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PROCESSING TECHNOLOGIES FOR RARE EARTH ELEMENTS FROM PERALKALINE IGNEOUS DEPOSITS: A SYSTEMATIC REVIEW

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Abstract

Peralkaline igneous deposits have gained increased attention as strategic sources of heavy rare earth elements (HREEs) and critical metals such as Zr, Nb, and Hf, providing a potential alternative to carbonatite and ion-adsorption clay deposits within a diversified global supply chain. Their processing remains technologically challenging due to complex silicate mineralogy—dominated by eudialyte-group minerals and steenstrupine—slow dissolution kinetics, and the widespread formation of silica gel during leaching, all of which require specialized "chemical-cracking" methods, including acid baking, dry digestion, sulfation or chloride roasting, and alkali fusion. Significant progress has been made in beneficiation (e.g., improved magnetic and gravity separation, enhanced mineral liberation through automated mineralogy) and hydrometallurgical processing, especially in approaches that prevent silica polymerization, boost selectivity for HREEs, and lower reagent use through optimized thermochemical decomposition. Recent research also includes innovations in solvent extraction, residue stabilization strategies, and life-cycle assessments, highlighting both improved technical feasibility and changing environmental considerations. Compared to carbonatites, which generally contain more acid-soluble LREE phases, peralkaline deposits demand more energy-intensive processing flowsheets; however, they provide significantly higher HREE concentrations than ion-adsorption clays, supporting long-term supply resilience. Overall, these advancements indicate that many of the historical metallurgical challenges associated with peralkaline REE ores are becoming increasingly manageable, positioning these deposits as promising sources for future REE production.

Keywords. peralkaline igneous rocks; eudialyte; steenstrupine; loparite; Zr–Nb–REE deposits; hydrometallurgy; roasting; chloride leaching.

Highlights

- Peralkaline igneous deposits provide some of the world's richest natural concentrations of HREEs along with critical co-products such as Zr, Nb, and Hf..
- Complex silicate mineralogy, including eudialyte-group minerals and steenstrupine, causes slow dissolution rates and requires specialized chemical-breaking strategies.
- Thermochemical innovations (sulfation/chloride roasting, alkali fusion) greatly reduce silica gel formation and improve overall REE extraction efficiencies.

- Compared to carbonatites, peralkaline ores require more energy-intensive processing; compared to ion-adsorption clays, they provide significantly higher HREE grades.
- Technological progress and new LCA data suggest that peralkaline deposits can significantly help build a diverse and resilient global REE supply chain.

1. Introduction

The rising global demand for high-performance permanent magnets, advanced alloys, and low-carbon technologies has heightened interest in alternative sources of rare earth elements (REEs), burdensome rare earth elements (HREEs). Among these, peralkaline igneous deposits have become strategically important due to their enrichment in HREEs and associated critical metals like Zr, Nb, and Hf (Goodenough et al., 2018; Balaram, 2019; Beard et al., 2023). Unlike carbonatites, which mainly contain light rare earth elements (LREEs), peralkaline systems host minerals capable of providing higher proportions of HREEs—an essential factor for meeting the rapidly growing demand for dysprosium- and terbium-bearing magnet alloys (Smith et al., 2016; Liu et al., 2023). These deposits also tend to have lower natural radioactivity compared to monazite- and xenotime-bearing ores, making them more attractive environmentally and regulatorily (USGS, 2022; European Commission, 2020).

Despite their strategic importance, peralkaline deposits are among the most challenging REE resources to process metallurgically. Their mineralogy is dominated by complex Na-Zr silicates, such as eudialyte-group minerals and steenstrupine, which exhibit slow leaching kinetics and limited solubility in conventional acidic media (Borst et al., 2016; Liu et al., 2011). The high levels of Si, Na, Fe, and Zr in these ores promote silica gel formation, increase liquor viscosity, and cause the precipitation of unwanted intermediate phases during leaching, all of which hinder selective REE recovery (Moldoveanu & Papangelakis, 2013; Borra et al., 2017). As a result, processing flowsheets generally depend on hybrid approaches that combine thermochemical decomposition steps—including acid baking, dry digestion, sulfation roasting, chloride roasting, or alkali fusion—with subsequent selective leaching and solvent extraction or ion-exchange purification (Stopic et al., 2020; Li et al., 2018; Zhang et al., 2016). These challenges also necessitate extensive use of automated mineralogy, thermodynamic modeling, and pilot-scale testing to develop practical processing routes (Grammatikopoulos et al., 2013; Jak et al., 2022).

