



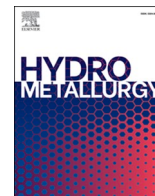
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Review

Hydrometallurgical processing of complex rare earth ores: trade-offs between REE recovery and radionuclide mobility

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ABSTRACT

Rare earth elements (REEs) are critical to low-carbon and advanced technologies, yet their extraction remains challenging due to complex mineralogy and the frequent presence of naturally occurring radioactive materials (NORM), particularly thorium (Th) and uranium (U). This review provides an integrated analysis of hydrometallurgical processing routes for REE-bearing ores, with a specific focus on the mechanisms governing Th and U mobility during mineral dissolution. Unlike conventional reviews that treat mineralogy, leaching chemistry, and radionuclide behavior separately, this work links these factors through a speciation-driven framework to explain and predict radionuclide partitioning across process streams. A systematic evaluation of literature published between 2000 and 2026 is presented, examining the performance of major lixiviants and the influence of mineralogical and geochemical variables on REE recovery and radionuclide behavior. The analysis shows that Th and U mobility is controlled by competing hydrolysis, complexation, polymerization, and redox reactions, which are highly sensitive to process conditions such as pH, temperature, and acid-to-ore ratio. Across processing routes, a consistent trade-off is identified: conditions that maximize REE recovery, particularly low-temperature sulfuric acid baking at high acid dosages, tend to promote significant co-dissolution of Th and U, whereas high-temperature roasting and alkaline treatment routes suppress radionuclide mobility but may reduce extraction efficiency or shift radiological burdens to solid residues. These relationships define a continuum of process performance and reveal the existence of ore-specific operational windows in which REE recovery can be balanced with controlled radionuclide partitioning and manageable impurity levels. The position of these windows is strongly governed by mineralogical characteristics, including REE host phases and gangue composition. This review therefore reframes REE hydrometallurgy as a speciation-controlled, mineralogy-constrained system, where process optimization must consider not only extraction efficiency but also radionuclide behavior and downstream separability. The proposed framework provides a basis for developing more selective, predictable, and environmentally compliant REE processing strategies.

1. Introduction

Rare earth elements (REEs) are indispensable components of modern low-carbon and advanced technologies, including wind turbines, electric vehicles, high-efficiency motors, solid-state batteries, hydrogen energy systems, and advanced electronic devices (Smethurst et al., 2008; Jowitt, 2022; Danouche et al., 2024). Their unique magnetic, catalytic, and electronic properties underpin many emerging technologies

associated with energy transition and decarbonization. Consequently, global demand for REEs has increased substantially and is projected to continue rising sharply. In particular, magnet-critical elements such as neodymium (Nd) and dysprosium (Dy) are expected to dominate future demand, with total REO consumption projected to reach approximately 519,000 t by 2030, of which Nd and Dy may account for approximately 75% and 9%, respectively (Zhao et al., 2025). This rapid growth has intensified the need not only for expanding resource availability but also

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for developing efficient, sustainable, and environmentally responsible processing routes.

Despite their strategic importance, REE extraction remains technically challenging due to their complex mineralogical occurrence and the chemical similarity of lanthanides. REEs are distributed across a wide range of mineral hosts, including fluorocarbonates (e.g., bastnäsite), phosphates (e.g., monazite and xenotime), oxides, and silicates (Zhu et al., 2015; Krishnamurthy and Gupta, 2016). However, economically viable extraction is restricted to a limited number of deposits due to low concentrations and complex mineral associations. Moreover, the lanthanide contraction leads to subtle but critical chemical similarities across REEs, necessitating multistage hydrometallurgical processing involving aggressive reagents and energy-intensive conditions (Brown et al., 2026).

A critical and often underintegrated aspect of REE processing is the co-occurrence of naturally occurring radioactive materials (NORM), particularly thorium (Th) and uranium (U), within REE-bearing minerals. Their presence classifies REE mining and processing as NORM activities, requiring stringent radiological control and regulatory compliance (Egidi, 2022; Kanojia et al., 2025). In minerals such as monazite, Th concentrations may range from 1 to 15 wt%, while U is typically present in smaller but still significant quantities. Radiological characterization studies have reported activity concentrations exceeding 1 Bq g^{-1} , highlighting the potential environmental and health risks associated with these materials (García-Tenorio et al., 2018).

The behavior of Th and U during REE processing is highly dynamic and strongly dependent on processing route and operating conditions. During beneficiation and hydrometallurgical treatment, these radionuclides may either co-dissolve with REEs into the leach solution or remain preferentially in solid residues (Demol et al., 2022; Basque et al., 2023; Aziman and Ismail, 2020). This variability introduces a fundamental challenge in process design, as it directly affects downstream separation, waste management, and environmental compliance. While U may, in some cases, be recovered as a valuable by-product (Zhu et al., 2015), Th remains problematic due to the absence of established large-scale applications, leading to its accumulation in process residues or effluents. The long half-life of Th and its decay products further amplify its radiological significance (P. Yang et al., 2021; Özkan et al., 2024).

The environmental implications of inadequate radionuclide management are well documented. Industrial operations, such as those at the Bayan Obo deposit in China and processing facilities in Malaysia have generated significant volumes of radioactive residues that require management and disposal in accordance with applicable regulatory frameworks (Aziman and Ismail, 2020; Su et al., 2021; Chadirji-Martinez et al., 2022). If inadequately contained, radionuclide-bearing residues may present long-term environmental concerns because weathering, rainfall infiltration, and surface runoff can promote the mobilization and transport of radionuclides and associated contaminants into surrounding soils and waters. Elevated natural radioactivity and evidence of contaminant transfer have been reported in soils surrounding former REE-processing facilities, demonstrating the importance of appropriate residue containment, monitoring, and long-term management. A study of a decommissioned REE-processing plant in Guangdong reported substantially elevated radionuclide activities in surrounding soils and identified rain leaching, runoff, and airborne transport as pathways by which processing wastes can enter environmental media. (Huang et al., 2022) A separate monazite-processing study also found very high radionuclide activities in several solid processing residues, supporting the need for radiation protection and controlled waste management, although it did not itself establish long-term environmental leaching (Hamed et al., 2016).

From a hydrometallurgical perspective, the mobility of Th and U is governed by complex interactions involving hydrolysis, redox transformations, and ligand complexation. These processes are highly sensitive to solution chemistry, including pH, temperature, ionic strength, and the presence of ligands such as sulfate, chloride, and phosphate.

Under strongly acidic conditions, hydrolysis is suppressed and both Th (IV) and U(VI) may remain in solution as stable complexes, whereas increasing pH promotes hydrolysis, polymerization, and precipitation. Similarly, ligand competition can significantly alter radionuclide solubility and stability, thereby controlling their partitioning between aqueous and solid phases.

These interactions give rise to a fundamental trade-off in REE processing: conditions that maximize REE dissolution often also enhance the mobility of Th and U, transferring radiological burdens to the aqueous phase. Conversely, conditions that suppress Th and U dissolution retains radionuclides within the primary process residue, necessitating long-term management and disposal of radioactive solids. Conversely, promoting Th and U dissolution transfers radionuclides to the aqueous phase, where they must subsequently be removed during downstream purification, generating secondary radioactive waste streams. The fundamental trade-off therefore lies not in whether radioactive waste is produced, but in where radionuclides are partitioned within the process and how the resulting waste streams are managed. (Qin et al., 2017; Xaba et al., 2018).

Despite significant advances in REE processing technologies, existing studies typically address mineralogy, leaching chemistry, and radionuclide behavior as separate aspects. As a result, the relationships between process conditions, REE recovery, and Th/U mobility are not systematically integrated, limiting the ability to design optimized and environmentally responsible flowsheets.

This review addresses this gap by providing an integrated, process-oriented analysis of REE hydrometallurgy that explicitly links mineralogical characteristics, dissolution chemistry, and radionuclide speciation. Through a systematic evaluation of literature published between 2000 and 2026, the work identifies key process variables governing REE recovery and Th/U partitioning, with particular emphasis on monazite processing.

A further limitation is that process performance is often compared across studies without sufficient normalization for ore mineralogy, gangue composition, or radionuclide host phases. As a result, differences attributed to operating conditions alone may in fact reflect underlying geo-metallurgical variability. This complicates the identification of transferable process rules and highlights the need for a framework that distinguishes intrinsic mineralogical effects from controllable process variables.

The discussion begins with an overview of REE mineral resources and compositional characteristics, followed by an evaluation of lixiviant performance and gangue interactions. The speciation and mobility of radioactive components are then examined in detail, emphasizing their dependence on solution chemistry. Building on this foundation, the review critically analyzes operational windows for monazite processing, highlighting the trade-offs between REE recovery, impurity control, and radionuclide management.

This review advances current understanding by linking ore mineralogy and leaching chemistry with the speciation and partitioning of Th and U. Particular attention is given to monazite processing, for which sufficient data are available to compare alkaline cracking and sulfuric acid baking. On this basis, the review identifies ore-specific operational windows for balancing REE recovery, impurity control, and radionuclide management.

2. Review methodology

The literature reviewed in this study was collected from major scientific databases, including Scopus, Web of Science, ScienceDirect, and SpringerLink. Searches were conducted using combinations of keywords related to rare earth element mineral resources, hydrometallurgical processing, leaching chemistry, thorium, uranium, radionuclide speciation, and REE recovery.

The selected literature was evaluated with emphasis on mineralogical characterization, hydrometallurgical processing conditions,

radionuclide behavior, and process performance. Particular attention was given to studies reporting Th and U partitioning during REE extraction, as well as investigations linking mineralogy, solution chemistry, and recovery mechanisms. The reviewed literature primarily covers the period from 2000 to 2026, while selected earlier studies were included where they provide foundational insights into REE processing and radionuclide behavior.

3. Rare earth elements abundances and exploited minerals composition

3.1. Rare earth elements abundances

The REEs are widely distributed in the Earth's crust, yet their economic extraction is constrained by their dispersion across diverse mineralogical hosts rather than true scarcity. Their natural abundance generally decreases with increasing atomic number due to the lanthanide contraction, resulting in a predominance of light rare earth elements (LREEs) such as cerium and lanthanum over heavy rare earth elements (HREEs).

From a processing perspective, this uneven distribution has direct implications for resource utilization. LREE-rich deposits account for the majority of global REE production, whereas economically viable HREE deposits are comparatively rare (Goodenough et al., 2018; Jordens et al., 2013). Consequently, the economic and metallurgical value of an ore body depends not only on total REE grade but also on the distribution of individual elements and their mineralogical associations.

Although REEs occur in discrete mineral phases such as bastnäsite, monazite, and xenotime, these phases are often finely disseminated, intergrown with gangue minerals, or hosted in refractory structures, which complicates liberation and hydrometallurgical extraction. They are incorporated into a limited number of mineral structures, often in association with gangue minerals and, critically, with NORM, particularly Th and U. This mineralogical coupling is a primary factor governing both extraction efficiency and radionuclide behavior during processing.

3.2. Compositional characterization of the exploited minerals

The mineralogical composition of REE-bearing ores is the primary factor controlling their processing behavior, as it governs dissolution kinetics, reagent consumption, and impurity interactions. REEs are commonly classified into light (LREEs: La–Gd) and heavy (HREEs: Tb–Lu, including Y), a distinction that is critical from both economic and metallurgical perspectives (van Wyk et al., 2024). Deposits enriched in HREEs are generally more valuable due to the strategic importance of these elements; however, their extraction is often complicated by their association with refractory minerals such as xenotime, fine-grained dissemination, and complex gangue assemblages that hinder liberation and recovery. (European Union, 2020; 2023). Beyond this conventional classification, the tetrad effect provides additional insight into REE geochemical behavior, particularly in magmatic and hydrothermal systems. The division into four tetrads (La–Nd, Pm–Gd, Gd–Ho, Er–Lu) reflects subtle variations in electronic structure and bonding, arising from the lanthanide contraction, which leads to a progressive decrease in ionic radius and coordination number (from ~9 to ~8) across the series (Monecke et al., 2002; Abedini et al., 2020; Ekberg et al., 2012). These variations influence not only mineral formation but also REE reactivity and separation behavior in hydrometallurgical systems.

REE resources are economically exploited from a limited number of deposit types, broadly categorized into magmatic (e.g., carbonatites), sedimentary (e.g., heavy mineral sands), and weathering-related deposits (e.g., ion-adsorption clays) (Oliveira and Inverno, 2014; Cotton, 2020; Thomas et al., 2024). Among these, carbonatite deposits represent the dominant global source, accounting for approximately 75% of

REE production (Batapola et al., 2020). These deposits are characterized by carbonate-rich lithologies (>50% Ca-bearing minerals such as calcite, dolomite, and ankerite) and relatively low silica content (<20% SiO₂). The substitution of REEs for Ca within these mineral structures, facilitated by similar ionic radii, leads to enrichment in LREEs (Elzinga et al., 2002).

