligand coordination, adsorption, and extraction work together in industrial processes. This explains why optimization needs careful regulation of acidity, ligand levels, ionic strength, temperature, and residence time.

Despite progress in separation chemistry, key issues remain. Many studies use synthetic solutions that do not mimic the complex industrial liquids containing sulfate, phosphate, silica, iron, aluminum, calcium, uranium, and organic compounds. These conditions can reduce thorium selectivity and lead to REE losses. Few studies assess long-term extractant durability, adsorbent stability under radiation, or process performance in continuous operation.

The principles here underpin practical separation strategies, with precipitation and co-precipitation being key industrial methods. They exploit Th(IV)'s tendency to hydrolyze and its lower solubility compared to REE(III). The next section reviews these precipitation-based thorium separation strategies and their limitations.

6. Precipitation and Co-precipitation Strategies

Precipitation methods are popular for thorium removal from REE streams because they exploit Th(IV)'s stronger hydrolysis and lower solubility compared to REE(III). They are industrially attractive due to simple operation, low equipment requirements, and suitability for

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large-scale hydrometallurgy. Often used early in REE processing to reduce radioactive impurities before solvent extraction, these systems face significant selectivity challenges in real conditions.

Most precipitation methods depend on controlling pH, reagent destabilization, or forming low-solubility thorium compounds. Industrial selectivity is affected by acidity, sulfate, ionic strength, temperature, phosphate, and competing ions like Fe^{3+}, Al^{3+}, Ca^{2+}, and UO_2^{2+}. Many studies report thorium removal rates of 95–99% but also show significant loss of light rare earth elements (LREEs) such as La, Ce, and Nd due to co-precipitation and limited selectivity control (Guo et al., 2021; Azimi et al., 2025).

Before discussing individual precipitation mechanisms, it helps to compare key parameters of thorium removal systems. The main process variables and limitations are summarized in Table 5.

Table 5. Comparative operational parameters and limitations associated with precipitation and co-precipitation strategies for thorium removal from REE hydrometallurgical systems. Adapted from Guo et al. (2021), Azimi et al. (2025), Zhou et al. (2025), and Hou et al. (2025).

Strategy	Typical pH range	Main reagent	Main advantage	Main limitation
Hydroxide precipitation	1.0–3.5	NaOH, NH_4OH, $Ca(OH)_2$	Rapid Th hydrolysis	REE co-precipitation
Carbonate precipitation	2.0–5.0	Na_2CO_3, $MgCO_3$	Improved selectivity	Sludge generation
Sulfate/phosphate precipitation	Highly acidic to moderate pH	Sulfates/phosphates	Strong Th stabilization	Complex residue chemistry
Co-precipitation systems	Variable	Mixed reagents	Enhanced impurity removal	Difficult process control

Table 5 shows that precipitation selectivity depends on reagent chemistry and pH. Hydroxide systems quickly remove thorium but often poorly discriminate Th(IV) from LREEs industrially. Carbonate and phosphate systems may enhance selectivity but produce complex sludge with secondary precipitates and entrained REEs.

6.1. Hydroxide precipitation

Hydroxide precipitation is a traditional method for thorium removal, as Th(IV) hydrolyzes and precipitates at a lower pH than most REEs. Industrial and lab systems use NaOH, NH_4OH, $Mg(OH)_2$, or $Ca(OH)_2$ to form thorium hydroxide in acidic to moderately acidic conditions. In sulfate liquors, thorium may begin precipitating near pH 1–2, while REEs stay stable until higher pH levels (Guo et al., 2021).

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Despite the thermodynamic advantage, hydroxide precipitation often shows limited selectivity in practice. Factors like pH gradients, incomplete mixing, high sulfate levels, and co-hydrolysis of Fe^{3+} and Al^{3+} can lead to extensive entrainment of REEs into thorium-rich precipitates. Though thorium removal exceeds 95–99%, light REEs, especially cerium and lanthanum, are often lost. Additionally, gelatinous hydroxide sludges can hinder filtration, washing, and separation processes (Demirelli et al., 2022; Gao et al., 2023).

Hydroxide precipitation systems consume significant amounts of reagents in highly acidic, concentrated sulfate liquors, necessitating substantial alkali before thorium hydrolysis. In industrial monazite processing, with free acidity over 50–150 g L^{-1} H_2SO_4, efficiency alone isn't enough; reagent costs, sludge handling, and neutralization affect overall economics.

6.2. Carbonate precipitation

Carbonate precipitation enhances thorium selectivity and reduces hydroxide sludge. Sodium, ammonium, and magnesium carbonates are studied for their use in thorium precipitation in REE hydrometallurgy. Magnesium carbonate is promising for the removal of Fe, Al, and Th while minimizing REE losses (Azimi et al., 2025).

Carbonate systems operate within pH 2-5, depending on feed and sulfate levels. Thorium carbonate and hydroxycarbonate are less soluble than many REE carbonate complexes under mildly acidic conditions, allowing partial selective separation. However, selectivity heavily depends on solution chemistry and residence time. In high-calcium systems, secondary precipitation can consume the carbonate reagent and form large precipitates, thereby lowering efficiency (Courchesne, 2020).

One advantage of carbonate precipitation is that it reduces gelatinous sludge compared with hydroxide systems. However, carbonate routes can still produce significant secondary solids with sulfate, phosphate, calcium, silica, and REEs. Under high acidity, carbonate consumption may become excessive because acid neutralization competes with thorium precipitation. Industrial application thus requires optimizing thorium removal, carbonate use, and REE recovery (Rahman et al., 2025).25).

6.3. Sulfate/phosphate precipitation

Sulfate- and phosphate-based systems leverage thorium's affinity for sulfate and phosphate ligands. In phosphate-rich systems, thorium phosphate phases are highly insoluble and may precipitate under strongly acidic conditions, where REEs are only partially soluble. This is relevant to monazite processing, as phosphate species are naturally present in digestion liquors (Teixeira, 2020).

Sulfate/phosphate precipitation systems are complex, with amorphous thorium phosphate complicating filtration, and phosphate species interacting with REEs, Fe^{3+}, Al^{3+} to form variable mixed precipitates. Sulfate-rich systems stabilize dissolved thorium in acidic conditions, delaying precipitation and reducing selectivity (Silva et al., 2020; Brückner et al., 2020).

Another limitation is residue stability. Thorium-bearing phosphate sludges may remain in the environment and are hard to reprocess, complicating disposal. They reduce thorium mobility but produce complex residues with radionuclides, sulfates, phosphates, and heavy metals. Environmental stabilization is vital despite thorium removal.

6.4. Selective co-precipitation systems

Selective co-precipitation improves thorium removal by manipulating hydrolysis, complexation, and impurities, often using mixed reagents, staged steps, oxidation, or additives to enhance selectivity and reduce REE losses (Chen et al., 2025).

Recent studies explore impurity removal systems that precipitate thorium with Fe and Al at optimized acidity levels. Magnesium carbonate-assisted systems show promising performance in impurity removal and REE recovery, but industrial use remains uncertain, as many tests use simplified synthetic liquors and lack long-term data.

Co-precipitation systems face kinetic limits often underestimated in lab studies. Thorium removal might seem effective in batch tests but can worsen during continuous use due to incomplete particle growth, colloidal stabilization, or changes in acidity. Also, many co-precipitation systems produce fine residues that are hard to filter, retain moisture, and increase disposal costs (Kornilov et al., 2025).

Before comparing industrial precipitation systems, visualize the main mechanisms controlling thorium precipitation and the factors influencing selectivity and REE losses. Figure 5 summarizes the dominant pathways and limitations in hydrometallurgical REE processes.

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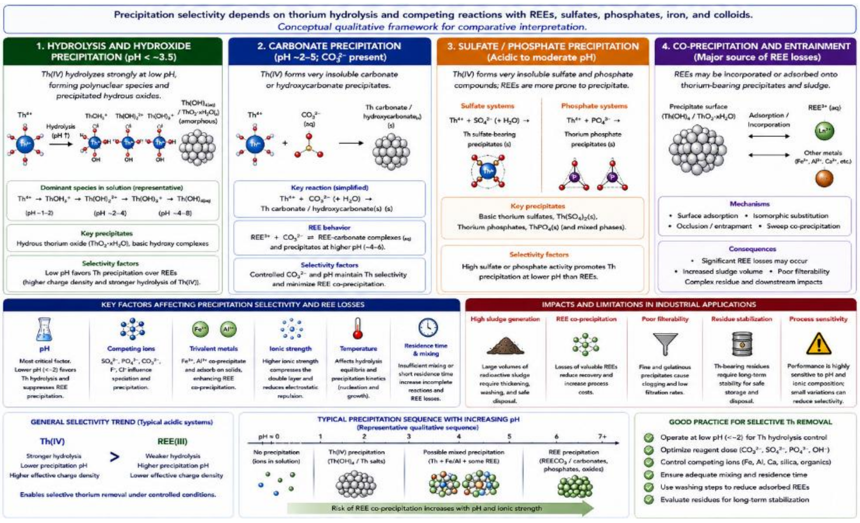

Figure 5. Schematic representation of the principal precipitation and co-precipitation mechanisms governing thorium removal from REE hydrometallurgical systems, including hydrolysis, carbonate formation, sulfate/phosphate interactions, and REE co-precipitation phenomena. Adapted from Guo et al. (2021), Azimi et al. (2025), Gao et al. (2023), and Zhou et al. (2025a).

Figure 5 shows that precipitation selectivity depends on thorium hydrolysis and competing reactions with REEs, sulfates, phosphates, iron, and colloids. Even lab systems with high thorium removal may perform poorly in industrial settings due to sludge, REE entrainment, or residue stabilization issues.

A key issue in the literature is the focus on thorium removal percentage without considering REE losses, reagent demand, sludge, or radioactive residue management. Many studies report >99% thorium removal but also show significant REE losses or produce large volumes of radioactive sludge. This is critical because precipitation systems are often proposed as scalable solutions despite limited pilot testing.