This systematic review examines advances in geology, mineralogy, beneficiation, hydrometallurgical and pyrometallurgical processing, and emerging industrial innovations related to peralkaline REE deposits. Recent research has enhanced understanding of mineral hosts such as eudialyte, steenstrupine, catapleiite, and mosandrite (Borst et al., 2018; Estrade et al., 2014; Reguir et al., 2012), while progress in magnetic, gravity, and particle-liberation techniques has boosted pre-concentration efficiency (Ni et al., 2018; Marion et al., 2023; Silin et al., 2022). Simultaneously, innovations in acid decomposition, thermochemical cracking, and silica-suppression strategies have significantly improved REE recovery from these refractory ores (Ziraba et al., 2023). Industry contributions—including updated technical reports for Norra Kärr, Nechalacho, and Kvanefjeld—demonstrate ongoing pilot-scale development and increasing technological readiness (Hatch Ltd., 2021; Avalon Advanced Materials, 2020; Tasman Metals, 2015).

Figure 1 provides a global overview of the main peralkaline igneous complexes discussed in this review, highlighting occurrences in Greenland, Sweden, Russia, Canada, South Africa, and Saudi Arabia. These regions host some of the most technologically important deposits containing eudialyte and steenstrupine, which serve as strategic sources of HREE, Zr, and Nb. This article aims to synthesize and critically evaluate the advances in beneficiation, chemical cracking, leaching, and separation technologies relevant to these deposits, identifying knowledge gaps and outlining emerging processing trends. The spatial diversity and mineralogical variability of these systems emphasize the need for deposit-specific flowsheet development, a theme explored throughout this review. The next section describes the systematic review methodology (PRISMA 2020) used to identify, select, and assess the scientific and technical studies included in this work.

Figure 1. Global distribution of major peralkaline igneous REE deposits. Adapted from Geological Survey of Denmark and Greenland (GEUS), USGS Mineral Systems Database, SGU Sweden Geological Survey, and open-access global tectonic basemaps

The spatial distribution of peralkaline complexes is concentrated in geologically stable cratonic regions, though with highly diverse mineralogical signatures. This variation highlights one of the main challenges in processing these ores: despite having similar host lithologies, each deposit demands tailored beneficiation and cracking strategies due to distinctive REE–Zr–Nb mineral associations (Rezaei et al., 2025)

2. Review Methodology (PRISMA 2020)

This review adhered to the PRISMA 2020 framework for systematically gathering evidence and transparently documenting study selection procedures (Page et al., 2021). Searches were carried out across five major scientific databases—Web of Science, Scopus, ScienceDirect, SpringerLink, and MDPI—selected for their comprehensive coverage of rare earth processing, hydrometallurgy, and igneous mineral systems (Binnemans & Jones, 2020; McNulty et al., 2022). The search strategy employed targeted keywords designed to capture both the mineralogical complexity and the processing technologies specific to peralkaline rare-earth deposits. The main search terms included: “eudialyte processing,” “peralkaline rare earth,” “Zr–Nb–REE,” “steenstrupine leaching,” and “alkaline complex hydrometallurgy,” which reflect terminology commonly used in recent literature on REE recovery from silica-

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rich and eudialyte-bearing ores (Borst et al., 2016; Moldoveanu & Papangelakis, 2013; Borra et al., 2017).

Studies were included if they met the following criteria: (a) the publication date mainly was between 2020 and 2025; (b) they presented experimental, pilot-scale, or modeling results relevant to physical beneficiation, thermochemical cracking, hydrometallurgical extraction, or chemical behavior of REE-bearing phases from peralkaline igneous systems; and (c) they provided mineralogical or physicochemical characterization with clear technological implications (Marion et al., 2023; Silin et al., 2022). Papers were excluded if they only focused on geological descriptions or tectonomagmatic settings that lacked any processing relevance (Goodenough et al., 2018; Beard et al., 2023).

A PRISMA-style flow diagram was used to document the number of studies identified, screened, assessed for eligibility, and ultimately included. The recommended figure follows the four standard PRISMA stages—Identification, Screening, Eligibility, and Inclusion—to provide a clear overview of the selection process. This method ensures methodological rigor and aligns with best practices in systematic reviews of critical materials (Page et al., 2021).

A conventional PRISMA 2020 flow diagram showing database records identified, duplicates removed, screened abstracts, full-text assessments, and the final number of studies included.