The principal REE-bearing mineral in carbonatites is bastnäsite ((La, Ce, Y)CO₃F), which accounts for approximately 70% of global REE production and over 50% of known reserves (Guo and Liu, 2019). Bastnäsite typically contains 65–75 wt% REEs and can reach up to 30–92% REO following beneficiation (Liu et al., 2022a; Julapong et al., 2023). However, it also contains measurable concentrations of Th (~0.3 wt%) and U (~0.09 wt%), necessitating careful handling and processing to mitigate environmental risks (Talan and Huang, 2022; Murty et al., 2024; Kaizhong et al., 2017).

Phosphate minerals represent another major class of REE resources, particularly monazite ((Ce, LREE, Th, U, Ca)PO₄) and xenotime (YPO₄). Monazite is a key source of LREEs and contains approximately 55–60% REO, with significant thorium content (typically 4–12 wt%) and minor uranium (Jordens et al., 2013; Patel et al., 2023). Its robust phosphate structure contributes to its refractory nature, making it resistant to direct acid leaching and requiring aggressive pre-treatment methods such as alkaline cracking or acid baking. Monazite deposits are commonly found in heavy mineral sands, particularly in regions such as South Africa, Brazil, India, and Australia (Batapola et al., 2020; W. Chen et al., 2017). Unlike monazite, bastnäsite typically contains comparatively low concentrations of Th and U, which partly explains its lower radiological burden during processing (Castor and Hedrick, 2006).

Xenotime, in contrast, is a major source of HREEs and is widely distributed across magmatic, sedimentary, and metamorphic environments. It typically contains approximately 60% YPO₄ and up to 30% other HREEs, along with minor thorium (~2.5% ThO₂) (Behrsing et al., 2014). Xenotime is often associated with a complex gangue mineralogy, including silica (SiO₂), iron oxides (Fe₃O₄), titanium minerals (FeTiO₃, TiO₂), and zircon (ZrSiO₄) (Udayakumar et al., 2020; Castroviejo, 2023), which can significantly influence leaching behavior and impurity dissolution (Udayakumar et al., 2020; Castroviejo, 2023). For instance, silicate phases (SiO₂ and ZrSiO₄) can promote the formation of gelatinous silica, which may coat mineral surfaces and hinder leaching kinetics (Rivera et al., 2019; Tsaousi et al., 2023). Iron oxides can contribute to leachate impurities (Fe²⁺/Fe³⁺) (Santawaja et al., 2022). Titanium- and zirconium-bearing phases are generally refractory (Srikanth et al., 2015), however, once dissolved, these elements are highly prone to hydrolysis and can co-precipitate with REEs thereby reducing REE recovery.

Ion-adsorption clay deposits represent a distinct and increasingly important class of REE resources, particularly for HREE supply. These deposits form through the weathering of granitic rocks, where REEs are mobilized and subsequently adsorbed onto clay minerals such as kaolinite and halloysite as exchangeable hydrated cations (L. Zhou et al., 2024; Hoshino et al., 2016). Although these deposits are typically low grade and difficult to beneficiate due to their fine particle size and high clay content (40–70%), they account for approximately 90% of global HREE production (Wu et al., 2023; Gao et al., 2023). Importantly, their relatively low Th and U concentrations (~20–30 mg/kg) make them more favorable from an environmental and regulatory standpoint compared with monazite and carbonatite systems. Ion-adsorption clay deposits generally contain lower concentrations of Th and U than monazite and other phosphate-hosted REE deposits. Nevertheless, radionuclides may still become concentrated in specific process streams or residues during extraction and purification, necessitating appropriate waste management and radiological control measures (Su et al., 2021; Azimi, 2025).

In addition to these major deposit types, oxide-based REE minerals such as fergusonite, polycrase, and aeschynite are also recognized, particularly in Nb–Ta–REE-rich systems (Yang et al., 2020a, 2020b).

Fergusonite (ABO_4) exhibits significant compositional variability, with REEs, Th, U, or Ca occupying the A site and Nb, Ta, or Ti in the B site. This compositional flexibility leads to multiple mineral species (e.g., fergusonite-(Y), -(Ce), -(Nd)) and contributes to complex processing behavior (Zozulya et al., 2020).

From a hydrometallurgical standpoint, the REE and gangue mineralogy dictates processing strategy. Carbonate minerals such as bastnäsite are generally more amenable to acid leaching, whereas phosphate minerals like monazite require prior structural breakdown. Ion-adsorption clays allow for relatively mild leaching conditions but present challenges in solid–liquid separation. Moreover, the association of REEs with gangue minerals (e.g., carbonates, silicates, and iron oxides) introduces additional complexity through acid consumption, impurity dissolution, and potential formation of secondary phases.

Crucially, mineralogy also governs the occurrence and distribution of Th and U within REE ores. Phosphate minerals, particularly monazite, are the primary hosts for Th, whereas carbonatite and clay deposits typically exhibit lower radionuclide concentrations. Monazite commonly contains several weight percent thorium and may exceed 10 wt% ThO_2 in some deposits, making it one of the most important naturally occurring hosts of radioactive elements in REE processing systems (Gupta and Krishnamurthy, 2005). This variability has direct implications for radionuclide mobility during processing and must be considered in the design of leaching systems and waste management strategies. Critically, this means that hydrometallurgical performance cannot be evaluated independently of deposit type. Ores with similar total REE grades may behave very differently during leaching if REEs and radionuclides reside in different mineral hosts or are associated with different gangue assemblages. Therefore, mineralogical characterization should be regarded not as a supporting exercise, but as a prerequisite for meaningful process comparison and flowsheet selection. For example, the refractory phosphate structure of monazite requires aggressive pretreatment such as acid baking or alkaline cracking, whereas bastnäsite can often be processed under substantially milder conditions (Gupta and Krishnamurthy, 2005).

4. Radioactive components and speciation

4.1. Radioactive components

The occurrence of Th and U in REE-bearing minerals arises primarily from their incorporation into crystal structures during mineral formation through co-precipitation and solid-solution substitution mechanisms. As a result, these radionuclides remain intimately associated with REE phases throughout beneficiation and hydrometallurgical processing. During extraction, they are progressively mobilized and redistributed across process streams, including leach solutions, solid residues, and secondary waste products.

At the leaching stage, Th and U may exhibit partial or complete co-mobility with REEs, depending on the physicochemical conditions of the system. In addition to their chemical behavior, both radionuclides continue their natural radioactive decay chains, producing a series of daughter isotopes that contribute to the overall radiological hazard (Lucas et al., 2015; B. Zhou et al., 2017; Yang et al., 2020b).

The Th and U occur as members of naturally occurring radioactive decay series that generate a range of daughter radionuclides, including radium, actinium, and lead isotopes. Although daughter radionuclides may influence radiological assessment and waste management, the present review focuses on the behavior, speciation, and partitioning of Th and U as the principal parent actinides commonly associated with REE-bearing minerals. Daughter radionuclides may exhibit different chemical behavior and may therefore deport independently during processing.

The partitioning of Th and U during REE processing is highly variable and depends on mineralogy, reagent dosage, thermal treatment, and subsequent leaching conditions. In many industrial and laboratory

studies, a large fraction of Th reports to the solid residue, although the extent of dissolution varies considerably between processing routes (Nisbet et al., 2022).

At Bayan Obo, where REEs occur in a mixed bastnäsite–monazite assemblage, the sulfate-based processing route has been reported to result in limited Th dissolution, with approximately 6% of Th entering the leach solution, while uranium is preferentially transferred to aqueous process streams (Pecht et al., 2011).

In laboratory studies of monazite sulfuric acid baking, Demol et al. (2022) reported partial Th dissolution under specific combinations of temperature, acid dosage, feed mineralogy, and leaching conditions. These results should not be interpreted as evidence that higher temperature alone increases Th dissolution. Rather, Th deportment reflects the combined effects of mineral conversion, sulfate availability, phosphate-phase formation, and the chemistry of the subsequent leaching step.

Reported Th and U dissolution values cannot be interpreted independently of mineralogical and chemical context. Similar partitioning percentages may result from different mechanisms, including dissolution of the host mineral, oxidation-state changes, aqueous complexation, hydrolysis, or precipitation of secondary phases. Consequently, the deportment of Th and U should be evaluated together with information on the radionuclide host phases, solution pH, redox conditions, and the concentrations of relevant ligands.

Thermodynamic speciation calculations, including Eh–pH and aqueous-complexation diagrams, are commonly used to evaluate the stability of dissolved, hydrolyzed, and precipitated Th and U species under hydrometallurgical conditions (Gontijo et al., 2022; Kim and Osseo-Asare, 2012; Smedley and Kinniburgh, 2023). These approaches provide a framework for interpreting the contrasting behavior of Th and U in sulfate-, phosphate-, and chloride-bearing systems. The following sections therefore examine their aqueous chemistry and speciation in these media.

4.2. Thorium chemistry and speciation

Thorium in aqueous systems exists almost exclusively in the tetravalent state (Th(IV)), reflecting its strongly redox-inert character under typical hydrometallurgical conditions. As a result, its speciation is primarily governed by pH and ligand interactions rather than redox transformations (Ekberg et al., 2000; Albrecht et al., 2011; Saha et al., 2023).

In simple aqueous systems ($\text{Th-H}_2\text{O}$), thorium exhibits a strong tendency toward hydrolysis due to its high charge density. Under strongly acidic conditions ($\text{pH} \approx 0\text{--}1$), hydrolysis is effectively suppressed, and Th remains as hydrated Th^{4+} species (Fig. 1a). However, as pH increases, hydrolysis proceeds rapidly, leading to the formation of mononuclear hydroxo complexes such as ThOH^{3+} , Th(OH)^{2+} , Th(OH)_2^{2+} , and Th(OH)_3^{+} . These species emerge progressively around $\text{pH} \approx 3$ (Fig. 1a), although their individual identification remains experimentally challenging (Torapava et al., 2009; Ekberg et al., 2000; Bentouhami et al., 2004).

At higher pH values ($\geq 3\text{--}5$), polymerization reactions become dominant, ultimately leading to the precipitation of amorphous $\text{Th(OH)}_4(\text{s})$, which significantly reduces thorium mobility (Fig. 1a) (Myllykylä et al., 2017; Gontijo et al., 2022). This strong tendency toward hydrolysis and precipitation explains the frequent retention of Th in solid residues during hydrometallurgical processing.

The presence of complexing ligands can substantially modify this behavior. In sulfate-rich systems (H_2SO_4), thorium forms stable aqueous complexes such as the cationic $\text{Th(SO}_4)_2^{2+}$ and the neutral $\text{Th(SO}_4)_2^0$. These complexes increase Th solubility and suppress hydrolysis by stabilizing Th in solution (Di Bernardo et al., 2018). In particular, the neutral $\text{Th(SO}_4)_2^0$ species plays a key role in the pH range 2–4, delaying the onset of hydrolysis and shifting precipitation of $\text{Th(OH)}_4(\text{s})$ to higher pH values (≈ 5), compared with sulfate-free systems (Fig. 1b) (Natrajan