The limitations of precipitation selectivity have heightened interest in solvent extraction systems that leverage stronger coordination differences between Th(IV) and REE(III) under controlled acidity. The next section examines solvent extraction and liquid-liquid separation for thorium removal from REE liquors.

7. Solvent Extraction and Liquid–Liquid Separation

Solvent extraction is one of the most important technologies for selective thorium removal from REE hydrometallurgical systems because it offers high selectivity, operational flexibility, and compatibility with continuous industrial processing. Compared with precipitation systems, solvent extraction generally provides better process control, reduced

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sludge generation, and improved purification efficiency, particularly in monazite digestion and nitrate-based circuits (Chung et al., 2020a; Chung et al., 2020b).

Selective extraction of Th(IV) is primarily associated with its higher charge density and stronger affinity for organophosphorus ligands compared with REE(III) species. Industrial extractants exploit differences in cation exchange, solvating extraction, ion-pair formation, and synergistic coordination to improve selectivity. However, extraction performance remains highly sensitive to acidity, aqueous speciation, competing ions, phase stability, and extractant degradation.

Organophosphorus extractants, particularly D2EHPA, remain among the most widely studied reagents for thorium separation due to their strong affinity for Th(IV) in nitrate and chloride media at moderate acidity. Nevertheless, increasing acidity may suppress extraction due to proton competition and the stabilization of aqueous thorium complexes (Lv et al., 2022; Wang et al., 2024). Cyanex-based systems have also attracted attention because of their tunable selectivity and improved extraction performance under highly acidic conditions. However, these systems require strict control of acidity, extractant concentration, O/A ratio, and stripping conditions to minimize co-extraction of REEs and impurities (Sert & Yusan, 2023; Wang et al., 2024).

TBP (tributyl phosphate) and other solvating systems are commonly applied in nitrate media, where neutral thorium nitrate complexes are extracted through solvation mechanisms (Elatontsev & Mukhachev, 2021). Although these systems are industrially established, they generally exhibit lower selectivity than stronger organophosphorus extractants in highly contaminated liquors.

More recently, synergistic extraction systems combining acidic extractants, solvating agents, ionic liquids, or aminophosphorus reagents have been investigated to improve thorium selectivity and reduce REE co-extraction (Li et al., 2025a; Yu et al., 2025). These systems may enhance separation factors and extraction kinetics, although their industrial applicability is limited by process complexity, extractant aging, viscosity effects, and sensitivity to acidity and phase composition.

Before discussing process limitations in greater detail, the principal solvent extraction systems investigated for thorium separation are summarized in Table 6

Table 6. Principal solvent extraction systems investigated for selective thorium removal from REE hydrometallurgical solutions, including operating media, selectivity characteristics, and main process

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limitations. Adapted from Chung et al. (2020a), Lv et al. (2022), Wang et al. (2024), Li et al. (2025a), and Yu et al. (2025).

Extractant/system	Main medium	Main mechanism	Main advantage	Main limitation
D2EHPA	Sulfate/nitrate	Cation exchange	Strong Th affinity	Acid sensitivity
Cyanex systems	Sulfate/chloride	Organophosphorus coordination	Improved selectivity	Co-extraction of impurities
TBP	Nitrate	Solvating extraction	Stable nitrate extraction	Lower selectivity
Ionic liquids	Acidic systems	Ion-pair/synergistic extraction	High tunability	Cost and viscosity
Mixed synergistic systems	Variable	Combined coordination	Enhanced separation factors	Complex process control

Solution acidity plays a critical role in Th/REE selectivity because it directly influences extractant deprotonation and aqueous speciation equilibria. Sulfate-rich systems often suppress extraction because thorium sulfate complexes remain stable in solution, whereas nitrate systems may favor extraction through neutral nitrate complex formation. Interference from Fe^{3+}, Al^{3+}, and UO_2^{2+} also represents a major challenge because these ions may compete for organophosphorus extractants and reduce purification efficiency (Kanojia et al., 2025). Consequently, industrial circuits commonly require multistage extraction, scrubbing, and stripping operations to achieve adequate thorium selectivity and REE recovery.

Although McCabe–Thiele analysis is widely used to estimate stage requirements, many laboratory investigations report only equilibrium distribution coefficients without evaluating stage efficiency, entrainment, phase disengagement, hydrodynamic behavior, or long-term extractant degradation. Before discussing industrial scalability limitations, Figure 6 illustrates the principal extraction equilibria and operational factors governing selective thorium separation.

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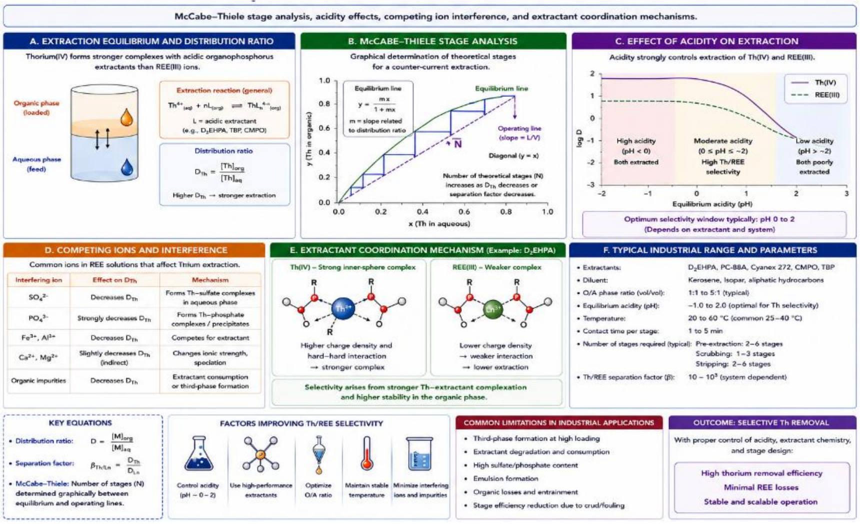

Interfering ion	Effect on D_{Th}	Mechanism
SO_4^{2-}	Decreases D_{Th}	Forms Th–sulfate complexes in aqueous phase
PO_4^{3-}	Strongly decreases D_{Th}	Forms Th–phosphate complexes / precipitates
Fe^{3+}, Al^{3+}	Decreases D_{Th}	Competes for extractant
Ca^{2+}, Mg^{2+}	Slightly decreases D_{Th} (indirect)	Changes ionic strength, speciation
Organic impurities	Decreases D_{Th}	Extractant consumption or third-phase formation

Extractants:	D_2EHPA, PC-88A, Cyanex 272, CMPO, TBP
Diluent:	Kerosene, Isopar, aliphatic hydrocarbons
O/A phase ratio (vol/vol):	1:1 to 5:1 (typical)
Equilibrium acidity (pH):	−1.0 to 2.0 (optimal for Th selectivity)
Temperature:	20 to 60 °C (common 25–40 °C)
Contact time per stage:	1 to 5 min
Number of stages required (typical):	Pre-extraction: 2–6 stages Scrubbing: 1–3 stages Stripping: 2–6 stages
Th/REE separation factor (β):	10 – 10^3 (system dependent)

- Distribution ratio: $D = \frac{[M]_{org}}{[M]_{aq}}$
- Separation factor: $\beta_{Th/Ln} = \frac{D_{Th}}{D_{Ln}}$
- McCabe–Thiele: Number of stages (N) determined graphically between equilibrium and operating lines.

- Third-phase formation at high loading
- Extractant degradation and consumption
- High sulfate/phosphate content
- Emulsion formation
- Organic losses and entrainment
- Stage efficiency reduction due to crud/fouling

With proper control of acidity, extractant chemistry, and stage design:
High thorium removal efficiency
Minimal REE losses
Stable and scalable operation

Figure 6. Representative schematic of solvent extraction equilibria for selective thorium removal from REE hydrometallurgical systems, including McCabe–Thiele stage analysis, acidity effects, competing ion interference, and extractant coordination mechanisms. Adapted from Chung et al. (2020b), Lv et al. (2022), Wang et al. (2024), and Li et al. (2025a).

Figure 6 highlights that solvent extraction performance depends not only on thermodynamic selectivity but also on phase chemistry, acidity control, stage configuration, and long-term operational stability. Consequently, systems demonstrating favorable laboratory selectivity may still face industrial limitations.

Extractant degradation remains one of the most underestimated operational challenges. Organophosphorus reagents may degrade through hydrolysis, oxidation, viscosity increase, or third-phase formation during prolonged exposure to acidic and radioactive environments. Degradation products may reduce selectivity, slow phase separation, and increase solvent losses. Similarly, ionic liquids frequently present high viscosity and stripping difficulties despite promising laboratory selectivity (Yu et al., 2025).

A recurring limitation in solvent extraction research is the emphasis on extraction efficiency rather than industrial operability. Many studies report favorable distribution coefficients under simplified laboratory conditions while neglecting emulsion formation, radiolytic stability, extractant aging, entrainment, solvent losses, and continuous-operation performance. In addition, synthetic feeds often fail to reproduce the ionic strength and impurity complexity of industrial REE liquors.

Despite these limitations, solvent extraction remains one of the most technologically mature approaches for thorium removal because of its high purification efficiency and compatibility with continuous operation. However, its operational complexity and cost have

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stimulated growing interest in adsorption, ion exchange, and advanced functional materials as complementary polishing technologies. The next section therefore examines adsorption-based systems for selective thorium separation from REE hydrometallurgical streams

8. Adsorption, Ion Exchange, and Functional Materials

Adsorption systems are increasingly used to remove thorium from REE liquors due to high selectivity, modularity, and low sludge. They reduce radioactive residues and facilitate thorium recovery at lower concentrations, with advances in materials like nanostructured adsorbents, MOFs, and COFs expanding options.