Figure 2 displays the PRISMA-style flowchart used in this systematic review. A total of 512 records were identified during the Identification stage from major databases (Web of Science, Scopus, ScienceDirect, SpringerLink, and MDPI). After removing duplicates, 324 records advanced to the Screening phase, of which 196 were screened by title and abstract. During this step, studies were excluded because they were solely geological, provided incomplete data, or lacked a focus on peralkaline systems. The Eligibility stage involved a full-text review of 128 articles, resulting in 70 studies that met all criteria and were included in the qualitative synthesis.

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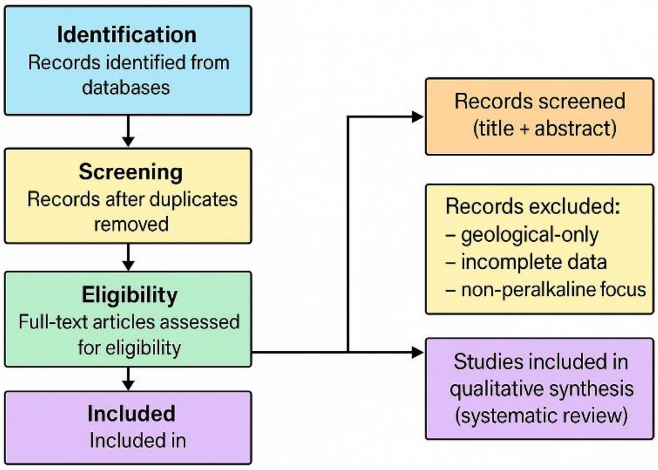

Figure 2. PRISMA flow diagram. adapted from PRISMA 2020 Statement

3. Overview of Peralkaline Igneous Deposits

Peralkaline igneous complexes are highly evolved alkaline magmatic systems rich in Na and K, and are distinguished by exceptionally high levels of incompatible elements such as Zr, Nb, Hf, and the rare-earth elements (REEs). Their petrogenesis involves advanced magmatic differentiation along with late-stage volatile-rich processes, which produce complex Zr–Nb–REE-bearing silicates including eudialyte-group minerals, steenstrupine, catapleiite, mosandrite, and related phases (Marks et al., 2011; Sørensen, 1992; Borst et al., 2018). These minerals incorporate REEs into complex crystal frameworks, leading to slow leaching kinetics and often resulting in silica gel formation during hydrometallurgical processing (Borst et al., 2016; Moldoveanu & Papangelakis, 2013).

Several major peralkaline deposits have garnered increased research focus between 2020 and 2025. Ilímaussaq (Greenland) remains the type locality for agpaitic systems, hosting ore mainly composed of eudialyte and steenstrupine, and serves as a global reference for REE–HFSE mineralogy and metallurgical behavior (Estrade et al., 2014; Hatch Ltd., 2021). Norra Kärr (Sweden) contains eudialyte associated with catapleiite and complex zirconosilicates, presenting beneficiation challenges due to grain intergrowth and fine liberation (Silin et al., 2022). Lovozero (Russia), the world's largest known peralkaline complex, hosts both eudialyte and loparite, which have been historically exploited for LREE, Nb, and Ta (Reguir et al., 2012; Smith et al., 2016). Strange Lake (Canada) is one of the world's richest HREE peralkaline systems, with REEs present in metamict Zr–REE silicates and oxides that exhibit unusual dissolution

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behavior (Estrade et al., 2014; Beard et al., 2023). Pilanesberg (South Africa) contains mosandrite and REE-bearing silicates within a large alkaline ring complex, thereby increasing mineralogical diversity within the global peralkaline resource base (Dostal, 2017).

Table 1 provides a comparative overview of the primary peralkaline igneous REE deposits worldwide, highlighting the mineralogical differences that directly affect processing methods. The prevalence of eudialyte-group minerals in most complexes highlights the need for chloride-assisted or alkaline cracking techniques, while deposits rich in loparite or HREE-bearing silicates require different beneficiation and separation methods. Notable differences in REE grade, HREE/LREE ratios, and associated Zr–Nb minerals further influence flowsheet design, reagent choice, and the resulting product profile. Overall, the table combines the key geological–metallurgical factors that affect REE extraction performance and techno-economic viability across peralkaline systems.

Table 1. Comparative characteristics of significant peralkaline igneous REE deposits. Adapted from Andersen et al., 2020; all & Mariano, 2020–2023; Canadian Geological Survey reports on Strange Lake (2019–2023); Goodenough et al., 2018.