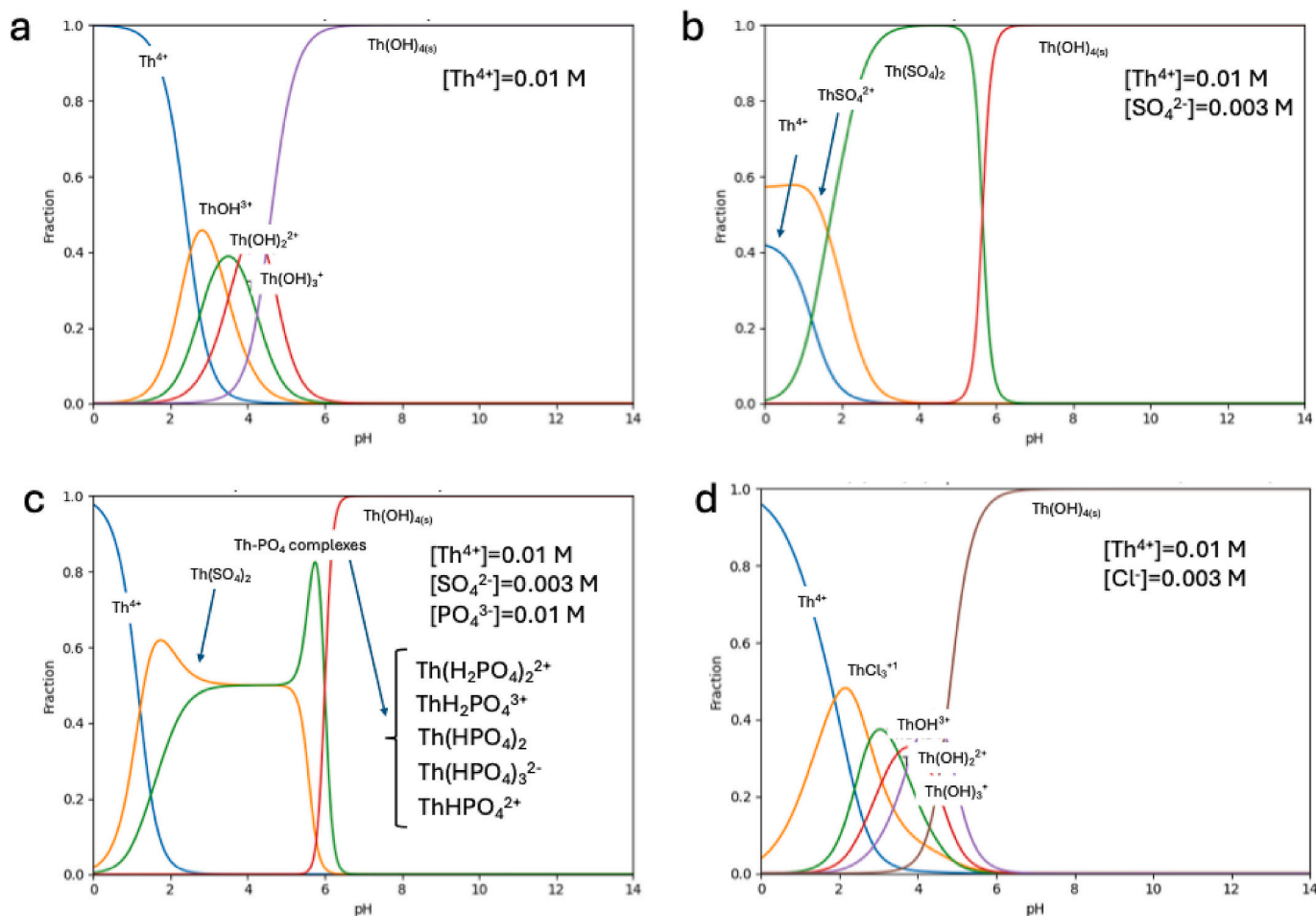


Fig. 1. (a) Th–H₂O system, (b) Th–SO₄ system, (c) Th–PO₄ system, (d) Th–Cl system. Speciation diagrams were generated using OLI Studio Version 12.0.011 based on thermodynamic equilibrium calculations under the specified solution conditions.

et al., 2014; Nisbet et al., 2019; Nisbet et al., 2022).

Phosphate systems exhibit even stronger complexation effects. In the presence of phosphate, thorium forms highly stable anionic oxophosphato complexes such as $(\text{ThO}(\text{HPO}_4)_4(\text{H}_2\text{PO}_4))^{5-}$ and $(\text{ThO}(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)_2)^{6-}$, which can maintain Th in solution up to near-neutral pH (Fig. 1c) in the range of ~ 0.1 – 1 M PO_4^{3-} (Fourest et al., 1994). However, the behavior of Th in sulfate–phosphate systems is highly competitive. At sufficiently high phosphate activities, typically above approximately 1 M phosphate under the conditions represented in the speciation diagram, insoluble thorium phosphate phases become thermodynamically stable and precipitate from solution. The precise precipitation boundary depends on pH, ionic strength, and the presence of competing complexing ligands. Under strongly acidic and sulfate-rich conditions, precipitation as $\text{Th}(\text{SO}_4)_2(\text{s})$ may occur, whereas under conditions of higher phosphate activity, Th-phosphate phases may form even at relatively low pH (Fig. 1c) (Gontijo et al., 2022; R. Kim et al., 2016). These apparently conflicting observations reflect the balance between ligand availability, protonation state, and nucleation kinetics.

In perchlorate media (HClO_4), no significant complexation is observed, whereas in HCl solutions chloride complexation becomes progressively more important as chloride activity increases (Ekberg et al., 2000; Nisbet et al., 2022). Because the relative abundance of thorium chloride complexes depends on several factors, including pH, ionic strength, temperature, and total thorium concentration, no single chloride concentration can be defined as a universal threshold for the onset of significant complexation. Experimental studies have nevertheless demonstrated that chloride complexation remains important in concentrated chloride media, including solutions containing up to at

least 2.5 M Cl^- (Nisbet et al., 2018). Under such conditions, a range of neutral and charged complexes may form, including ThCl_2^{2+} , ThCl_3^+ , ThCl_4 , ThCl_5^- and ThCl_6^{2-} (Fig. 1d) (Johansson et al., 1991; Maiorov et al., 2006). Structurally, these species correspond to coordination environments ranging from 8- to 9-fold coordination, with mixed aquo–chloro complexes (Wacker et al., 2021).

Thorium speciation is dominated by a strong competition between hydrolysis and ligand complexation. In the absence of strong ligands, hydrolysis leads to rapid immobilization, whereas sulfate and especially phosphate ligands can significantly enhance Th solubility and mobility.

4.3. Uranium chemistry and speciation

In contrast to Th, U exhibits multiple oxidation states in aqueous systems (+3, +4, +5, and +6), although U(IV) and U(VI) are the most relevant under natural and hydrometallurgical conditions (Smedley and Kinniburgh, 2023). Uranium speciation is therefore controlled by both redox conditions and solution chemistry.

Under oxidizing conditions, uranium exists predominantly as the uranyl ion (UO_2^{2+}), which is highly soluble and mobile. In reducing environments, U(IV) dominates and forms sparingly soluble species, leading to immobilization (Faizrahmanov, 2024; Judge and Azimi, 2020). The relative stability of these oxidation states follows the order $\text{U(VI)} > \text{U(IV)} > \text{U(III)} > \text{U(V)}$, reflecting the strong tendency of U(VI) to persist in aqueous systems.

In simple aqueous systems (U–H₂O), UO_2^{2+} is the dominant species at low pH (~ 1 – 3) (Smedley and Kinniburgh, 2023). As pH increases, hydrolysis leads to the formation of species such as UO_2OH^+ ($\text{pH} \approx 2.5$),

followed by more complex hydrolysed and polymeric species, including $\text{UO}_2(\text{OH})_2$, and $(\text{UO}_2)_3(\text{OH})_5^+$ in the pH range 3–6 (Fig. 2a) (Drobot et al., 2015; Faizrahmanov, 2024). At higher pH values, precipitation of uranyl hydroxides (e.g., $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$) occurs, reducing U mobility (Fig. 2a).

In sulfate-bearing media, uranyl forms aqueous sulfate complexes whose relative importance depends strongly on sulfate activity. Under the conditions represented in Fig. 2b ($[\text{UO}_2^{2+}] = 0.01 \text{ M}$ and $[\text{SO}_4^{2-}] = 0.003 \text{ M}$), $\text{UO}_2\text{SO}_4(\text{aq})$ is the principal sulfate complex at acidic pH. As pH increases, sulfate complexation becomes less important and hydrolysed uranyl species become dominant, followed by precipitation of $\text{UO}_2(\text{OH})_2(\text{s})$. Higher-order sulfate complexes, including $\text{UO}_2(\text{SO}_4)_2^{2-}$ and $\text{UO}_2(\text{SO}_4)_3^{4-}$, are reported in sulfate-rich solutions (Hennig et al., 2007), particularly when sulfate is present in excess, but they do not reach appreciable fractions under the sulfate concentration selected for Fig. 2(b) (Bertoli et al., 2019).

The presence of phosphate significantly alters uranium speciation because phosphate strongly competes with sulfate and hydrolysis reactions. Under the sulfate–phosphate conditions represented in Fig. 2(c), protonated uranyl–phosphate species become important as pH increases. The species $\text{UO}_2\text{H}_2\text{PO}_4^+$ is favoured under more acidic conditions, whereas the neutral complex $\text{UO}_2\text{HPO}_4(\text{aq})$ becomes increasingly important at moderately acidic to near-neutral pH. At higher pH, hydrolysed uranyl species and ultimately $\text{UO}_2(\text{OH})_2(\text{s})$ become thermodynamically favoured. The relative proportions of these species depend on phosphate activity, sulfate concentration, pH, and ionic

strength.

Uranium(VI) can form soluble uranyl–phosphate complexes in phosphate-bearing solutions. The stability of these aqueous species depends on pH and phosphate activity, whereas at sufficiently high phosphate concentrations uranium may precipitate as insoluble uranyl phosphate minerals, such as chernikovite $[\text{H}_3\text{O}(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}]$ (Mehta et al., 2014).

In chloride systems, uranyl remains largely uncomplexed at low chloride concentrations, with UO_2^{2+} dominating up to $\text{pH} \approx 5$. Chloride complexes (e.g., UO_2Cl^+) are generally weak and only become significant at high chloride activity. As pH increases, hydrolysis again becomes dominant, leading to the formation of hydroxide species and eventual precipitation (Fig. 2d). However, in the presence of phosphate, uranyl speciation shifts strongly toward phosphate complexes, even under mildly acidic conditions, due to the higher stability of these species compared to chloride complexes (Fig. 2d).

The speciation of Th(IV) and U(VI) in hydrometallurgical systems is governed by a dynamic interplay between hydrolysis, polymerization, and ligand complexation. While hydrolysis is suppressed under strongly acidic conditions, even modest increases in pH can trigger the formation of hydroxo species, leading to precipitation and immobilization, particularly in the case of thorium.

Sulfate-rich systems tend to stabilize both Th and U through the formation of aqueous complexes (e.g., $\text{Th}(\text{SO}_4)_2^{2+}$, $\text{Th}(\text{SO}_4)_2^0$, UO_2SO_4 , $\text{UO}_2(\text{SO}_4)_2^{2-}$), thereby promoting their dissolution under acidic conditions. However, as pH increases, hydrolysis competes with

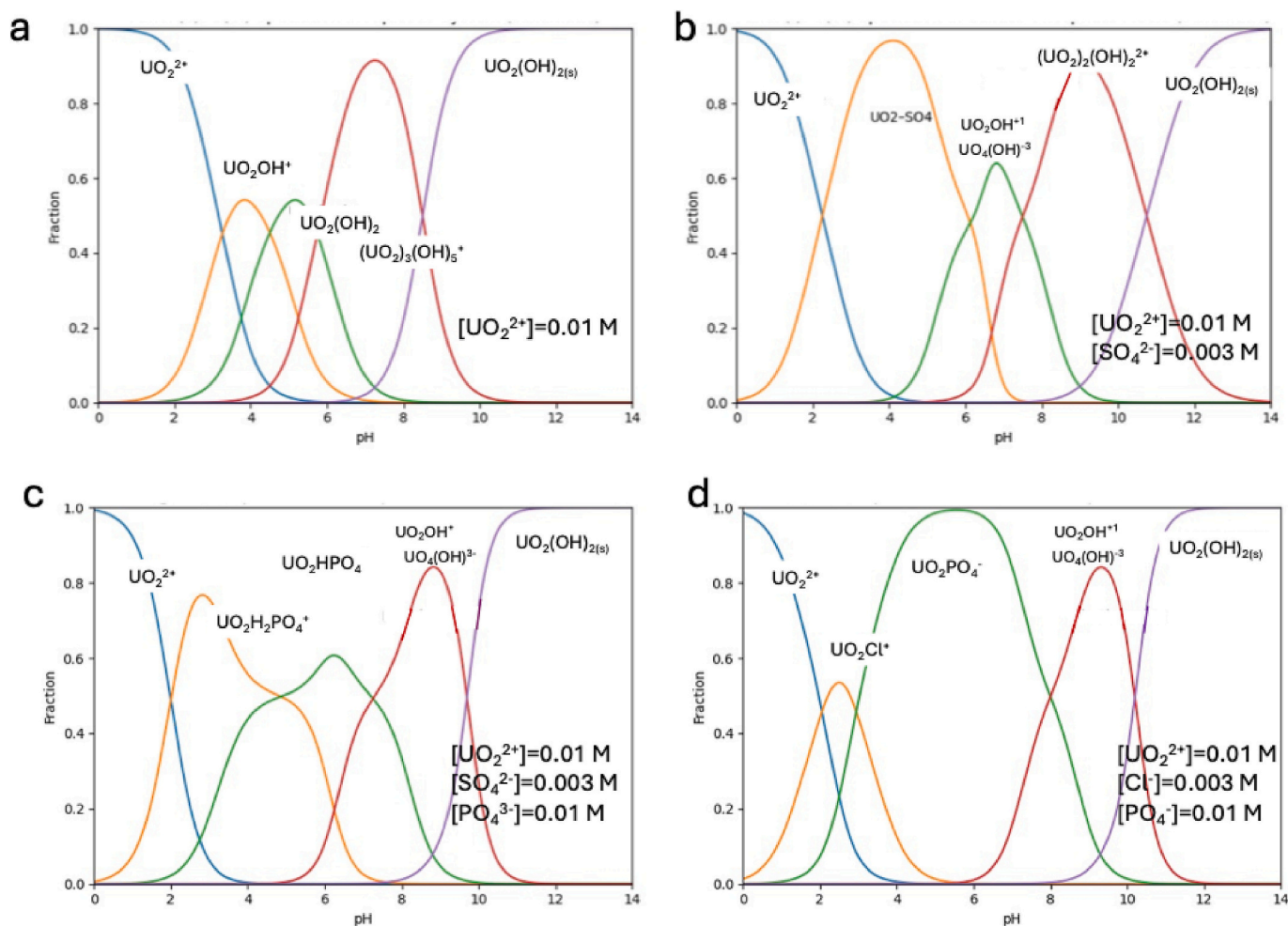


Fig. 2. (a) U–H₂O system, (b) U–SO₄ system, (c) U–SO₄–PO₄ system, (d) U–Cl–PO₄ system. Speciation diagrams were generated using OLI Studio Version 12.0.011 based on thermodynamic equilibrium calculations under the specified solution conditions.

complexation, reducing solubility. Chloride systems, by contrast, generally provide weaker complexation, making hydrolysis more dominant unless chloride concentrations are high.