Despite these advances, adsorption systems remain strongly affected by solution chemistry and industrial operating conditions. Many materials that exhibit high thorium uptake under laboratory conditions lose selectivity in real pregnant leach solutions (PLS) due to competition from Fe^{3+}, Al^{3+}, Ca^{2+}, sulfate, phosphate, and dissolved organics. In addition, most published studies rely on simplified batch systems with low ionic strength and synthetic feeds.

Before discussing individual material classes, the principal adsorption and ion-exchange systems investigated for thorium separation are summarized in Table 7.

Table 7. Principal adsorption, ion exchange, and functional-material systems investigated for selective thorium removal from REE hydrometallurgical solutions, including dominant adsorption mechanisms, operational advantages, and practical limitations. Adapted from Alotaibi and Ismail (2022), Liu et al. (2023), Huang et al. (2025), and Wang et al. (2026a).

Material class	Main mechanism	Main advantage	Main limitation
Ion exchange resins	Ionic exchange/coordination	Mature technology	Competitive ion interference
Functionalized adsorbents	Surface complexation	High selectivity potential	Reduced performance in real PLS
MOFs/COFs/nanomaterials	Tailored coordination sites	Ultrahigh adsorption capacity	Stability and scalability issues
Biomimetic systems	Specific coordination interactions	Selective binding	Limited industrial validation

Table 7 indicates that adsorption selectivity is mainly governed by surface chemistry and coordination environment. However, adsorption capacity alone is insufficient for industrial implementation, as regeneration behavior, chemical stability, hydraulic performance, and resistance to fouling often limit long-term operation.

8.1. Ion exchange resins

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Ion exchange resins are among the most mature technologies for thorium removal because of their long industrial use in hydrometallurgy and nuclear chemistry. Selectivity depends on coordination between Th(IV) and resin functional groups, such as phosphonic, aminophosphonic, carboxylic, and sulfonic groups, which favor thorium due to its high charge density and affinity for oxygen donors (Salem & Fattah, 2021). Effective thorium removal has been reported in mildly acidic nitrate and chloride systems.

However, resin performance frequently deteriorates under industrial PLS conditions because high sulfate concentration, ionic strength, and competition from Fe^{3+} and Al^{3+} reduce thorium selectivity. Fouling caused by solids, silica, organics, or precipitates may also decrease adsorption capacity and flow stability during continuous operation (Talan & Huang, 2020a). Advanced extraction resins containing ionic liquids or organophosphorus functionalities have demonstrated improved selectivity, although large-scale implementation remains limited by synthesis cost, regeneration complexity, and insufficient long-term stability data (Zhou et al., 2025b; Wang et al., 2025).

8.2. Functionalized adsorbents

Functionalized adsorbents include polymeric, mineral, carbonaceous, magnetic, and hybrid materials modified with phosphonate, phosphate, amidoxime, amino, or oxygen-rich groups to improve thorium affinity (Hu et al., 2022; Chen et al., 2022). Several studies report adsorption capacities exceeding 100–300 mg g^{-1} using modified zeolites, graphene oxide, chitosan, phosphonic materials, and magnetic adsorbents (Alotaibi & Ismail, 2022; Yan et al., 2024; Guo et al., 2024).

Many reported capacities are from ideal lab conditions with single-component solutions, low ionic strength, and batch equilibrium. In industrial REE liquors, competition from Fe^{3+}, Al^{3+}, Ca^{2+}, phosphate, and sulfate often decreases thorium uptake and selectivity. Regeneration issues persist because repeated acid stripping can degrade surfaces, hydrolyze ligands, cause pore collapse, or cause irreversible metal binding, especially in strongly acidic sulfate or chloride media (Zahakifar & Khanramaki, 2024; Utesheva et al., 2025).

8.3. MOFs and nanomaterials

MOFs, COFs, and nanostructured adsorbents have attracted increasing attention for their tunable pores, large surface areas, and highly selective Th(IV) coordination sites (Liu et al., 2023). Recent studies involving phosphonate MOFs, oxygen-rich COFs, thiophene

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frameworks, and nanocomposites report rapid adsorption kinetics and strong thorium affinity, even under acidic conditions (Zhong et al., 2024; Wang et al., 2026a; Khan et al., 2026).

Despite promising lab results, industrial use is uncertain. Many nanostructured systems lack stability under acidic conditions, and issues like high synthesis costs, mechanical fragility, pressure drop, and sensitivity to solids hinder scale-up. Radiological stability is rarely tested, although prolonged alpha radiation exposure could affect framework integrity and pore structure (Hassan et al., 2024; He et al., 2026). High adsorption in synthetic systems doesn't guarantee industrial feasibility.

8.4. Biomimetic and bio-inspired systems

Biomimetic and bio-inspired materials represent an emerging class of thorium-selective adsorbents designed to mimic natural coordination and mineralization mechanisms. These systems commonly employ phosphate-rich coatings, biopolymers, modified biomass, algal composites, or nano-biochar to improve Th(IV) binding (Chen et al., 2025; Abu Shawer et al., 2025; Orabi et al., 2020).

While these materials are renewable and recyclable, they often have poor acid resistance, low stability, biological degradation, and reduced selectivity in sulfate-rich industrial liquors with competing ions. As a result, industrial validation remains limited.

Before discussing broader technological limitations, Figure 7 summarizes the principal adsorption and coordination mechanisms governing selective thorium uptake in advanced adsorption systems.

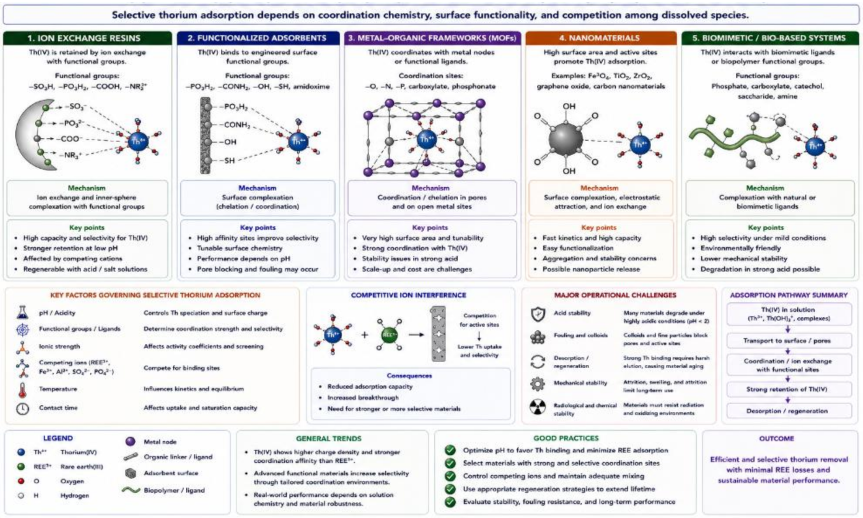

Figure 7. Schematic representation of the principal adsorption and coordination mechanisms governing selective thorium uptake in ion exchange resins, functionalized adsorbents, MOFs, nanomaterials, and

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biomimetic systems, including competitive ion interference and regeneration limitations. Adapted from Liu et al. (2023), Huang et al. (2025), Chen et al. (2026a), and Wang et al. (2026a).

Figure 7 highlights that adsorption selectivity is strongly influenced by coordination chemistry, surface functionality, ionic competition, and material stability. A recurring limitation in the literature is the excessive emphasis on equilibrium adsorption capacity without adequate evaluation of regeneration behavior, hydraulic stability, radiological durability, pressure drop, or long-term continuous operation. Most investigations remain restricted to laboratory-scale batch experiments and lack validation using real industrial process streams.

Despite these limitations, adsorption and functional-material systems remain promising as polishing technologies integrated with precipitation and solvent extraction circuits. Their modular operation, low sludge generation, and potential for trace-thorium removal make them attractive for future hybrid purification flowsheets. However, substantial technological gaps remain before large-scale industrial implementation becomes feasible

Limitations of adsorption and ion exchange methods have spurred interest in membrane and electrochemical techniques that cut reagent use and enhance selective separation during continuous operation. The next section reviews these technologies for removing thorium from REE hydrometallurgical systems.

9. Membrane and Electrochemical Approaches

Membrane and electrochemical technologies are increasingly investigated for selective thorium removal from REE hydrometallurgical systems because they enable continuous operation, reduce reagent consumption, lower sludge generation, and can be integrated into advanced purification circuits. Unlike precipitation systems, these approaches rely on engineered ionic transport, charge selectivity, or electrochemical behavior to improve separation performance, particularly for low-concentration thorium polishing and hybrid flowsheets.

Despite these advantages, industrial implementation remains limited by membrane fouling, chemical degradation, poor acid resistance, high energy demand, and instability under acidic conditions during REE processing. Although several studies report promising laboratory selectivity, such performance is often difficult to maintain in industrial pregnant leach solutions (PLS) containing sulfate, silica, suspended solids, phosphate species, and competing multivalent ions.

Before discussing individual technologies, the principal membrane and electrochemical approaches investigated for thorium separation are summarized in Table 8.

Table 8. Principal membrane and electrochemical technologies investigated for selective thorium removal from REE hydrometallurgical systems, including dominant separation mechanisms, operational advantages, and major limitations. Adapted from Milani et al. (2022), Nechifor et al. (2024), Iskandar et al. (2024), and Fu et al. (2025)

Technology	Main mechanism	Main advantage	Main limitation
Nanofiltration	Charge/size exclusion	Partial selective retention	Fouling and pressure demand
Ultrafiltration	Particle/colloid separation	Sludge reduction	Limited ionic selectivity
Hybrid membranes	Functionalized transport	Improved selectivity	Membrane degradation
Electrodialysis	Ionic migration under electric field	Continuous separation	High energy consumption
Electrochemical systems	Redox/electrosorption	Reduced reagent use	Electrode instability

Table 8 indicates that membrane and electrochemical systems generally offer lower chemical consumption and improved process control compared with precipitation systems. However, long-term operational stability remains a major barrier for industrial implementation under highly acidic conditions.