Phosphate is the most influential ligand in REE systems, particularly in monazite processing. Its strong affinity for both Th and U allows the formation of highly stable complexes that can maintain these elements in solution up to near-neutral pH or alternatively promote precipitation depending on local chemical conditions and kinetics.

From a process perspective, these behaviours have critical implications. Control of pH, ligand concentration, and ionic strength enables the manipulation of Th and U partitioning between aqueous and solid phases. This control is essential for minimizing interference with REE recovery, enabling selective separation, and ensuring compliance with environmental regulations.

Consequently, speciation analysis provides a fundamental basis for designing hydrometallurgical processes that balance REE recovery efficiency with effective radionuclide management. Importantly, speciation analysis also helps explain why seemingly contradictory processing outcomes may both be correct within different chemical windows. Variations in pH, sulfate activity, phosphate release, and oxidation state can shift radionuclides across narrow stability boundaries, leading to abrupt changes in partitioning. This reinforces the need to define operational windows rather than rely on single-point processing conditions when evaluating process selectivity.

5. Process chemistry for rare earth ore bodies dissolution

The REE processing typically begins with beneficiation to concentrate the ore prior to hydrometallurgical treatment, a stage widely recognized as the most cost-intensive component of the value chain (Verbaan et al., 2015). The complexity of REE extraction arises primarily from the refractory nature of many REE-bearing minerals, which require aggressive chemical conditions to disrupt the crystal lattice and enable metal dissolution (Entezari-Zarandi and Larachi, 2019; Cuadros-Muñoz et al., 2024).

In practice, complete REE recovery is rarely achieved in a single leaching step. Industrial processing routes commonly involve sequential dissolution and precipitation stages, producing intermediate phases that simplify downstream separation but simultaneously introduce additional complexity in process control (García et al., 2020). For highly refractory ores, thermal pre-treatment such as roasting or conversion is often required to enhance mineral reactivity. Following leaching, the pregnant leach solution (PLS) is typically neutralized using alkaline reagents (e.g., MgO, MgCO₃, Na₂CO₃) to remove impurities and recover REEs.

However, these approaches often lack selectivity between REEs and associated radionuclides (Th and U), leading to co-dissolution and the generation of significant radioactive residues. For instance, processing 100 kt of REE concentrate may produce approximately 200 t of thorium-rich sludge (ThO₂) (Whitty-Léveillé et al., 2018). Additional environmental challenges arise from airborne emissions (dust, fluorine compounds) and sulfur-based gases, which further increase the regulatory burden associated with REE production (Schüler et al., 2011).

Mineralogical variability further complicates REE extraction. Gangue elements such as Ca can promote co-precipitation reactions (e.g., gypsum formation), reducing REE recovery if solution chemistry is not carefully controlled (Verbaan et al., 2015). These effects are particularly pronounced in monazite-, bastnäsite-, and mixed-ore systems, where complex mineral associations require tightly controlled process conditions. Current extraction routes remain constrained by a combination of aggressive operating conditions, limited selectivity, and environmental challenges.

5.1. Monazite processing and dissolution

Monazite ((Ln,Th)PO₄) is one of the most important REE-bearing

minerals but also among the most refractory, owing to the strong stability of its phosphate lattice (Gibson et al., 2022; Qin et al., 2023). As a result, direct dissolution in dilute acids is ineffective, and processing typically requires a prior conversion step to disrupt the mineral structure.

This conversion is governed by temperature, pressure, residence time, and solution chemistry, with typical conditions involving elevated temperatures (~200 °C), pressures (~5 atm), and extended reaction times (up to 4 h) (Khoshoei et al., 2026). Two principal industrial routes are widely employed: caustic digestion (alkaline cracking) and acid-based treatment (e.g., sulfuric acid baking).

5.1.1. Comparison of alkaline and salt roasting routes

Caustic cracking using concentrated NaOH is widely applied to high-grade monazite concentrates (55–65% REO) (Liu et al., 2022a). The process involves reacting (Ln,Th)PO₄ with 60–70% NaOH at temperatures above 140 °C, producing mixed REE–Th hydroxides and trisodium phosphate (Na₃PO₄).

While effective, this process suffers from limited selectivity, as up to 50% of silicate gangue (SiO₂) may dissolve, increasing reagent consumption and reducing efficiency (Huang et al., 2025). Partial U dissolution (15–40%) has also been reported (Anvia, 2015; Traoré, 2025), whereas Th is largely retained in the solid phase.

Following solid–liquid separation, Na₃PO₄ can be recovered and recycled through precipitation as Ca/Mg phosphates. The remaining hydroxide phase is subsequently leached in HCl (pH ≈ 3.2–3.7, 80 °C), achieving REE recoveries of approximately 85–95%, while retaining most Th (95–99%) and U (~90%) in the solid residue (Samin et al., 2025; Krishnamurthy and Gupta, 2016).

This behavior is consistent with the speciation trends discussed earlier. Under these mildly acidic chloride conditions, thorium predominantly undergoes hydrolysis rather than chloride complexation, leading to precipitation as insoluble hydroxides (Fig. 1d) (Ekberg et al., 2000; Bentouhami et al., 2004). In contrast, U remains largely immobile due to its persistence as U(IV) within the monazite lattice, requiring oxidative conditions to convert into soluble U(VI) species (Ballini et al., 2020; Lahrouch et al., 2022).

To reduce NaOH consumption, modified systems such as CaO–NaOH–H₂O have been developed. Huang et al. (2025) demonstrated improved decomposition efficiency (~90.6%) and reduced reagent consumption (25–33%) compared with conventional NaOH treatment. Under subsequent HCl leaching, Th and U are more readily mobilized due to increased acidity, consistent with the enhanced solubility predicted for strongly acidic chloride systems (Fig. 2d).

Similarly, roasting with MgCl₂•6H₂O has been shown to enhance phosphate removal (~97%) and enable high REE, Th, and U recovery (~96%) during subsequent HCl leaching (Ma et al., 2026). In this case, the high mobility of Th reflects the suppression of hydrolysis under strongly acidic conditions, while U dissolution is facilitated by oxidation to U(VI) and the formation of stable aqueous complexes.

A wide range of monazite processing routes have been investigated, including caustic roasting, salt roasting, smelting, and mechanical activation. Reported decomposition efficiencies range from ~79% (salt roasting) to >98% (smelting and caustic treatment) (Kumari et al., 2015; Shuchen et al., 2007; Xing et al., 2010). More recent approaches, such as ultrasound-assisted leaching, have demonstrated improved efficiency under milder conditions (Khoshoei et al., 2026; Bu et al., 2024).

However, these processes differ significantly in terms of energy requirements, selectivity, and environmental impact. High-temperature routes (e.g., smelting, salt roasting) are often economically and environmentally prohibitive, while lower-temperature methods may suffer from incomplete conversion or limited selectivity.

To facilitate comparison of these processing routes, Table 1 summarizes the key operational parameters, decomposition efficiencies, REE recoveries, and associated radionuclide behavior for alkaline treatment and salt roasting as monazite treatment methods. The

Table 1

Comparative analysis of caustic cracking and salt roasting conditions highlighting the trade-off between REE recovery, impurity dissolution, and Th/U partitioning.