Nanofiltration (NF) is a well-studied membrane technique for thorium separation, differentiating ions by charge, size, and surface interactions. In sulfate-rich REE liquids, thorium often shows higher retention than REEs due to its charge density and hydrolyzed complexes (Man et al., 2023). Studies report rejection rates above 80–95% under optimal conditions, but NF performance depends on feed composition, membrane chemistry, and fouling control. Factors like sulfate, silica, colloids, and hydrolysis products can reduce permeability and membrane stability, often requiring pretreatment or cleaning (Milani et al., 2022; Yussuf et al., 2024).

Ultrafiltration (UF) systems exhibit lower ionic selectivity because they primarily remove colloids and suspended particles rather than dissolved ions. However, UF may still assist with thorium management by removing colloidal thorium hydroxides, radioactive particulates, and sludges generated during upstream precipitation stages (Aziman & Ismail, 2020b). Because of its lower pressure requirements and energy consumption, UF is mainly used in the clarification and polishing stages rather than for direct ionic separation.

Hybrid membrane systems incorporating functionalized surfaces, graphene oxide derivatives, phosphonate groups, ionic liquids, MOFs, or nanocomposite layers have

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demonstrated improved thorium selectivity under laboratory conditions (Fu et al., 2025; Chen et al., 2026b). These systems combine physical separation with selective chemical interactions between thorium species and membrane ligands. However, industrial applicability remains uncertain because membrane degradation, swelling, pore collapse, and acid hydrolysis may progressively reduce long-term stability under aggressive hydrometallurgical conditions.

Electrodialysis and electrochemical systems attract interest due to their potential to improve thorium selectivity and reduce reagent use through electrically driven ionic transport. Technologies like electro-assisted adsorption, capacitive deionization, electrocoagulation, and electrosorption show moderate separation performance (Ma et al., 2025). However, acidic sulfate-rich environments often increase electrical resistance, cause membrane scaling, electrode degradation, gas evolution, and operational instability, especially in large-scale continuous systems.

Before discussing the limitations of membrane and electrochemical systems, Figure 8 illustrates the principal transport pathways, fouling mechanisms, and electro-assisted separation processes governing thorium separation under hydrometallurgical conditions.

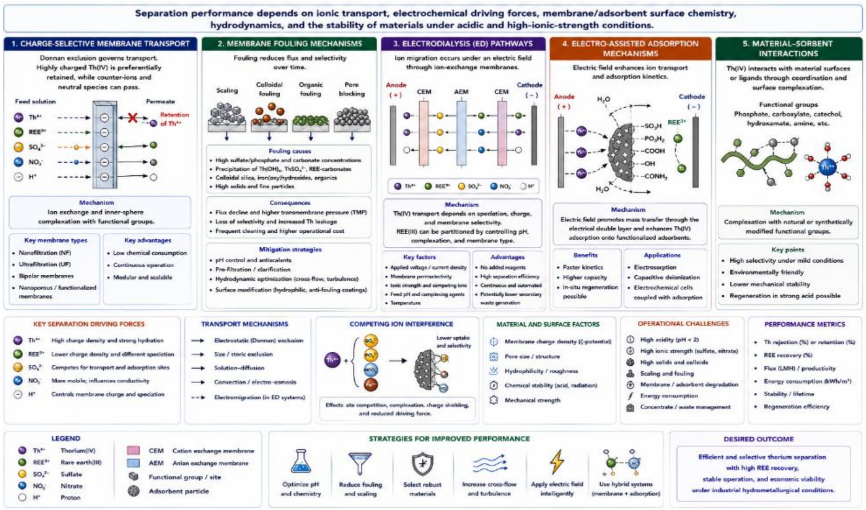

Figure 8. Schematic representation of the principal membrane and electrochemical mechanisms governing thorium separation from REE hydrometallurgical systems, including charge-selective transport, membrane fouling, electrodialysis pathways, and electro-assisted adsorption mechanisms. Adapted from Milani et al. (2022), Nechifor et al. (2024), Fu et al. (2025), and Chen et al. (2026b).

Figure 8 highlights that membrane and electrochemical systems are strongly influenced by ionic transport, hydrodynamics, surface chemistry, and long-term material stability. Consequently, high laboratory selectivity does not necessarily translate into industrial

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robustness under high-acidity and high-solids conditions typical of industrial REE process streams.

A major limitation in the literature is the lack of long-duration operational studies. Many investigations report only initial thorium rejection or adsorption performance without evaluating membrane lifespan, fouling evolution, cleaning requirements, electrode degradation, or long-term energy demand. Economic feasibility also remains uncertain because these systems frequently require substantial capital investment, pretreatment infrastructure, pressure-resistant equipment, and high electrical energy input.

Despite these limitations, membrane and electrochemical systems remain promising as complementary technologies integrated with precipitation, solvent extraction, or adsorption in hybrid purification circuits. Their reduced secondary residue generation and continuous-operation capability may become increasingly important as REE hydrometallurgical systems evolve toward more integrated and environmentally controlled flowsheets.

Table 9 summarizes the principal advantages, limitations, operational characteristics, and technological challenges associated with precipitation, solvent extraction, adsorption, and membrane systems for separating thorium from REE in hydrometallurgical systems.

Table 9. Comparative assessment of the principal thorium separation technologies applied to REE hydrometallurgical systems. Adapted from Chung et al. (2020a), Aziman et al. (2021b), Liu et al. (2023), Man et al. (2023), Kanojia et al. (2025), and the comparative engineering analysis developed in the present review.

Criterion	Precipitation	Solvent Extraction (SX)	Adsorption	Membrane Systems
Selectivity toward Th(IV)	Moderate to high	High	Moderate to very high	Moderate to high
REE co-losses	Often significant	Generally low when optimized	Variable depending on adsorbent	Moderate
Operating acidity tolerance	Moderate	High	Frequently limited at high acidity	Membrane-dependent
Process complexity	Low	High	Moderate	Moderate to high
Reagent consumption	High	Moderate to high	Low to moderate	Moderate
Sludge/residue generation	High	Moderate	Low	Low
Continuous-operation suitability	High	High	Moderate	Moderate
Regeneration requirements	Limited	Essential	Essential	Essential

Sensitivity to competing ions	High	Moderate	High	Moderate
Fouling/degradation tendency	Low	Extractant degradation possible	Adsorbent aging possible	Membrane fouling significant
Scalability	Commercially established	Commercially established	Mostly pilot/laboratory scale	Mostly pilot scale
Technological maturity	High	High	Moderate	Moderate
Main advantages	Simplicity and low capital cost	High selectivity and industrial applicability	High selectivity using advanced materials	Reduced sludge generation
Main limitations	REE co-precipitation and sludge generation	Solvent degradation and process complexity	Limited industrial validation	Fouling and membrane stability

Table 9 shows that no single technology simultaneously maximizes selectivity, simplicity, scalability, and environmental performance. Precipitation and solvent extraction remain the most industrially mature approaches, whereas adsorption and membrane systems demonstrate promising selectivity but still face limitations related to fouling, regeneration, long-term stability, and pilot-scale validation. Consequently, future industrial implementation will likely depend on integrated hybrid flowsheets combining multiple complementary separation technologies.

The limitations of isolated separation technologies have spurred greater interest in integrated and hybrid purification strategies that combine precipitation, solvent extraction, adsorption, and membrane systems in multi-stage setups. The next section examines integrated and hybrid flowsheets for the selective removal of thorium from REE hydrometallurgical systems.

10. Integrated and Hybrid Separation Flowsheets

Integrated and hybrid purification flowsheets are increasingly important in REE hydrometallurgy because isolated separation methods rarely achieve high thorium selectivity, low REE losses, operational stability, environmental safety, and economic viability simultaneously. Industrial thorium management, therefore, relies on combining precipitation, solvent extraction, adsorption, membrane systems, and recirculation strategies within integrated process circuits (Verbaan et al., 2022; Kanojia et al., 2025).

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Thorium behavior changes significantly throughout hydrometallurgical circuits because speciation, hydrolysis, and complex stability depend on acidity, sulfate concentration, impurities, and internal recirculation. Consequently, technologies that perform well under specific laboratory conditions may exhibit reduced selectivity or stability in industrial PLS. Hybrid flowsheets help distribute purification tasks across multiple stages, improving overall robustness and process flexibility.

A common industrial strategy combines selective precipitation with solvent extraction. Initial precipitation stages partially remove thorium, iron, and other impurities before solvent extraction polishing, thereby reducing extractant consumption, organic degradation, and the number of extraction stages required (Demirelli et al., 2022). Partial hydroxide or carbonate precipitation may significantly decrease dissolved thorium levels, although excessive precipitation can still promote undesirable REE co-losses and sludge generation.

Recent investigations have also explored adsorption-assisted hybrid systems integrated with membrane concentration or solvent extraction polishing stages (Larochelle et al., 2024; Talan et al., 2023). Adsorption columns are often proposed for trace-thorium polishing, whereas membrane systems may assist in reagent recovery, stream concentration, or solids reduction prior to adsorption. However, industrial implementation remains limited because of membrane fouling, operational complexity, pressure requirements, and uncertain long-term stability under acidic conditions.

Recirculation strategies are another critical aspect of hybrid thorium management. Although process liquor recycling improves reagent utilization and water efficiency, thorium accumulation in recycle loops may destabilize purification stages and increase ionic strength, impurity buildup, and sludge generation, particularly in sulfate-rich systems (Verbaan et al., 2025). Effective thorium management, therefore, requires integrated control of the entire hydrometallurgical circuit rather than optimization of isolated separation units.

Before discussing the broader industrial implications of hybrid systems, the principal integrated separation strategies investigated for thorium removal are summarized in Table 10.