Reference	Monazite (%) Feed Composition	Experimental Setup (Conditions)	Performance (REE, Th, U Recovery)	Time (h)	Process Weaknesses	Environmental Impact (Th/U deportment)
Samin et al. (2025)	Ce ≈ 25.648 La ≈ 11.225 Nd ≈ 9.452 Th ≈ 5.521 U ≈ 0.253 Y ≈ 3.095 P ≈ 8.343	NaOH decomposition of monazite (<325 mesh): water:NaOH:monazite = 1.7:1.5:1, 140 °C, reported experimentally as 4 h; hot filtration/washing to pH 9. Then partial dissolution of the RE/Th/U hydroxide precipitate using 14 N HCl, hydroxide:HCl = 1:1, 80 °C for 2 h, to pH 3.7. Th and U subsequently precipitated with 1 M NaOH at pH 6.14–6.30. RE hydroxides then precipitated at pH 9.8.	At pH 6.14–6.30, recovery to the Th/U hydroxide precipitate: U = 96.41%, Th = 90.85%, La = 2.83% on average. Under optimized RE(OH) ₃ precipitation conditions, RE ₂ O ₃ recovery = 99.79%, while Th recovery in that RE precipitate was 4.52%.	Caustic cracking = 4 HCl leach = 2	High NaOH consumption (1.5 kg NaOH per 1 kg monazite), concentrated 14 N HCl dissolution, multiple pH-controlled precipitation stages, several filtration steps, and repeated calcination. The process is effective for Th/U removal but is relatively complex and reagent-intensive.	After partial dissolution, Th and U are deliberately precipitated as hydroxides at pH 6.14–6.30, with approximately 90.85% Th and 96.41% U reporting to this precipitate. The optimized RE(OH) ₃ product contains only 55 ppm Th and 21.6 ppm U
	94% monazite, TREE+Y 51%, Th 6.0%, U 0.26%	Caustic conversion: P80 ≈ 35 µm; 68% NaOH, NaOH: monazite = 1:1, 150 °C, 3.5 h. Slurry diluted and hot-filtered. HCl leach: RE hydroxide residue leached at pH 3.2, 70 °C, 6 h. Downstream impurity removal: BaCl ₂ /Na ₂ SO ₄ for Ra sulfate precipitation and Na ₂ S for PbS precipitation.	Monazite decomposition: 96%. During HCl leaching, REE dissolution = 94% to RECl ₃ liquor. Th dissolution <0.1% as elemental Th; 238 U dissolution ≈9.7–10% to RECl ₃ liquor.	3.5 h caustic conversion +6 h HCl leaching	High-concentration NaOH at elevated temperature; long HCl leach; generates trisodium phosphate liquor and a Th/U-rich hydroxide residue. Importantly, several daughter radionuclides remain highly mobile even when parent Th is retained. Additional impurity-removal steps are required before final REE recovery.	After caustic conversion, <0.1% Th and 40% U reported to the trisodium phosphate liquor; most Th remained in the hydroxide residue. During HCl leaching, <0.1% elemental Th and ~10% U entered the RECl ₃ liquor. However, 226Ra = 93%, 210Pb = 48%, 231 Pa = 46%, and 227Ac = 38% also entered the RECl ₃ liquor. Subsequent impurity removal achieved >99.9% Ra, 87% 210Pb, 99% 210Po, 95% 231 Pa, ~80–85% Th isotopes, but only 18% 238 U and 39% 227Ac removal. U release is low with (NH ₄) ₂ SO ₄ and most U remains in the leach residue. The authors state that ammonium sulfate releases substantially less U than 6 M HCl. However, Th concentrations in ammonium sulfate leach liquors were significant, likely due to enhanced ThO ₂ solubility in sulfate media. Exact Th and U recovery percentages are not reported numerically in the paper.
Liu et al. (2022a)	Ce ≈ 18.80% Nd ≈ 12.68 La ≈ 5.18 Sm ≈ 4.68 Pr ≈ 3.06 Gd ≈ 2.38 Y ≈ 1.49 other REEs ≈0.66% Th ≈ 7.68 U ≈ 0.22 P ≈ 9.57	Monazite ground to d80 = 14.61, 8.25, or 4.95 µm. NaOH pretreatment: 10–50% w/v NaOH, 60–80 °C, 24 h, 600 rpm. Main ammonium sulfate leach: 0.5 M (NH ₄) ₂ SO ₄ , pH 4, room temperature or up to 65 °C, 2 h. Comparison tests used 6 M HCl.	With d80 = 14.61 µm, 50% NaOH at 80 °C for 24 h followed by 0.5 M (NH ₄) ₂ SO ₄ at pH 4: TREE recovery ~60% at room temperature. At d80 = 4.95 µm, TREE recovery reached 77.7%, with Nd recovery up to 86.5%. At 65 °C ammonium sulfate leaching, TREE recovery improved further to ~65–70% for d80 = 14.61 µm.	24 h NaOH pretreatment +2 h leaching.	Mild temperature but very long pretreatment time (24 h); requires fine grinding, especially for high recovery; 50% NaOH still needed for practical decomposition. Ammonium sulfate leaching is slower than 6 M HCl at room temperature, although higher temperature improves kinetics.	
Huang et al. (2025)	Ce ≈ 14.60 La ≈ 9.01 Nd ≈ 7.36 Pr ≈ 1.75 Sm ≈ 1.28 Gd ≈ 0.95 P ≈ 8.55 Th ≈ 4.45 Al ≈ 0.90 Si ≈ 1.42	CaO–NaOH–H ₂ O mixed-alkali decomposition in a high-pressure reactor. Optimum: CaO/monazite mass ratio 0.18, 8 M NaOH, 160 °C, L/S mass ratio 5, 9 h. After decomposition, hot-water dilution/filtration followed by acid leaching of the decomposition product with 2 M HCl + H ₂ O ₂ at 80 °C for 2 h.	under optimum conditions gave 87.6–93.1% RE leaching, average 90.6%. Without CaO, RE leaching was only 70.4%. Approximately 20 percentage-point improvement in RE recovery and 25–33% lower NaOH consumption compared with conventional NaOH decomposition. Th and U extraction/deportment were not quantified.	9 h mixed-alkali decomposition +2 h HCl leaching.	Relatively long reaction time (9 h); requires a pressurized reactor at 160 °C; addition of CaO increases the mass of decomposition products and causes some P to remain/disperse in the decomposition products. Authors identify increased by-product mass and phosphorus dispersion as the principal technical challenges.	Not reported. Feed contains 4.45 wt% Th, but the study does not quantify Th deportment or recovery during mixed-alkali decomposition or subsequent HCl leaching.
Ma et al. (2026)	REO ≈ 53.95%; ThO ₂ ≈ 6.64%; U ≈ 0.25%.	Mechanical activation to D90 < 100 µm; 70 wt% MgCl ₂ •6H ₂ O relative to monazite; roasting at 600 °C for 60 min; gravity separation; REE-rich	Monazite decomposition 96.85%. After gravity separation: REE recovery 94.21%, ThO ₂ recovery 94.83%, U recovery 94.65% to concentrate. Final REE	1 h roasting +1 h HCl leaching	Requires 600 °C roasting, high MgCl ₂ •6H ₂ O addition (70 wt%), mechanical activation, multistage gravity separation, and subsequent 6 M HCl/H ₂ O ₂	4.72% of ThO ₂ and 4.84% of U report to the tailings; 94.83% ThO ₂ and 94.65% U follow the REE-rich concentrate

(continued on next page)

Table 1 (continued)

Reference	Monazite (%) Feed Composition	Experimental Setup (Conditions)	Performance (REE, Th, U Recovery)	Time (h)	Process Weaknesses	Environmental Impact (Th/ U deportment)
		concentrate leached in 6 M HCl + small H ₂ O ₂ at 70 °C for 60 min.	recovery to RECl ₃ solution: 96.27%		leaching. HCl is evolved during MgCl ₂ hydrolysis/ roasting	

comparison highlights that no single process provides an optimal balance between efficiency, selectivity, and environmental performance. The data also show that the apparent superiority of a process depends strongly on the evaluation criterion selected. Routes that minimize aqueous radionuclide mobility often do so by transferring Th and U to solid residues, whereas highly extractive routes may simply relocate the radiological burden to the leachate. Accordingly, Table 1 should be interpreted as a comparison of radionuclide management strategies as much as a comparison of extraction performance.

Caustic digestion offers effective separation of REEs from Th and U but at the cost of high reagent consumption and wastewater generation (Anvia, 2015; Samin et al., 2025). Emerging hybrid and modified processes (e.g., CaO–NaOH–H₂O systems, MgCl₂ roasting) demonstrate improved performance by combining enhanced mineral breakdown with better control of radionuclide partitioning (Huang et al., 2025).

Importantly, the data compiled in Table 1 reinforce that process selection must be tailored to ore characteristics and desired radionuclide management strategy, rather than relying on a single universal approach. A critical implication is that decomposition efficiency alone is not an adequate metric for comparing monazite processing routes. A process may achieve high structural breakdown yet still perform poorly from a radiological or downstream purification perspective if Th and U are mobilized into difficult-to-treat streams. Comparative assessment must therefore consider not only conversion extent, but also radionuclide destination and the form in which they are retained or released.

It has become evident that successful REE processing requires ore-specific process selection combined with dedicated radionuclide control strategies. Integrating mineralogy, dissolution chemistry, and speciation behavior is therefore essential to achieve both technical efficiency and regulatory compliance in modern REE extraction systems.

5.1.2. Sulfuric acid baking

Sulfuric acid baking is the dominant industrial route for processing monazite concentrates of variable grade ($\leq 50\%$ REO), with the advantage that it is not restricted to finely ground materials (Borai et al., 2016). In this process, monazite ((Ln,Th)PO₄) is mixed with concentrated sulfuric acid ($\approx 93\%$ H₂SO₄) and roasted at temperatures ranging from ~ 200 to 800 °C, resulting in the conversion of REEs into water-soluble sulfate species ((Ln,Th,U)SO₄). The efficiency of REE recovery and the partitioning behavior of Th and U are strongly governed by roasting temperature, acid-to-ore ratio (A/O), and ore mineralogy.

At elevated roasting temperatures (>300 °C), the resulting leach solutions are generally cleaner, with reduced co-dissolution of gangue elements such as Fe, Ca, and Ti. This behavior is attributed to the formation of refractory metal–phosphate (Me–P–O) phases, promoted by dehydration and polycondensation of orthophosphoric acid generated during early stages of sulfation (Teixeira et al., 2019; Demol et al., 2022; Demol et al., 2024; Traoré, 2025). Thorium follows a similar trend, forming insoluble phosphate species (e.g., Th–P–O phases such as Th(PO₃)₄), which are stable at temperatures around ~ 230 °C (Aziman and Ismail, 2020).

However, excessively high temperatures (~ 500 °C) may lead to partial REE recovery ($\sim 85\%$) due to the stabilization of refractory REE–phosphate phases such as CePO₄ and PrPO₄ (Demol et al., 2018). Under these conditions, Th is almost completely retained in the solid phase ($\approx 100\%$ rejection). To mitigate REE losses, additives such as muscovite and goethite have been proposed to inhibit the formation of refractory

REE–phosphate phases. These additives promote the formation of soluble aluminosilicate or iron–sulfate polyphosphate species during roasting (Demol, 2020).

For example, Fe-bearing phases may form Fe₂(SO₄)₃, which subsequently reacts with pyrophosphoric acid to produce iron pyrophosphate (Fe₄(P₂O₇)₃). This reaction consumes phosphoric acid, reducing its availability to reprecipitate REEs as phosphate phases, thereby enhancing REE solubilization at higher roasting temperatures (Traoré, 2025).

At lower roasting temperatures (<300 °C), the leaching behavior becomes highly sensitive to the acid-to-ore ratio (A/O) and mineralogical composition. Increasing the A/O ratio enhances sulfation efficiency, enabling REE recoveries exceeding 90%, but also promotes extensive co-dissolution of Th (≈ 95 – 100%) and significant impurity loading (Fe, Al, Mg, Ca) in the leachate (Traoré, 2025; Demol et al., 2022). Such impurity-rich solutions pose significant challenges for downstream solvent extraction and ion exchange processes (Judge and Azimi, 2020). This observation is particularly important because it shows that high REE recovery and good overall process selectivity are not synonymous. Under these conditions, the process may appear favorable when judged only by extraction percentage, yet become substantially less attractive once impurity management, radionuclide removal, and effluent treatment are included in the evaluation.

To mitigate impurity accumulation, pre-treatment strategies have been proposed. For instance, Borai et al. (2016) demonstrated that pre-washing with HCl (6 M, 60 °C, S/L = 5%, 0.5 h) effectively removes Ca, Na, Ti, and Fe with efficiencies of $\sim 80\%$, 100% , $\geq 90\%$, and $\geq 90\%$, respectively.

Iron behavior is particularly influenced by mineralogical form. Goethite (FeOOH) and magnetite (Fe₃O₄) exhibit significantly higher reactivity than hematite (Fe₂O₃), reflecting differences in crystallinity and structural stability (Gontijo et al., 2020). Using a geo-metallurgical approach, Demol et al. (2022) reported Fe dissolution in the order: goethite (≈ 74 – 77%) $\geq$ magnetite (≈ 74 – 84%) $\gg$ hematite (≈ 14 – 17%). The higher reactivity of magnetite is attributed to its mixed Fe(II)/Fe(III) valence, which facilitates sulfation, whereas hematite's dense structure limits its reactivity. This finding highlights a broader limitation in the current literature: gangue iron is often treated as a bulk chemical constituent rather than a mineralogically distinct process variable. However, the results clearly show that iron deportment is phase-specific, meaning that total Fe assays alone are insufficient for predicting sulfation behavior or impurity loading.

Ore matrix composition further defines process performance. In Fe-free monazite systems, high recoveries ($\sim 95\%$) of both REEs and Th/U have been reported following roasting at 210 – 220 °C with A/O ≈ 3 – 4 , followed by water leaching at 70 °C (Jeon et al., 2022; Berry et al., 2018). In contrast, Borai et al. (2016) achieved complete Th dissolution ($\approx 100\%$) but limited REE recovery ($\sim 35\%$) using dilute H₂SO₄ (10%) and low A/O (~ 0.3). This suggests preferential Th solubilization via sulfate complexation relative to REEs, consistent with the stronger complexation behavior of Th(IV) in sulfate media (Fig. 1b).

This behavior can be explained by the higher charge density and coordination flexibility of Th(IV), which enhances its interaction with sulfate ions compared with trivalent REEs. Consequently, increasing A/O promotes more complete sulfation of REEs and improves their dissolution.

At the same time, these results caution against interpreting higher

acid dosage as a universally beneficial strategy. While greater acid availability may improve REE sulfation, it can also intensify radionuclide dissolution and gangue attack, shifting the process from a recovery-limited regime to a separation-limited regime. The optimal acid input is therefore constrained by downstream processability rather than extraction alone.

Gangue interactions further complicate process behavior. In Fe–Ca-rich matrices (Fe $\approx$ Ca $\approx$ 30–35%), Traoré (2025) reported moderate recoveries ($\approx$ 66% REEs, 50% Th, 65% Ca, 75% Fe) under roasting at 200 °C and A/O $\approx$ 1.5, although the specific mineral phases were not fully characterized.

In Fe-rich systems dominated by goethite (α -FeOOH) with subordinate ilmenite (FeTiO₃), Gontijo et al. (2023) observed high REE recoveries ($\approx$ 85–93%) while Fe dissolution remained limited ($\sim$ 10–22%). The selective behavior was attributed to the different reactivities of the Fe-bearing gangue minerals during sulfation and leaching, with ilmenite remaining relatively refractory under the applied conditions (Long et al., 2026).

In contrast, Ca-rich systems exhibit lower REE recovery ($\sim$ 57%) due to gypsum (CaSO₄•2H₂O) formation, which reduces sulfate availability and inhibits REE dissolution (Gontijo et al., 2023). Although Th behavior was not explicitly measured, its stability in sulfate-rich systems is expected to exceed that of REEs, depending on pH and competing complexation reactions (E. Kim and Osseo-Asare, 2012). The contrast between Fe-rich and Ca-rich matrices demonstrates that ore mineralogy does more than modify process efficiency; it changes the nature of the governing process limitation. In Fe-rich systems, the challenge is primarily impurity sulfation and phase reactivity, whereas in Ca-rich systems it is sulfate consumption and secondary gypsum formation. This distinction is important for process design because it implies that different ores require different optimization targets, even within the same nominal roasting route.