Table 10. Principal integrated and hybrid separation flowsheets were investigated for selective thorium removal from REE hydrometallurgical systems, including process integration strategies, operational advantages, and main industrial limitations. Adapted from Verbaan et al. (2022), Larochelle et al. (2024), Rahman et al. (2025), and Pereira (2026b).

Hybrid strategy	Main integration concept	Main advantage	Main limitation
Precipitation + SX	Bulk impurity removal followed by polishing	Reduced extractant loading	Sludge generation

Adsorption + membrane	Fouling reduction and polishing	Improved trace-thorium control	Membrane instability
Multi-stage SX circuits	Sequential selective extraction	High purification efficiency	Complex operation
Integrated recycle systems	Reagent and water recovery	Lower operating cost	Thorium accumulation
Hybrid polishing circuits	Combined polishing technologies	Improved selectivity	Increased CAPEX

Table 10 shows that hybrid systems improve overall process performance by distributing operational limitations among multiple purification stages rather than eliminating them. This approach increases selectivity and flexibility but also introduces greater process complexity and control requirements.

The industrial focus in REE hydrometallurgy is therefore shifting from the search for a single “universal” thorium separation technology toward optimized hybrid flowsheets that balance selectivity, reagent consumption, environmental performance, and operational stability. This transition is especially important because many advanced adsorbents, membrane systems, and functional materials still exhibit limited scalability or insufficient pilot-scale validation.

Integrated flowsheets may also improve environmental performance by reducing radioactive residue generation and enhancing thorium containment through combined purification and recycling strategies. Nevertheless, these systems pose engineering challenges, including hydrodynamic instability, impurity recirculation, reagent interactions, and long-term operational control. Many hybrid flowsheets remain insufficiently validated under continuous industrial conditions.

Before comparing the principal separation technologies, Figure 9 presents a representative hybrid thorium management flowsheet illustrating the interactions among precipitation, solvent extraction, adsorption, membrane polishing, and recycle stages in REE hydrometallurgical circuits.

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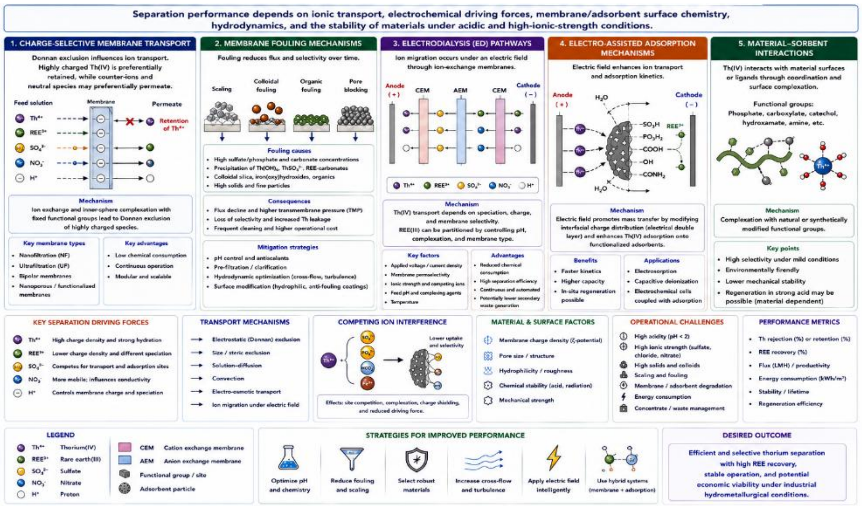

Separation performance depends on ionic transport, electrochemical driving forces, membrane/adsorbent surface chemistry, hydrodynamics, and the stability of materials under acidic and high-ionic-strength conditions.

1. CHARGE-SELECTIVE MEMBRANE TRANSPORT

Donnan exclusion influences ion transport. Highly charged Th(IV) is preferentially retained, while counter-ions and neutral species may preferentially permeate.

Mechanism
Ion exchange and inner-sphere complexation with fixed functional groups lead to Donnan exclusion of highly charged species.

Key membrane types
- Nanofiltration (NF)
- Ultrafiltration (UF)
- Bipolar membranes
- Nanoporous / functionalized membranes

Key advantages
- Low chemical consumption
- Continuous operation
- Modular and scalable

2. MEMBRANE FOULING MECHANISMS

Fouling reduces flux and selectivity over time.

Fouling causes
- High sulfate/phosphate and carbonate concentrations
- Precipitation of $Th(OH)_4$, $ThSO_4^{2+}$, REE-carbonates
- Colloidal silica, iron(oxy)hydroxides, organics
- High solids and fine particles

Consequences
- Flux decline and higher transmembrane pressure (TMP)
- Loss of selectivity and increased Th leakage
- Frequent cleaning and higher operational cost

Mitigation strategies
- pH control and antiscalants
- Pre-filtration / clarification
- Hydrodynamic optimization (cross-flow, turbulence)
- Surface modification (hydrophilic, anti-fouling coatings)

3. ELECTRODIALYSIS (ED) PATHWAYS

Ion migration occurs under an electric field through ion-exchange membranes.

Mechanism
Th(IV) transport depends on speciation, charge, and membrane selectivity. REE(III) can be partitioned by controlling pH, complexation, and membrane type.

Key factors
- Applied voltage / current density
- Membrane permselectivity
- Ionic strength and competing ions
- Feed pH and complexing agents
- Temperature

Advantages
- Reduced chemical consumption
- High separation efficiency
- Continuous and automated
- Potentially lower secondary waste generation

4. ELECTRO-ASSISTED ADSORPTION MECHANISMS

Electric field enhances ion transport and adsorption kinetics.

Mechanism
Electric field promotes mass transfer by modifying interfacial charge distribution (electrical double layer) and enhances Th(IV) adsorption onto functionalized adsorbents.

Benefits
- Faster kinetics
- Higher capacity
- In-situ regeneration possible

Applications
- Electrosorption
- Capacitive deionization
- Electrochemical cells coupled with adsorption

5. MATERIAL–SORBENT INTERACTIONS

Th(IV) interacts with material surfaces or ligands through coordination and surface complexation.

Functional groups: Phosphate, carboxylate, catechol, hydroxamate, amine, etc.

Mechanism
Complexation with natural or synthetically modified functional groups.

Key points
- High selectivity under mild conditions
- Environmentally firendly
- Lower mechanical stability
- Regeneration in strong acid may be possible (material dependent)

KEY SEPARATION DRIVING FORCES

Th^{4+}	High charge density and strong hydration
REE^{3+}	Lower charge density and different speciation
SO_4^{2-}	Competes for transport and adsorption sites
NO_3^-	More mobile; influences conductivity
H^+	Controls membrane charge and speciation

TRANSPORT MECHANISMS
- Electrostatic (Donnan) exclusion
- Size / steric exclusion
- Solution–diffusion
- Convection
- Electro-osmotic transport
- Ion migration under electric field

COMPETING ION INTERFERENCE

Effects: site competition, complexation, charge shielding, and reduced driving force.

MATERIAL & SURFACE FACTORS
- Membrane charge density (ζ-potential)
- Pore size / structure
- Hydrophilicity / roughness
- Chemical stability (acid, radiation)
- Mechanical strength

OPERATIONAL CHALLENGES
- High acidity (pH < 2)
- High ionic strength (sulfate, chloride, nitrate)
- High solids and colloids
- Scaling and fouling
- Membrane / adsorbent degradation
- Energy consumption
- Concentrate / waste management

PERFORMANCE METRICS
- Th rejection (%) or retention (%)
- REE recovery (%)
- Flux (LMH) / productivity
- Energy consumption (kWh/m^3)
- Stability / lifetime
- Regeneration efficiency

LEGEND

Th^{4+}	Thorium(IV)
REE^{3+}	Rare earth(III)
SO_4^{2-}	Sulfate
NO_3^-	Nitrate
H^+	Proton
CEM	Cation exchange membrane
AEM	Anion exchange membrane
	Functional group / site
	Adsorbent particle

STRATEGIES FOR IMPROVED PERFORMANCE

DESIRED OUTCOME

Efficient and selective thorium separation with high REE recovery, stable operation, and potential economic viability under industrial hydrometallurgical conditions.

Figure 9. Representative integrated and hybrid thorium separation flowsheets for REE hydrometallurgical systems, including precipitation, solvent extraction, adsorption, membrane polishing, and internal recycle strategies. Adapted from Verbaan et al. (2022), Demirelli et al. (2022), Vaughan et al. (2023), and Pereira (2026b).

Figure 9 shows that effective thorium management relies on integrated processes, not just optimizing individual technologies. The literature often evaluates separation tech in isolation, ignoring upstream leaching, downstream purification, reagent recycling, residue stabilization, and economics. As a result, lab-scale systems may not be practical industrially.

This section's integrated perspective underpins the upcoming comparative analysis, which examines principal thorium separation technologies with respect to selectivity, REE losses, robustness, scalability, environmental impact, and industrial feasibility.

11. Comparative Critical Analysis

Thorium removal from REE hydrometallurgical systems isn't just about separation efficiency. While lab studies show high thorium removal, industrial success also depends on REE losses, stability, scalability, environment, residue management, and cost. Comparing technologies requires an engineering assessment of thermodynamics, process robustness, radioactive waste, and industrial relevance.

Technological maturity varies among separation systems. Most adsorption, MOF, membrane, and electrochemical methods are at low-to-intermediate readiness levels (TRL 2–5) due to limited pilot validation, long-term data, and stability issues under industrial conditions. Conversely, precipitation and solvent extraction are established (TRL 8–9) with proven large-scale use, despite operational and environmental limitations.

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A key conclusion from the current literature is that no single technology simultaneously achieves high thorium selectivity, low REE losses, low reagent consumption, minimal residue generation, operational simplicity, and industrial scalability under all process conditions. Instead, each separation method presents specific advantages and limitations that become more evident under industrial operation.