Low-temperature roasting ($\sim$ 200 °C) with high A/O result in high REE recovery ($\approx$ 90–95%) but extensive Th/U dissolution ($\geq$ 95%) and hence radionuclide-rich leachates are generated. High-temperature roasting ($>$ 300 °C) results in cleaner leachates which is strong in Th immobilization but there are potential REE losses due to refractory phase formation. Mineralogical complexity further amplifies this variability, influencing acid consumption, impurity dissolution, and radionuclide partitioning. From a process design perspective, these results demonstrate that optimal operating conditions must balance REE recovery efficiency, impurity management, and controlled Th/U partitioning. Sustainable monazite processing therefore requires selecting operational windows that not only maximize REE extraction but also ensure that radionuclides are directed into process streams where they can be effectively managed, whether through controlled dissolution and recovery or stable immobilization in solid residues.

To provide a consolidated comparison of sulfuric acid baking conditions and their impact on process performance, Table 2 summarizes key operational parameters reported in the literature, including roasting temperature, acid-to-ore ratio (A/O), leaching conditions, REE recovery, and the corresponding behavior of Th and U. The compiled data highlight the strong dependence of REE extraction efficiency and radionuclide partitioning on both thermochemical conditions and ore mineralogy. In particular, the table illustrates the trade-off between high REE recovery achieved at low-temperature, high A/O conditions and the increased co-mobility of Th and U under these regimes, compared with higher-temperature operations that favor radionuclide immobilization but may reduce REE recovery due to refractory phase formation. This comparison reinforces the need for process optimization strategies that balance recovery, selectivity, and radiological control.

An important limitation of the published sulfuric acid baking data is that comparable roasting temperatures and acid-to-ore ratios do not always produce comparable outcomes across studies. The variability in reported Th dissolution demonstrates that operating variables cannot be interpreted independently of feed mineralogy. Demol et al. (2022)

reported significantly higher Th dissolution during laboratory sulfuric acid baking of monazite concentrates than has been observed in some industrial processing routes. Differences in monazite grade, gangue composition, and the occurrence of Th-bearing accessory minerals are known to influence acid consumption, sulfation reactions, and radionuclide partitioning, contributing to the variability reported across studies (Aziman and Ismail, 2020; Su et al., 2021). Thus, Table 2 should be read not as a universal optimization chart, but as evidence that process windows are ore specific.

To further illustrate the differences mentioned above, Fig. 3 presents simplified flowsheets for the major monazite processing routes, highlighting the pathways of REEs and the partitioning of Th and U across process streams.

5.2. Th and U deportment during ion-adsorption clay processing

Ion-adsorption clay deposits differ fundamentally from monazite ores because a significant fraction of their REEs occurs as hydrated cations adsorbed to negatively charged clay-mineral surfaces rather than incorporated within a refractory phosphate lattice (Azimi, 2025). Consequently, REEs can commonly be recovered through ion exchange using relatively mild salt solutions, including ammonium sulfate, magnesium sulfate, and other electrolyte systems. The extractability of the REEs depends on whether they occur as weakly bound outer-sphere complexes, more strongly retained inner-sphere complexes, or within residual REE-bearing mineral phases (Borst et al., 2020; Liu et al., 2022a, 2022b).

Ion-adsorption clays generally contain lower concentrations of Th and U than monazite-rich ores. However, the distribution of these radionuclides among exchangeable, oxide-associated, and residual mineral fractions is more important than their bulk concentration for predicting their behavior during leaching. Unlike the exchangeable REE fraction, Th is commonly associated with resistant accessory minerals or strongly sorbed to Fe- and Mn-bearing phases because of the strong hydrolysis and surface-binding behavior of Th(IV). Uranium may occur in residual minerals, adsorbed forms, or oxidized U(VI)-bearing species, and its mobility is therefore more sensitive to redox conditions, pH, carbonate, and ligand availability.

Under the mildly acidic to near-neutral conditions generally used for salt leaching, dissolution of refractory Th- and U-bearing minerals is limited (Anawati and Azimi, 2022). This can permit preferential recovery of exchangeable REEs while retaining much of the Th and U in the leached clay residue. Nevertheless, radionuclide deportment remains deposit-specific because some ion-adsorption clay systems also contain discrete monazite, xenotime, zircon, or other accessory phases. More acidic treatment or alkaline pretreatment intended to liberate non-exchangeable REEs may attack these phases and increase the transfer of Th and U to the leach solution. Accordingly, radionuclide partitioning in ion-adsorption clay processing should be evaluated using sequential extraction, mineralogical characterization, and direct analysis of both leachates and residues rather than inferred solely from the total Th and U contents of the feed (Cunningham et al., 2025).

The limited availability of studies reporting complete Th and U mass balances remains an important knowledge gap. Most ion-adsorption clay investigations focus on REE extraction, ammonium consumption, permeability, or impurity dissolution, while radionuclide concentrations in the feed, leachate, and residue are not consistently reported. Further research is therefore required to establish how radionuclide host phases and leaching conditions affect their long-term partitioning during both ex-situ and in situ ion-exchange extraction.

5.3. Process selection and decision framework

The analysis of monazite processing routes highlights that hydrometallurgical extraction of REEs is inherently governed by a trade-off between recovery efficiency, impurity management, and radionuclide

Table 2

Comparative analysis of sulfuric acid baking conditions highlighting the trade-off between REE recovery, impurity dissolution, and Th/U partitioning.

Reference	Feed Composition (%)	Experimental Setup	Performance (REE / Th / U Recovery)	Time (Hours)	Process Weaknesses	Th/U in Residues (Quantified Where Data Exist)
Borai et al., 2016	Ce 12.21 La 6.899 Gd 4.063 Nd 3.841 Y 1.097% Pr 0.972 Sm 0.598 Th 4.338 U 0.242 P 4.47	HCl pre-washing for impurity removal followed by H ₂ SO ₄ digestion. The preferred low-acid route used concentrated H ₂ SO ₄ at approximately monazite:H ₂ SO ₄ = 1:1, 220 °C for 2 h, with a small BaCl ₂ addition; hot-water washing followed. Th was selectively precipitated by NH ₄ OH at pH 0.9. LREEs were subsequently precipitated using Na ₂ SO ₄ ; remaining REEs were converted to hydroxides at pH 7, HCl-leached at pH 3, and HREEs/Y precipitated with 3% oxalic acid.	Low-acid digestion enabled approximately 99.9% leaching of Th and phosphate, while most REEs and U remained undigested. Subsequent selective Th precipitation was 99.3% at pH 0.9. LREE double-sulfate precipitation efficiencies were Ce 92.1%, Nd 79.45%, La 82.2%	Principal digestion: 2 h at 220 °C	High-temperature concentrated H ₂ SO ₄ digestion; multistage flowsheet involving washing, BaCl ₂ treatment, pH-controlled Th precipitation, double-sulfate precipitation, hydroxide conversion, HCl leaching and oxalate precipitation; significant sensitivity of Th/REE selectivity to pH and BaCl ₂ dosage; incomplete/selectivity problems occurred under the high-acid route.	Under the preferred low-acid digestion, Th was extensively mobilized (~99.9%) while most U and REEs remained in the undigested residue. A complete quantitative final Th/U mass balance and waste-volume inventory were not reported.
	Th 3.0 P 7.8 Ce 1.3 Gd 0.9 Eu 0.8 U 0.0037	WLP dried, ground and sieved to <500 µm. Sulfuric-acid digestion at solid:acid = 1:5, generally 2 h with stirring at 600 rpm. Acid molarity varied from 3 to 18 M H ₂ SO ₄ ; temperature from 100 to 350 °C; leaching time from 0.5 to 2 h	About 50% Th dissolution at 6 M H ₂ SO ₄ ; with concentrated H ₂ SO ₄ , Th dissolution approached ~90% at 150 °C	2	Requires strong sulfuric acid, high acid-to-solid ratio (1:5), elevated temperature, and multistep digestion/leaching. Very concentrated acid improves Th dissolution but increases reagent demand and corrosion concerns. REE dissolution also occurs, so selectivity between Th and REEs is limited.	~90% of Th is transferred from WLP residue to sulfate leach solution, leaving roughly ~10% in the residual solid. U deportment during digestion was not quantified in detail
Demol et al., 2024	Ce 23.3 La 12 Nd 9.2 Pr 2.34 P 11.5	Monazite and hydroxyapatite ground to P80 ≈ 44 and 41 µm, respectively. Primarily 1:1 w/w monazite:apatite mixtures. H ₂ SO ₄ baking at 200–800 °C; acid addition corresponding to 250% stoichiometric requirement for monazite +150% for apatite (1600 kg H ₂ SO ₄ /t for 1:1 mixture). Bake held 2 h at final temperature. Baked solids leached in 0.9 M H ₂ SO ₄ , L/S = 40:1 w/w, 20–25 °C for 2 h. A goethite test used monazite:apatite:goethite = 1:1:3 at 500 °C and 1800 kg/t H ₂ SO ₄ .	For 1:1 monazite:apatite, REE dissolution was 90–99% at 200–300 °C, reaching 99% at 300 °C. At 500 °C, REE dissolution dropped to 29%, compared with 80% for monazite alone. Increasing apatite:monazite to 2:1 reduced REE dissolution further to ~12%. Addition of goethite at 500 °C increased REE dissolution from 29% to 85%. At 500 °C for monazite:apatite = 1:1, only about 4% Th dissolved, meaning the great majority remained in the solid residue. However, addition of goethite increased Th dissolution to 53%, while REE dissolution increased to 85%. At lower bake temperatures, Th dissolution was substantially higher.	2 h bake +2 h leach = 4 h principal reaction stages	Very high H ₂ SO ₄ consumption (1600 kg/t for 1:1 monazite/apatite; 1800 kg/t with goethite); elevated-temperature baking; apatite can severely suppress REE recovery above 300 °C through insoluble polyphosphate formation; high L/S ratio (40:1) during leaching; goethite restores REE recovery but also substantially increases Th dissolution and adds solid mass.	At 500 °C, 1:1 monazite/apatite: ~4% Th dissolved, so ~96% remained associated with the solid stream; the measured leach residue contained 547 mg Th from 597 mg in the feed in the reported mass balance. REE retention was also substantial because only 29% TRE dissolved. U was not reported.
	TRE 50.1 Th 5.97 P 11.5 Si 1.39 Zr 2.4 LRE (La–Nd) 46.9 HRE (Sm–Lu) + Y 3.21	Sulfuric acid baking using 1700 kg H ₂ SO ₄ /t concentrate, equivalent to 250% of stoichiometric sulfate requirement. Bake temperatures 200–800 °C. At 200–250 °C: heat at 5 °C/min and hold 2 h. Above 250 °C: initial stage at 250 °C for 2	REE dissolution: 90% at 200 °C, 96% at 250 °C, 99% at 300 °C. Above 300 °C, REE dissolution progressively decreased because of insoluble Th–REE polyphosphate formation; at 800 °C only	Low-temperature route: 2 h bake +2 h leach = 4 h principal stages. For bake temperatures >250 °C: 2 h at 250 °C + 2 h at final temperature + 2 h leach = 6 h	Very high H ₂ SO ₄ consumption (1700 kg/t); high leach L/S (40:1); elevated-temperature operation; low-temperature baking gives excellent REE recovery but high Th dissolution; higher-temperature baking suppresses Th but	At ~250 °C, >90% Th dissolution was obtained. At 300 °C, Th dissolution fell sharply to ~35% because Th pyrophosphate precipitated during leaching. At 500 °C, Th dissolution was <10%,

(continued on next page)

Table 2 (continued)