Before discussing individual aspects in greater detail, it is important to summarize the principal operational trade-offs associated with the major thorium separation technologies. The comparative performance of the principal approaches reviewed in this study is summarized in Table 11.

Table 11. Comparative evaluation of the principal thorium separation technologies investigated for REE hydrometallurgical systems, including thorium removal efficiency, REE losses, operational pH range, scalability, and main process limitations. Adapted from Azimi et al. (2025), Wang et al. (2024), Zhou et al. (2025b), Li et al. (2026), and Yu et al. (2025).

Method	Typical Th removal (%)	Typical REE loss (%)	Main pH range	Scalability	Main limitation
Hydroxide precipitation	90–99	5–25	1–3.5	High	REE co-precipitation
Carbonate precipitation	80–98	3–15	2–5	Moderate to high	Sludge generation
Sulfate/phosphate precipitation	85–99	5–20	Acidic to moderate	Moderate	Complex residue chemistry
Solvent extraction	90–99+	<5–15	Strongly acidity-dependent	High	Multi-stage complexity
Adsorption/ion exchange	70–99	<5–10	Variable	Moderate	Competitive ion interference
MOFs/nanomaterials	80–99+	Low in synthetic systems	Variable	Low	Poor industrial validation
Membrane systems	60–95	Variable	Variable	Low to moderate	Fouling and energy demand
Hybrid systems	90–99+	<5–10	Multi-stage	High potential	Process complexity

Table 11 shows that high thorium removal efficiency alone isn't a good measure of process quality. Many methods removing over 95–99% of thorium cause significant REE losses, unstable sludge, high reagent use, or operational issues in industry.

11.1. Removal efficiency vs REE losses

The relationship between thorium removal efficiency and REE losses is a key trade-off in REE hydrometallurgy. Many studies focus on removing thorium but overlook the economic impact of losing valuable REEs. This is especially true in precipitation systems, where high pH or excess reagents often cause light REEs like La, Ce, and Nd to co-precipitate (Azimi et al., 2025).

Hydroxide and phosphate precipitation often report thorium removals above 95–99%, but studies show REE losses of over 10–20% under lab conditions (Zhou et al., 2025a). Such losses may be economically unacceptable in industry, as REE recovery affects profitability. Solvent extraction systems generally improve selectivity with optimized acidity, but may still co-extract REEs when Fe^{3+}, Al^{3+}, or uranium levels are high (Dash et al., 2021).

Advanced functional materials and MOF-based systems often exhibit low REE losses and high thorium uptake in laboratory settings (Li et al., 2026; Yu et al., 2025). However, these results rely on simplified feeds that do not replicate the chemistry of industrial PLS, so real-world selectivity advantages may be less pronounced.

11.2. Selectivity and process stability

Selectivity alone isn't enough without process stability. Some advanced materials show high equilibrium selectivity but lack long-term robustness due to fouling, degradation, extractant instability, or acidity sensitivity.

Solvent extraction systems are highly selective, leveraging strong coordination differences between Th(IV) and REE(III). However, extractant performance depends on acidity, ionic strength, and impurities. High sulfate levels or Fe^{3+} loading can lower separation efficiency and accelerate extractant degradation (Karmakar et al., 2021; Wang et al., 2025).

Adsorption systems with MOFs, COFs, and nanostructured materials often show high thorium uptake in batch tests but decline under continuous use due to pore blockage, ligand breakdown, structural issues, or competing ions (Liu et al., 2023; Zhong et al., 2024). Radiological stability is also a concern, as long-term alpha radiation can affect framework integrity.

Membrane systems face stability issues like fouling, polarization, and acid degradation. Long-term flux decline and cleaning needs can hinder industrial use, making process stability a key barrier to large-scale adoption of advanced separation tech.

11.3. Scalability and industrial feasibility

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Industrial scalability is a major gap between lab research and real-world use. Many thorium separation systems are tested only on small synthetic samples under batch conditions, leaving engineering challenges such as hydrodynamics, continuous operation, solids handling, residue management, and process integration unclear.

Precipitation systems are industrially attractive due to their simplicity and scalability, but are limited by large sludge volumes, poor filtration, and radioactive residue stabilization needs. Solvent extraction circuits are more mature, integrated into REE purification, but require complex operation, solvent management, and high capital costs (Rahman et al., 2025).

Advanced adsorbents, nanomaterials, and electrochemical systems are less mature industrially. Many involve costly synthesis, limited durability, or lack long-term validation in acidic conditions. Few studies assess continuous column operation, pressure drop, radiological degradation, or large-scale regeneration (Iskandar et al., 2024; Larochelle et al., 2024).

Hybrid flowsheets offer long-term potential by spreading operational limitations across multiple units. Rather than a single “perfect” separation method, integrated systems combine precipitation, solvent extraction, adsorption, and membrane stages based on their respective strengths and weaknesses (Talan, 2021; Kanojia et al., 2025).

11.4. Environmental and radiological impacts

Environmental and radiological issues limit the use of thorium separation methods. High removal rates do not guarantee a better environmental impact if the process produces unstable radioactive sludge, large volumes of waste, or hard-to-manage residues.

Precipitation systems produce radioactive solids with sulfate, phosphate, and metals, needing long-term storage, groundwater monitoring, and containment (Aziman et al., 2021b). Solvent extraction can reduce sludge but raises concerns about solvent losses, extractant degradation, and secondary effluents.

Membrane and adsorption systems typically generate less solid waste, but fouled membranes, spent adsorbents, and contaminated regeneration liquids can still pose environmental hazards. Also, the radiological stability of advanced materials is poorly understood, particularly after long-term industrial use (Hassan et al., 2024).

A major weakness in the literature is the tendency to evaluate separation technologies without integrating full residue management analysis. Many studies discuss thorium removal efficiency while neglecting final residue stabilization, transportation, long-term monitoring, and regulatory compliance requirements. This omission may substantially overestimate the environmental attractiveness of several emerging technologies (Akhtar et al., 2025; García et al., 2020).

11.5. Economic considerations

Economic viability is key for thorium separation tech. Operational costs such as reagents, extractants, membrane replacement, sludge disposal, energy, and radioactive waste affect OPEX. Environmental licensing, radiological monitoring, and long-term residue storage can raise CAPEX for REE facilities (Talan, 2021).

Precipitation systems have low equipment costs but may incur high downstream residue management expenses due to sludge volume and the need for neutralization. Solvent extraction entails greater capital complexity, including multi-stage mixer-settlers, solvent inventory, and stripping, but can improve REE recovery and reduce sludge.

Advanced materials such as MOFs, ionic liquids, and nanocomposites show promising lab-scale selectivity but face economic challenges due to costly synthesis and limited durability data. Similarly, membrane and electrochemical systems can cut reagent use but increase energy demand and maintenance costs (Talan et al., 2023).

Before concluding, it is important to summarize the technological maturity and industrial applicability of the main thorium separation strategies discussed. Table 12 summarizes their comparative status.

Table 12. Comparative assessment of the principal thorium separation technologies according to operational advantages, technological limitations, and industrial maturity level. Adapted from Vaughan et al. (2023), Verbaan et al. (2022), Rahman et al. (2025), and Kanojia et al. (2025).

Strategy	Main advantage	Main limitation	Technological maturity
Precipitation	Simplicity and scalability	REE losses and sludge generation	High
Solvent extraction	High selectivity potential	Multi-stage complexity	High
Adsorption/ion exchange	Modular operation	Competitive interference	Moderate
MOFs/nanomaterials	High laboratory selectivity	Poor scalability	Low
Membrane systems	Continuous operation	Fouling and instability	Low to moderate
Hybrid systems	Improved integrated performance	Operational complexity	Moderate to high

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Table 12 emphasizes that thorium management in REE hydrometallurgy will likely rely on integrated hybrid systems rather than standalone technologies. Effective flowsheets must balance selectivity, REE recovery, environmental stability, scalability, and cost.

Before concluding the review, it is necessary to critically examine the principal unresolved issues and technological limitations that continue to restrict industrial progress in selective thorium separation. The next section, therefore, discusses the major current challenges and research gaps identified throughout the literature.

12. Current Challenges and Research Gaps

Despite advances in thorium separation over the past decade, significant scientific and engineering gaps hinder its industrial use in REE hydrometallurgical systems. A common issue is the gap between laboratory success and industrial validation. Many new technologies show promising thorium selectivity in lab tests but lack thorough evaluation under continuous operation, complex feeds, and long-term industrial conditions (Pereira, 2026a; Kanojia et al., 2025).

A key limitation in this review is the reliance on synthetic solutions, which often contain only Th(IV) and selected REE ions at low ionic strength. In contrast, industrial PLS contains high levels of sulfate, acidity, phosphate, silica, Fe^{3+}, Al^{3+}, Ca^{2+}, uranium, solids, and organics, all of which affect hydrolysis, adsorption, extraction, membrane performance, and precipitation.

Separation efficiencies often overestimate industrial results because laboratory conditions are ideal. Many advanced adsorbents, MOFs, membranes, and solvent systems show high thorium selectivity in synthetic media but drop in performance in real hydrometallurgical liquors due to ion interference and instability (Iskandar et al., 2024; Man et al., 2023).

A key research gap is the scarcity of pilot-scale and continuous-operation studies, mainly limited to batch experiments with simple hydrodynamics and short durations. This matters because thorium separation could change over time due to fouling, extractant degradation, pH shifts, ionic buildup, colloidal effects, or radiological effects. Continuous operation presents engineering challenges like slurry transport, pressure drops, stage efficiency, membrane cleaning, adsorbent regeneration, and stability—problems rarely explored in lab studies (Pereira, 2026b).

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Before discussing the broader technological implications, it is important to summarize the main unresolved issues in current thorium separation research. The key gaps identified are summarized in Table 13.