Reference	Feed Composition (%)	Experimental Setup	Performance (REE / Th / U Recovery)	Time (Hours)	Process Weaknesses	Th/U in Residues (Quantified Where Data Exist)
Jeon et al., 2022	Th 2.42 U 0.46 Ce 26.2 La 13.20 Nd 8.84 Pr 1.95 Sm 1.06 Gd 0.87 Y 1.33	h, followed by heating to final temperature and another 2-h hold. Baked solids ground and leached in 0.9 M H ₂ SO ₄ , L/S = 40:1, 20–25 °C, 2 h. Concentrated 99% H ₂ SO ₄ acid baking/sulfation. Temperature investigated: 220–260 °C; time: 0–180 min; H ₂ SO ₄ /concentrate mass ratio: 0.5–5, optimum: 220 °C, 180 min, H ₂ SO ₄ /monazite = 1. Water leach at 70 °C, 250 rpm, 10% pulp density. Th subsequently separated by SX using 0.1 M Primene JM-T at ~2 M acidity; downstream LREE separation investigated using Cyanex 572.	~52–55% REEs dissolved because monazite partially re-formed. ~88% REE and Th leaching under their stated optimum sulfation/ water-leach conditions. At H ₂ SO ₄ / ore ratios ≥3, ~95% REE and Th leaching was observed. From the resulting PLS, >95 ± 2% Th extraction was achieved using 0.1 M Primene JM-T at ~2 M acidity, with low REE co-extraction	3	progressively reduces REE recovery through insoluble polyphosphate formation; at 650–800 °C, monazite partially re-forms. Concentrated H ₂ SO ₄ and elevated-temperature baking; long 3 h sulfation; Th is intentionally co-leached with REEs, necessitating a downstream Th-removal stage; higher acid/ore ratios improve leaching but substantially increase acid consumption; multistage SX is required for subsequent REE separation.	with most Th rejected to the solid residue. U was not reported. Approximately 88% Th is mobilized with the REEs into the PLS under the stated optimum leaching conditions, followed by >95 ± 2% extraction of dissolved Th into the Primene JM-T organic phase. Feed contains 0.46 wt% U, but U deportment during baking/ leaching and downstream separation was not reported
Berry et al., 2018	Ce 23.00 La 10.30 Nd 8.39 Pr 2.20 Sm 1.39 Y 0.91 Th 2.60 U 0.34	H ₂ SO ₄ acid bake followed by water leaching. Baking: 180–250 °C, 1–4 h, H ₂ SO ₄ /concentrate (S/C) = 1:1–4:1, average particle size 48–137 µm. Water leach: 70 °C, 30 min, 500 rpm, 200 mL DI water per 5 g concentrate	At S/C = 4:1, 210 °C, 4 h, ≥90% extraction of REEs, U and Th was obtained, with Th approaching 100%. At S/C = 1:1, REE extraction was only ~60–70%, but Th ~2% and U ~ 5%, demonstrating strong selective retention of Th/U. At S/C = 2:1 and 210 °C, ≥97% REE extraction was achieved after 3 h, while Th/U extraction depended strongly on temperature/time.	1–4 h baking +30 min water leaching	Concentrated H ₂ SO ₄ ; elevated-temperature bake; high acid dosage required for simultaneous high REE/Th/U extraction; acid consumption increases with baking time and S/C ratio; Th/U mobility is highly sensitive to operating conditions; refractory silicate-bearing residue remains.	Highly condition-dependent. At S/C = 1:1, only ~2% Th and ~ 5% U were extracted, so ~98% Th and ~ 95% U remained in the residue, but REE extraction was only ~60–70%. At S/C = 4:1, Th approached 100% extraction and U ~ 90%, transferring most radionuclides to the PLS. Increasing baking temperature generally decreased Th/U extraction and increased their retention in the residue.
Gontijo et al., 2023 (Fe-rich)	REO 7.4% Fe ₂ O ₃ 45.6% P ₂ O ₅ 7.2% CaO 0.9% Th 0.0479 U 0.0099	Natural fines (<74 µm); H ₂ SO ₄ sulfation/acid baking at 25–240 °C, H ₂ SO ₄ /sample = 0.45:1–0.95:1, 0–60 min; followed by leaching in 0.9 M H ₂ SO ₄ at 30 ± 3 °C for 2 h, sample:solution = 1:9.	maximum REE extraction 93% at 25 °C, 30 min, H ₂ SO ₄ /sample 0.72:1; 91% at 0.95:1 with only ~6% Fe dissolution. Recommended selective condition (25 °C, 15 min, 0.45:1) gave ~85% TREE with ~12% Fe dissolution	15 min sulfation +2 h leaching = 2.25 h principal reaction time	Fe-rich gangue consumes H ₂ SO ₄ and can reduce REE extraction; higher acid addition can cause agglomeration/handling and potential scaling problems	Th and U extraction/deportment were not experimentally reported
Gontijo et al., 2023 (Ca-rich)	REO 2.1 CaO 24.9 P ₂ O ₅ 19.5 Fe ₂ O ₃ 17.2 Th 0.00707 U 0.01195	Natural fines (<74 µm); H ₂ SO ₄ sulfation/acid baking at 25–240 °C, H ₂ SO ₄ /sample = 0.45:1–0.95:1, 0–60 min; followed by leaching in 0.9 M H ₂ SO ₄ at 30 ± 3 °C for 2 h, sample:solution = 1:9.	Considerably lower REE extraction, approximately 55% under the recommended selective condition and ≤ 66–67% maximum, due largely to Ca-sulfate formation/ REE uptake	15 min sulfation +2 h leaching = 2.25 h principal reaction time	Ca-rich feed forms gypsum/CaSO ₄ coatings that passivate phosphate minerals and retain REEs; high Ca/P also increases impurity burden.	Th and U extraction/deportment were not experimentally reported
Teixeira et al., 2019	Three Fe-rich monazite-bearing natural fines (<74 µm): Bebedourite : 4.26% REO, 25.79% Fe, Th 352 mg/kg, U 46 mg/kg; Flogopitite : 4.70% REO, 21.81% Fe, Th 181 mg/kg, U 45 mg/kg; Foscorite : 4.86% REO, 24.05% Fe, Th 233 mg/kg, U 50 mg/kg. Main REE carrier = monazite , with ~5% of REEs in crandallite.	Natural fines (<74 µm); sulfation with 97.5 wt% H ₂ SO ₄ ; acid addition 0.21–0.34 kg H ₂ SO ₄ /kg ore; mixing; roasting 200–800 °C for 2 h; cooling; water leaching at 10 wt% solids for 2 h at room temperature, pH controlled at 1.5–2.0.	Optimum at ~700 °C: REO extraction 73–82%, depending on feed, while Fe and Th extraction <1%. Above 700–750 °C, REE extraction decreases sharply and approaches zero at 800 °C.	30 min sulfation/mixing +2 h roasting +2 h water leaching = 4.5 h principal process stages	High-temperature roasting (~700 °C); narrow selective temperature window; REE recovery only ~70–80%; REE extraction collapses above ~750 °C due to formation/decomposition of insoluble REE compounds; SO _x /SO ₃ -containing off-gas generated during sulfate decomposition and requires management/recovery.	Th extraction <1% at ~700 °C, indicating >99% Th remains with the solid residue. U extraction/deportment was not reported.

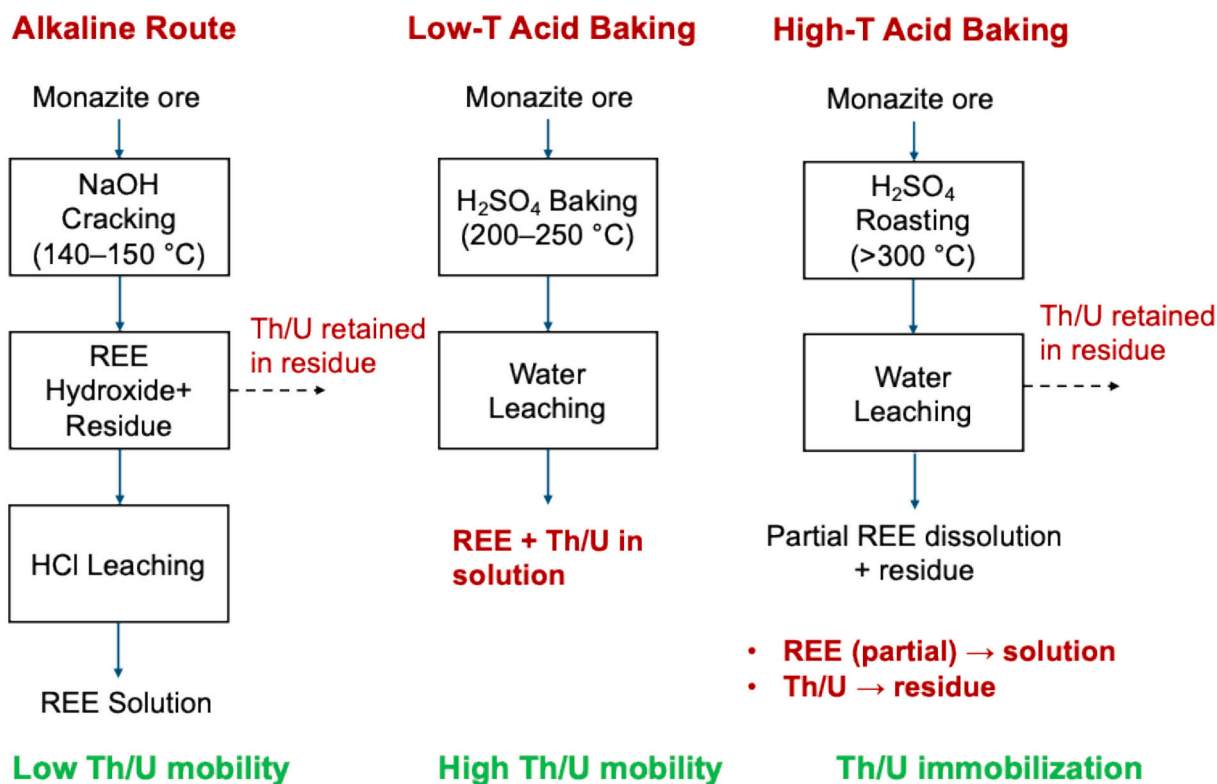


Fig. 3. Simplified flowsheets for major monazite processing routes illustrating REE extraction pathways and the partitioning behavior of Th and U.

mobility. While individual studies often report optimized conditions for maximizing REE dissolution, a broader comparison reveals that these conditions frequently coincide with increased transfer of Th and U into the leach solution. Conversely, process configurations that suppress

radionuclide mobility tend to limit REE recovery or shift radiological burdens to solid residues.

To synthesize these relationships, Fig. 4 presents a conceptual trade-off map linking REE recovery to Th/U dissolution into the leachate

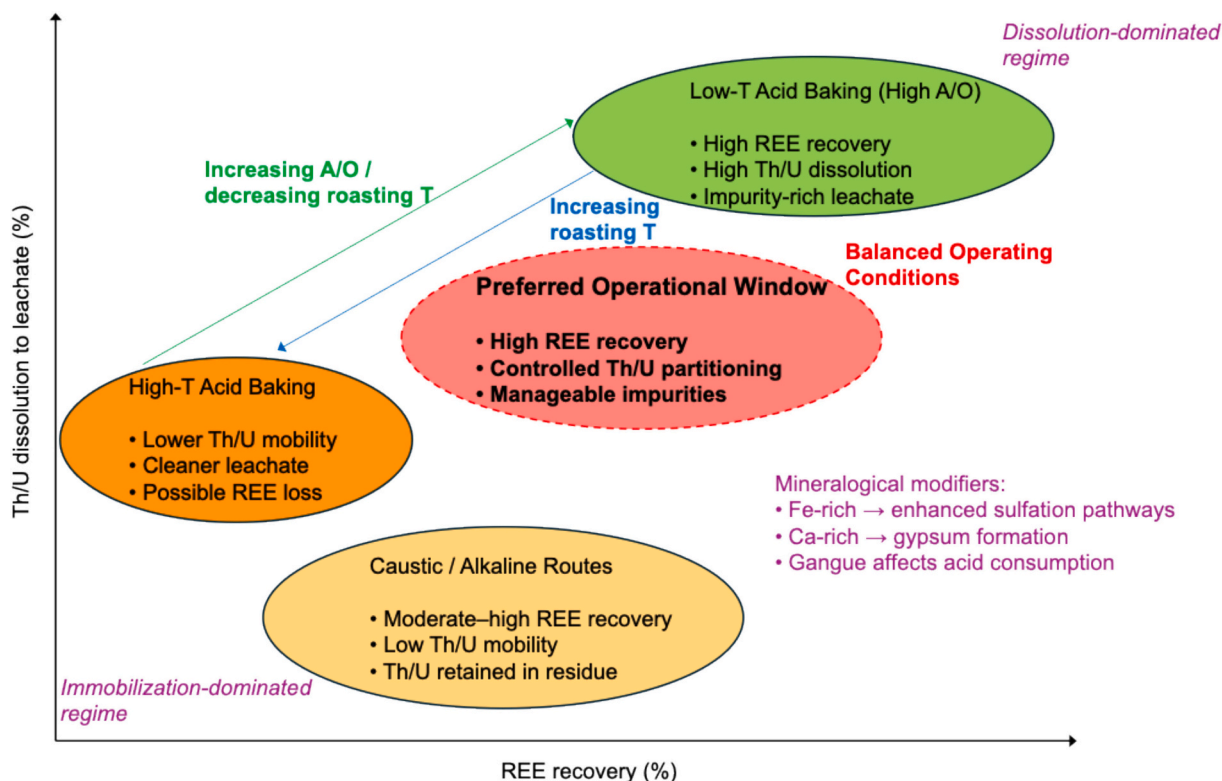


Fig. 4. Conceptual trade-off diagram illustrating the relationship between REE recovery and the transfer of Th and U to the leachate during monazite processing.

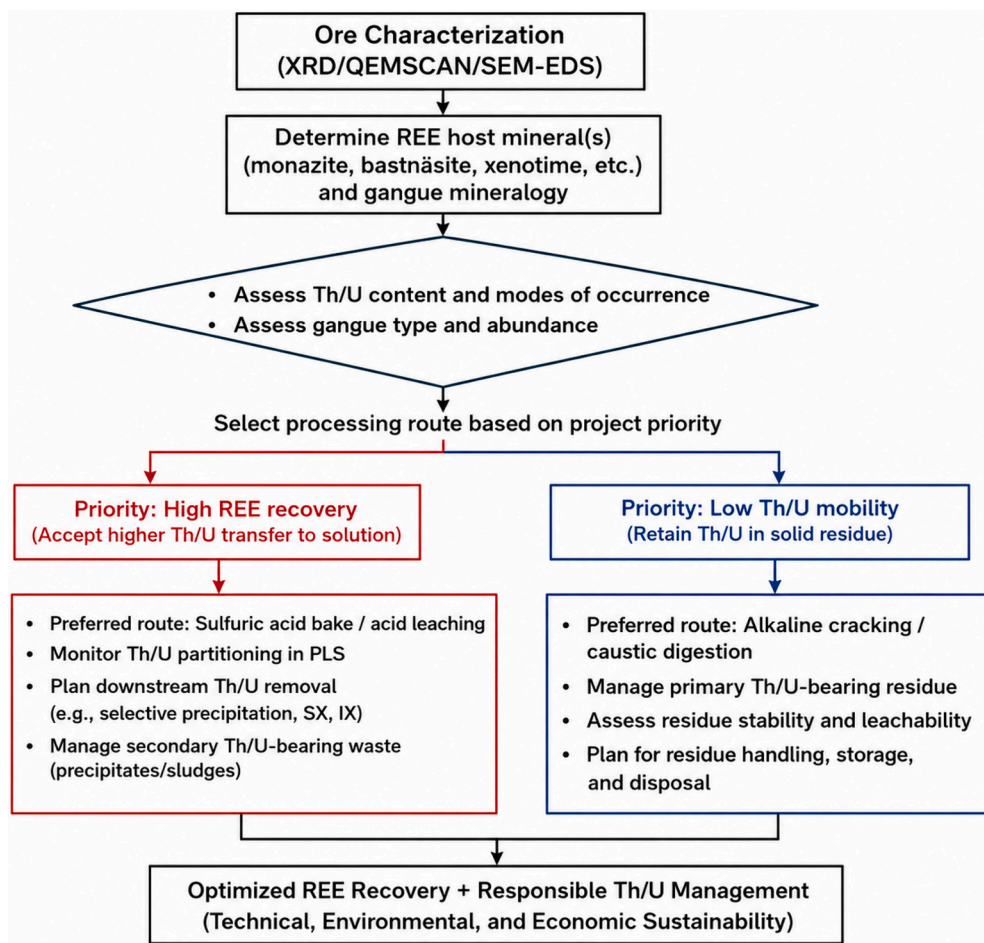


Fig. 5. Conceptual decision framework for selecting hydrometallurgical treatment routes for REE-bearing ores. The framework integrates mineralogical characterization, radionuclide occurrence, process objectives, and operational constraints to guide the selection of appropriate extraction strategies while balancing REE recovery, radionuclide mobility, environmental performance, and residue management requirements.

across different processing routes and operating conditions. The diagram identifies distinct process domains corresponding to alkaline treatment, low-temperature sulfuric acid baking, and high-temperature roasting, each characterized by specific performance outcomes.

Low-temperature acid baking at high acid-to-ore ratios (A/O) occupies the region of high REE recovery but is associated with extensive co-dissolution of Th and U, resulting in impurity-rich leachates that require complex downstream treatment. In contrast, high-temperature roasting shifts the system toward lower radionuclide mobility and cleaner solutions, primarily due to the stabilization of refractory phosphate phases and reduced solubility of Th-bearing compounds. However, these conditions may also reduce REE recovery through incomplete mineral decomposition or reprecipitation phenomena.

Alkaline processing routes represent a fundamentally different regime, in which Th and U are largely retained in solid residues due to limited solubility under mildly acidic to alkaline conditions. While this reduces immediate radionuclide transfer to the aqueous phase, it introduces challenges related to the long-term stability and management of radioactive solid wastes.

Importantly, the transitions between these regimes are not discrete but are controlled by continuous variations in operating parameters such as roasting temperature, acid-to-ore ratio, and leaching conditions. As illustrated in Fig. 4, increasing roasting temperature generally promotes radionuclide immobilization and reduces impurity dissolution, whereas increasing A/O and decreasing roasting severity enhance REE recovery at the expense of increased Th/U mobility. These opposing

trends define a continuum of process performance rather than isolated operating modes.

A key implication of this analysis is the existence of a preferred operational window, in which high REE recovery can be achieved while maintaining controlled radionuclide partitioning and manageable impurity levels. The position and extent of this window are strongly dependent on ore mineralogy. Fe-rich systems may facilitate sulfation reactions and improve REE extraction efficiency, whereas Ca-rich matrices can promote gypsum formation, reducing sulfate availability and limiting REE dissolution. Similarly, gangue composition influences acid consumption, secondary phase formation, and overall process selectivity.

Therefore, the trade-off between REE recovery and radionuclide mobility cannot be resolved through a single universal processing strategy. Instead, optimal process design requires a geo-metallurgical approach that integrates mineralogical characteristics with thermochemical conditions and solution chemistry. By explicitly considering these interactions, it becomes possible to tailor operating conditions that maximize extraction efficiency while ensuring effective control of Th and U across process streams. This perspective reframes REE processing not as a problem of maximizing extraction, but as a multi-objective optimization problem governed by competing chemical and mineralogical constraints. This shift in perspective is essential for moving from empirically optimized conditions toward predictive and mineralogy-informed process design.

Beyond metallurgical performance, the selection of a processing

route is strongly influenced by reagent consumption, energy requirements, waste management costs, and operational complexity. Sulfuric acid baking is attractive because it is a mature industrial technology capable of achieving high REE recoveries and processing large throughputs. However, it requires substantial sulfuric acid consumption and elevated roasting temperatures, resulting in increased energy demand and the generation of sulfate-bearing process streams that require treatment.

In contrast, alkaline cracking routes generally operate with lower radionuclide mobility and simplify downstream solution purification by retaining most Th and U within solid residues. Nevertheless, these processes require significant quantities of caustic reagents and generate alkaline waste streams that must be managed appropriately. In addition, the economic benefits associated with improved radionuclide control may be partially offset by costs related to residue handling and long-term storage.

From a practical perspective, neither route can be considered universally superior. Sulfuric acid baking may offer advantages where maximum REE recovery is prioritized and existing acid infrastructure is available, whereas alkaline processing may be preferred where radiological management, solution purity, or regulatory constraints are dominant considerations. Consequently, process selection should be based on a site-specific evaluation that integrates mineralogy, recovery targets, reagent availability, environmental obligations, and radionuclide management requirements.

The literature reviewed in this work demonstrates that no single hydrometallurgical route is universally optimal for all REE deposits. Instead, process selection should be guided by the interplay between mineralogical characteristics, radionuclide occurrence, gangue composition, recovery objectives, and environmental constraints. Based on the collective findings of the reviewed studies, a conceptual decision framework is proposed to assist in the selection of suitable processing routes (Fig. 5). The framework emphasizes the importance of integrating mineralogical characterization with radionuclide assessment prior to process development and highlights how different processing objectives may favor alternative treatment strategies.

The proposed framework begins with detailed characterization of the REE host minerals and associated radioactive components. Deposits dominated by monazite and containing elevated concentrations of Th and U require particular attention because radionuclide behavior becomes a key process constraint. Where maximum REE recovery is the primary objective, sulfuric acid baking may provide favorable performance, although increased radionuclide mobility and downstream treatment requirements must be considered. Conversely, where minimization of radionuclide transfer to solution is prioritized, alkaline processing routes may be advantageous because Th and U are largely retained within solid residues. In all cases, process selection should be supported by geometallurgical characterization and an assessment of waste management, environmental performance, and economic feasibility.

5.4. Implications of Th/U mobility for downstream REE recovery and purification

The partitioning of Th and U during leaching directly affects the complexity of downstream REE recovery. REEs are commonly recovered from PLS through precipitation, ion exchange, solvent extraction (SX), and crystallization, with SX being the principal industrial technology for separating individual REEs or producing mixed REE products (Xie et al., 2014). When Th and U are retained in the solid phase during primary extraction, their transfer to downstream REE separation circuits is minimized; however, the resulting Th/U-bearing residues require appropriate management and disposal (Amaral et al., 2018).

Conversely, dissolution of Th and U transfers these elements to the PLS and introduces additional separation requirements before or during REE recovery. The behavior of dissolved Th is strongly dependent on

solution chemistry, particularly pH and the presence of phosphate and sulfate species (Kim and Osseo-Asare, 2012). Th and U present in sulfate liquors can be separated from REEs through processes such as selective precipitation and solvent extraction; for example, simultaneous or sequential extraction of Th and U from sulfate solutions using amine extractants has been demonstrated (Amaral et al., 2018). Thus, mobilization of Th and U during primary extraction can necessitate additional downstream separation stages and generate Th/U-bearing process streams requiring further treatment.

Consequently, Th/U partitioning during primary extraction should be considered as part of the overall flowsheet rather than independently of downstream REE recovery. Greater transfer of Th/U to the PLS can increase downstream purification requirements and shift the radioactive inventory from the primary residue to downstream process streams. Conversely, retaining Th/U in the solid phase can simplify downstream REE purification but concentrates the radioactive inventory in the primary residue. Thus, process selection should balance REE recovery with Th/U partitioning and the resulting requirements for downstream purification and waste management.

6. Conclusions

This review examined how mineralogy and solution chemistry govern the partitioning of Th and U during hydrometallurgical processing of REE ores, with the most detailed evidence available for monazite. Th mobility is primarily controlled by hydrolysis, precipitation, and complexation with sulfate and phosphate, whereas U is generally more mobile under oxidizing conditions because of the stability of aqueous uranyl complexes.

The comparison of monazite-processing routes shows that low-temperature sulfuric acid baking at high acid-to-ore ratios can achieve high REE recovery but may also transfer substantial Th and U to the leachate. Higher-temperature roasting can suppress radionuclide dissolution through the formation of refractory phosphate phases, although REE losses may occur. Alkaline cracking generally retains radionuclides in the primary residue and produces cleaner process liquors but requires substantial caustic input and long-term management of the resulting solids.

These findings demonstrate that radionuclide control cannot be evaluated independently of REE recovery or waste management. Dissolving Th and U creates downstream separation requirements and secondary radioactive solids, whereas suppressing their dissolution concentrates them in primary process residues. The preferred route is therefore ore-specific and depends on radionuclide host phases, gangue mineralogy, solution chemistry, and the capacity to manage the resulting waste streams.

Future studies should combine quantitative mineralogy, aqueous speciation, kinetic measurements, and solid-phase characterization to establish predictive relationships between processing conditions and radionuclide deportment. Such data are needed to move monazite processing from empirical optimization toward mineralogy-informed flowsheet design.

CRediT authorship contribution statement

Kolela J. Nyembwe: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Christian Ekberg:** Writing – review & editing, Supervision, Conceptualization. **Martina Petranikova:** Writing – review & editing, Software. **Arushi Kanojia:** Writing – review & editing. **Ilyes Mahti:** Writing – review & editing. **Gisele Azimi:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Christian Ekberg reports financial support was provided by European Union. Gisele Azimi reports a relationship with University of Toronto that includes: employment. Given her role as Associate Editor, Gisele Azimi had no involvement in the peer review of this article and had no access to information regarding its peer review. Full responsibility for the editorial process for this article was delegated to another journal editor. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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