Table 13. Principal technological, operational, and scientific gaps limiting industrial implementation of thorium separation technologies in REE hydrometallurgical systems. Adapted from Pereira (2026a), Kanojia et al. (2025), Iskandar et al. (2024), and Vaughan et al. (2023).

Research gap	Main consequence	Industrial implication
Excessive use of synthetic solutions	Overestimated selectivity	Poor industrial predictability
Lack of pilot-scale studies	Uncertain scalability	Difficult industrial adoption
Limited long-term testing	Unknown operational stability	Reliability concerns
Insufficient economic analysis	Incomplete feasibility evaluation	Investment uncertainty
Poor radiological stability assessment	Unknown material degradation	Safety and durability risks
Incomplete residue management analysis	Underestimated environmental liability	Regulatory complications

Table 13 shows that many limits are not just chemical; key unresolved issues include engineering validation, operational robustness, economic assessment, and environmental management, not just separation efficiency.

Long-term operational stability remains unresolved. Many studies report initial thorium removal but do not assess material degradation over time, especially under prolonged acidic and radioactive conditions. This is critical for advanced adsorbents such as MOFs, functionalized membranes, and ionic-liquid systems, where framework integrity may be compromised. Radiological stability is also underexplored despite continuous alpha-emitting thorium exposure (Akhtar et al., 2025).

Solvent extraction and membrane systems are often assessed using short-term experiments, neglecting long-term issues such as extractant aging, third-phase formation, phase disengagement decline, fouling, cleaning, and membrane lifespan.

Another weakness in the literature is the limited evidence linking separation efficiency to environmental management. Many studies discuss thorium removal without considering residue stabilization, long-term storage, groundwater protection, or regulations. This omission can distort sustainability assessments because residue management is often a major economic and environmental burden in REE processing (Aziman et al., 2021b; Vaughan et al., 2023).

Economic evaluation is underdeveloped, mainly focusing on technical separation while neglecting costs like reagent use, energy, equipment, membrane replacement, adsorbent

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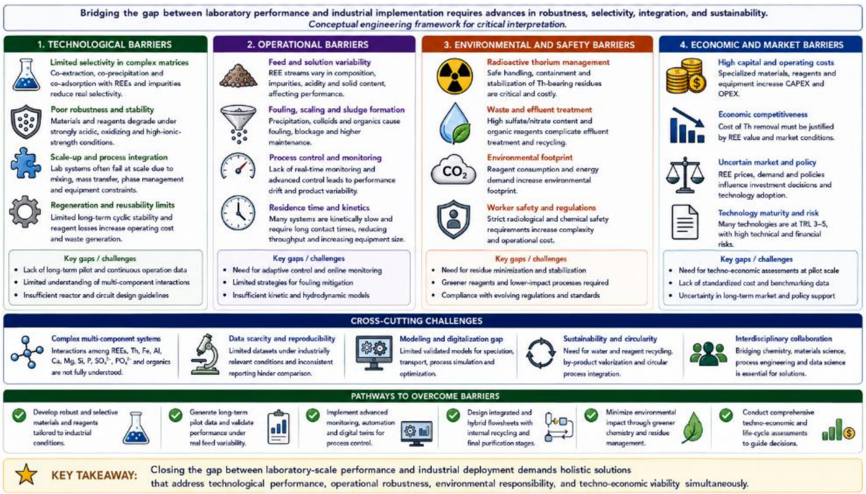
regeneration, and waste disposal. Favorable lab results may still be impractical industrially (Talan et al., 2023).

Another issue is the lack of standardized performance metrics, making it hard to compare thorium removal efficiencies due to variations in acidity, feed, concentrations, contact times, and setups. Sometimes, REE losses are unquantified, and interference and impurities are ignored. This inconsistency complicates comparing technologies and hampers industrial decisions.

The increasing complexity of REE feedstocks introduces new challenges. Secondary resources such as phosphogypsum, red mud, slags, electronic waste, and flotation residues exhibit highly heterogeneous levels of thorium and impurities. Existing separation technologies developed for conventional monazite or bastnäsite may require major adaptations for these emerging resources.

Before concluding, visualize the link between lab performance and barriers to industrial thorium separation. Figure 10 summarizes the key research gaps and engineering challenges identified in this review.



Bridging the gap between laboratory performance and industrial implementation requires advances in robustness, selectivity, integration, and sustainability.
Conceptual engineering framework for critical interpretation.

1. TECHNOLOGICAL BARRIERS

Limited selectivity in complex matrices
Co-extraction, co-precipitation and co-adsorption with REEs and impurities reduce real selectivity.

Poor robustness and stability
Materials and reagents degrade under strongly acidic, oxidizing and high-ionic-strength conditions.

Scale-up and process integration
Lab systems often fail at scale due to mixing, mass transfer, phase management and equipment constraints.

Regeneration and reusability limits
Limited long-term cyclic stability and reagent losses increase operating cost and waste generation.

Key gaps / challenges
- Lack of long-term pilot and continuous operation data
- Limited understanding of multi-component interactions
- Insufficient reactor and circuit design guidelines

2. OPERATIONAL BARRIERS

Feed and solution variability
REE streams vary in composition, impurities, acidity and solid content, affecting performance.

Fouling, scaling and sludge formation
Precipitation, colloids and organics cause fouling, blockage and higher maintenance.

Process control and monitoring
Lack of real-time monitoring and advanced control leads to performance drift and product variability.

Residence time and kinetics
Many systems are kinetically slow and require long contact times, reducing throughput and increasing equipment size.

Key gaps / challenges
- Need for adaptive control and online monitoring
- Limited strategies for fouling mitigation
- Insufficient kinetic and hydrodynamic models

3. ENVIRONMENTAL AND SAFETY BARRIERS

Radioactive thorium management
Safe handling, containment and stabilization of Th-bearing residues are critical and costly.

Waste and effluent treatment
High sulfate/nitrate content and organic reagents complicate effluent treatment and recycling.

Environmental footprint
Reagent consumption and energy demand increase environmental footprint.

Worker safety and regulations
Strict radiological and chemical safety requirements increase complexity and operational cost.

Key gaps / challenges
- Need for residue minimization and stabilization
- Greener reagents and lower-impact processes required
- Compliance with evolving regulations and standards

4. ECONOMIC AND MARKET BARRIERS

High capital and operating costs
Specialized materials, reagents and equipment increase CAPEX and OPEX.

Economic competitiveness
Cost of Th removal must be justified by REE value and market conditions.

Uncertain market and policy
REE prices, demand and policies influence investment decisions and technology adoption.

Technology maturity and risk
Many technologies are at TRL 3–5, with high technical and financial risks.

Key gaps / challenges
- Need for techno-economic assessments at pilot scale
- Lack of standardized cost and benchmarking data
- Uncertainty in long-term market and policy support

CROSS-CUTTING CHALLENGES

Complex multi-component systems
Interactions among REEs, Th, Fe, Al, Ca, Mg, Si, P, SO_4^{2-}, PO_4^{3-} and organics are not fully understood.

Data scarcity and reproducibility
Limited datasets under industrially relevant conditions and inconsistent reporting hinder comparison.

Modeling and digitalization gap
Limited validated models for speciation, transport, process simulation and optimization.

Sustainability and circularity
Need for water and reagent recycling, by-product valorization and circular process integration.

Interdisciplinary collaboration
Bridging chemistry, materials science, process engineering and data science is essential for solutions.

PATHWAYS TO OVERCOME BARRIERS

- ✓ Develop robust and selective materials and reagents tailored to industrial conditions.
- ✓ Generate long-term pilot data and validate performance under real feed variability.
- ✓ Implement advanced monitoring, automation and digital twins for process control.
- ✓ Design integrated and hybrid flowsheets with internal recycling and final purification stages.
- ✓ Minimize environmental impact through greener chemistry and residue management.
- ✓ Conduct comprehensive techno-economic and life-cycle assessments to guide decisions.

★ **KEY TAKEAWAY:** Closing the gap between laboratory-scale performance and industrial deployment demands holistic solutions that address technological performance, operational robustness, environmental responsibility, and techno-economic viability simultaneously.

Figure 10. Schematic representation of the principal technological, operational, environmental, and economic barriers limiting industrial implementation of thorium separation technologies in REE hydrometallurgical systems. Adapted from Pereira (2026a), Pereira (2026b), Iskandar et al. (2024), and Akhtar et al. (2025).

Figure 10 shows that the gap between lab research and industrial use depends on factors such as operational stability, radiological durability, process integration, residue management, and economic feasibility, not just on separation efficiency.

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A key conclusion is that future thorium management needs better integration of chemistry, process engineering, environmental science, and economics. Separation tech should focus not only on selectivity and thorium removal but also on operational robustness, compatibility with complex liquors, waste reduction, and economic viability.

The unresolved challenges in this section highlight key areas for future research and development. The next section explores future prospects for thorium separation and presents the review's conclusions.

13. Future Perspectives and Conclusions

The future of thorium separation in REE hydrometallurgy depends on advances in materials, process integration, digital tools, predictive modeling, and eco-friendly design. While progress has been made in thorium coordination, adsorption, solvent extraction, and membrane purification, future strategies need to achieve greater selectivity, robustness, environmental compatibility, and integration with complex REE supply chains.

Developing MOFs, COFs, and nanostructured materials for Th(IV) coordination is promising. Studies show ordered environments with phosphonate, amidoxime, or oxygen-donor sites enhance thorium affinity under acidic conditions (Chen et al., 2026a; Wang et al., 2026a). Future focus will be on improving stability, resistance, robustness, and scalability rather than just maximizing lab adsorption capacity.

An important trend is the rising use of AI, machine learning, and predictive thermodynamic modeling to optimize hydrometallurgical processes. As REE liquors become more complex, empirical development grows inefficient. Predictive models that include hydrolysis, extraction, adsorption, membrane transport, and impurity buildup could greatly enhance process design and control (Wang et al, 2026b).

Machine learning approaches are crucial for hybrid flowsheet optimization because multiple variables, such as acidity, ionic strength, sulfate concentration, residence time, extractant composition, and impurity recirculation, interact nonlinearly, thereby affecting thorium selectivity and REE recovery. AI-assisted modeling can help find optimal operating windows that minimize REE losses while ensuring thorium removal and operational stability.

Before discussing future process integration, it’s important to summarize key technological trends influencing next-generation thorium separation systems. The main research and development directions are in Table 14.

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Table 14. Principal future technological directions expected to influence selective thorium separation from REE hydrometallurgical systems, including emerging materials, process integration strategies, and industrial development priorities. Adapted from Chen et al. (2026a), Wang et al. (2026a), Wang et al (2026b), and Kanojia et al. (2025).

Future direction	Main objective	Main expected benefit	Main challenge
Advanced MOFs/COFs	Improved Th selectivity	High coordination specificity	Stability and scale-up
AI-assisted process optimization	Predictive process control	Reduced operational instability	Data availability
Smart hybrid flowsheets	Multi-stage optimization	Improved global selectivity	Process complexity
Green chemistry approaches	Reduced environmental impact	Lower waste generation	Industrial validation
Thorium recycling strategies	Resource recovery	Reduced radioactive liability	Regulatory acceptance
Digital process integration	Real-time monitoring	Improved operational control	Infrastructure cost

Table 14 shows that future thorium strategies will rely on integrating chemistry, engineering, digital monitoring, and sustainability, unlike earlier approaches that focused mainly on separation efficiency.

The concept of “smart separation” is increasingly relevant. Future REE hydrometallurgical plants might use real-time monitoring, adaptive reagent control, predictive maintenance, and dynamic algorithms to respond to feed variability and impurity build-up. These systems could enhance stability and cut reagent use compared to traditional thorium management.

Digital integration is key in this transition. Advanced process control systems can monitor parameters like pH, redox potential, ionic strength, phase composition, and impurities in real time to improve selectivity and safety. Digital twins and predictive simulations enable operators to anticipate fouling, extractant degradation, or impurity buildup before issues become critical (Pereira, 2026b).

Green chemistry principles are influencing thorium separation, emphasizing eco-friendly, low-energy, and recyclable methods (Akhtar et al., 2025). Many so-called “green” technologies lack comprehensive life-cycle evaluations, particularly regarding membrane disposal, nanomaterial persistence, and radioactive residues. Future assessments should consider reagent use, environmental impact, and radiological risks.

An important area is recycling thorium residues. Thorium has been viewed as waste in REE processing, but interest in nuclear systems and reactors might shift this view, positioning thorium as a recoverable resource (Man et al., 2026). While large-scale use is uncertain, selective recovery could become economically viable in the future.

Despite promising tech, key issues persist. Pilot validation is limited; long-term radiological stability is poorly understood. Most emerging techs are still tested with simplified solutions that do not reflect real industrial REE environments.

Before concluding, it is useful to visualize the key technological pathways shaping thorium management in REE processing. Figure 11 summarizes the main future directions and their interaction with industrial, environmental, and digital integration trends.

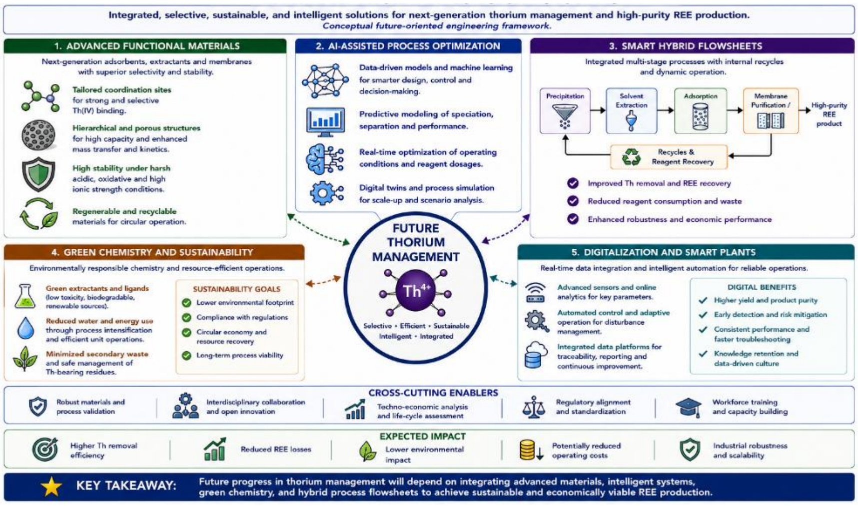

Figure 11. Schematic representation of the principal future technological directions for selective thorium separation in REE hydrometallurgical systems, including advanced functional materials, AI-assisted process optimization, smart hybrid flowsheets, green chemistry approaches, and digital process integration. Adapted from Chen et al. (2026a), Wang et al. (2026a), Wang and Zhu (2026), and Pereira (2026b).

Figure 11 shows that future thorium management will likely shift toward integrated, adaptive systems that use selective chemistry, predictive control, environmental optimization, and digital monitoring. The goal is no longer just maximizing removal efficiency but achieving stable, selective, cost-effective, and environmentally responsible operation amid variable hydrometallurgical conditions.

This review highlights that the separation of thorium remains a key challenge in REE hydrometallurgy. Progress has been made in understanding thermodynamics, coordination, and interfacial mechanisms, but gaps exist between lab success and industrial use. Precipitation systems are attractive but often lose REEs and produce sludge. Solvent extraction offers better selectivity but requires multi-stage processes and precise control of acidity. Advanced

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adsorbents, MOFs, and membrane technology show promise in the lab, but their industrial durability remains uncertain.

This review suggests future industrial progress will not rely on a single separation technology. Instead, it favors hybrid flowsheets with complementary purification under digital control. For REE hydrometallurgy, success depends on maximizing recovery and creating scalable, environmentally friendly thorium strategies that ensure long-term stability and safety.

14. Conclusions

Thorium management remains one of the principal challenges in rare earth element (REE) hydrometallurgy. Despite substantial advances in precipitation systems, solvent extraction, adsorption, membrane technologies, electrosorption, and hybrid purification approaches, no single technology currently meets all the requirements for high thorium selectivity, low REE losses, operational robustness, environmental safety, radioactive residue stability, and industrial scalability.

This review demonstrates that thorium separation is fundamentally governed by the tetravalent nature of Th(IV), its strong hydrolysis tendency, high coordination affinity toward oxygen-donor ligands, and complex aqueous speciation behavior. These characteristics create opportunities for selective separation from REE(III) species but also introduce important operational and thermodynamic challenges. The performance of thorium separation systems is strongly influenced by acidity, sulfate concentration, competing ions, residue recirculation, ionic strength, and feed variability, making direct comparison between technologies inherently difficult.

Precipitation systems remain attractive because of their simplicity, relatively low capital cost, and industrial familiarity; however, they frequently suffer from REE co-precipitation and the generation of radioactive sludge requiring stabilization and long-term management. Solvent extraction technologies generally offer superior selectivity and greater technological maturity, although they require complex multistage circuits, strict acid control, solvent management, and operational optimization. Emerging materials such as covalent organic frameworks (COFs), metal-organic frameworks (MOFs), functionalized nanomaterials, advanced adsorbents, and membrane systems have demonstrated promising selectivity under laboratory conditions, but their industrial applicability remains limited by fouling, competing-ion interference, material degradation, regeneration complexity, and insufficient pilot-scale validation.

A recurring limitation identified throughout the literature is the strong reliance on synthetic laboratory solutions and equilibrium-based batch experiments, which do not adequately capture the complexity of industrial pregnant leach solutions (PLS). Many studies report exceptionally high thorium removal efficiencies while providing limited discussion regarding REE co-losses, residue stabilization, continuous-operation performance, process integration, economic feasibility, or long-term operational stability. Consequently, direct extrapolation of laboratory-scale selectivity data to industrial systems remains highly uncertain.

The results of this review indicate that future industrial implementation will likely depend on integrated hybrid flowsheets that combine multiple complementary purification technologies rather than on isolated separation methods. Hybrid systems incorporating precipitation, solvent extraction, adsorption, membrane polishing, and controlled recirculation strategies may provide an improved balance between selectivity, REE recovery, operational stability, and environmental performance. In particular, integrating polishing technologies into conventional hydrometallurgical circuits appears especially promising for reducing radioactive residue generation while maintaining process efficiency.

The review also highlights the critical importance of radioactive residue management as an integral component of thorium separation strategies rather than as a secondary downstream issue. Long-term residue stabilization, radiological safety, transportation, environmental compliance, and waste minimization must be considered together with separation efficiency during process development and technology evaluation.

Emerging trends such as advanced functional materials, AI-assisted process optimization, digital process monitoring, and green chemistry approaches may contribute to improved thorium selectivity and process sustainability. Nevertheless, substantial research gaps remain regarding pilot-scale validation, long-term material stability, continuous-operation performance, techno-economic assessment, radiological durability, and industrial integration.

Future research should therefore prioritize continuous pilot-scale operation using real industrial process streams under representative hydrometallurgical conditions. Greater emphasis is needed on long-duration testing, fouling behavior, reagent aging, regeneration

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performance, residue stability, and integrated process economics. More comprehensive reporting of REE losses, operational instability, and radioactive waste generation is also necessary to improve the reliability and comparability of future studies.

Ultimately, the future of REE hydrometallurgy depends not only on maximizing rare-earth recovery but also on developing selective, economically viable, environmentally responsible, and industrially robust thorium management strategies that operate under realistic process conditions.

Declarations

Author Contributions

Antonio Clareti Pereira: Conceptualization, methodology, literature investigation, formal analysis, critical interpretation, visualization planning, writing—original draft preparation, writing—review and editing.

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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 upon reasonable request.

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