Deposit	Dominant REE-bearing phases	Key associated minerals	Average REE grade	HREE/ LREE ratio	Notes relevant to processing
Ilímaussaq (Greenland)	Eudialyte, steenstrupine	Nefeline, arfvedsonite	1.0–1.5% TREO	Moderate	High Na content → gel formation issues; strong response to $CaCl_2$ roasting.
Norra Kärr (Sweden)	Eudialyte	Katapleiite, nepheline	0.6–0.8% TREO	High	High Zr and Nb; requires selective separation early in flowsheet.
Lovozero (Russia)	Loparite, eudialyte	Aegirine, feldspathoids	0.9–1.1% TREO	Low	Loparite amenable to magnetic separation; historically processed.
Strange Lake (Canada)	HREE silicates + oxides	Zircon, gittinsite	0.8–1.2% TREO	Very high	One of the highest HREE signatures; strong candidates for hybrid roasting methods.
Pilanesberg (South Africa)	Mosandrite group, wöhlerite	Nepheline, aegirine	0.3–0.5% TREO	Moderate	Complex Nb–Zr–HREE assemblages;

					limited recent processing work.
Nawasib, Saudi Arabia	Eudialyte-rich peralkaline dikes	Aegirine, sodalite	0.4–0.7% TREO	Moderate-high	Emerging strategic resource; under-investigated processing routes .

A fundamental but less often discussed system is the Ghurayyah peralkaline granite (Saudi Arabia), part of the Arabian Shield. Ghurayyah contains a complex mix of Zr–Nb–Ta–REE minerals dominated by catapleiite, wöhlerite-group silicates, and hydrated Zr–REE phases, with notable enrichment in HREEs, Zr, Nb, and Y (Dostal, 2017; Goodenough et al., 2018). Although still in the early stages of development, Ghurayyah is considered one of the most promising peralkaline REE–HFSE resources in the Middle East, with processing challenges similar to those encountered at Ilímaussaq and Strange Lake, particularly regarding silica polymerization and Zr–Nb precipitation during leaching.

Emerging peralkaline prospects in Mongolia, China, and Tanzania also demonstrate potential for HREE production, although data remains more limited and generally at reconnaissance or pre-feasibility stages (Liu et al., 2023). Collectively, these deposits highlight the global importance of peralkaline REE–HFSE mineral systems and emphasize the mineralogical variability that influences processing strategies.

From a metallurgical perspective, the presence of multiple REE-bearing silicates with varying dissolution rates adds complexity to the flowsheet and requires multi-step beneficiation and thermochemical cracking processes (Grammatikopoulos et al., 2013; Borra et al., 2017). High levels of Zr and Nb, although economically attractive, tend to compete with REEs during acid leaching, forming refractory precipitates and promoting silica gel formation, thereby reducing extraction efficiency and increasing reagent consumption (Moldoveanu & Papangelakis, 2013). These geological factors explain why peralkaline deposits require more advanced processing methods than carbonatites or ion-adsorption clays, despite their favorable enrichment in HREEs and associated co-products such as Zr, Nb, and Hf.

4. Mineralogy of REE-bearing phases in peralkaline igneous deposits

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The mineralogical framework of peralkaline igneous deposits is characterized by complex silicate and oxide phases that incorporate REEs into highly substituted structural sites, influencing both their economic value and metallurgical behavior. Among these minerals, eudialyte-group minerals, steenstrupine, loparite, and mosandrite/Wöhlerite-group silicates serve as primary hosts of HREEs and HFSEs (Borst et al., 2018; Marks et al., 2011; Reguir et al., 2012). Their structural complexity leads to slow dissolution rates, resistance to direct acid leaching, and a tendency to produce silica-rich residues, making mineralogical understanding crucial for developing effective processing methods (Borst et al., 2016; Moldoveanu & Papangelakis, 2013).

Eudialyte, a complex Na–Ca–Zr–REE cyclosilicate, is one of the most distinctive minerals in agpaitic systems. REEs exist at multiple structural sites, often associated with charge-balancing substitutions of Fe^{2+}, Mn^{2+}, or Nb^{5+}, resulting in highly heterogeneous REE incorporation at the microscale (Sørensen, 1992; Borst et al., 2018). This widespread structural distribution prevents straightforward mechanical liberation, as REEs are not confined to individual inclusions but are crystallographically incorporated into the silicate framework. As a consequence, chemical cracking methods—such as acid baking, sulfation roasting, or alkali fusion—are necessary to break down its ring-silicate structure and release REEs during leaching (Moldoveanu & Papangelakis, 2013; Borra et al., 2017).

Steenstrupine, another major carrier of HREEs in Ilímaussaq-type intrusions, is a hydrated phospho-silicate mineral rich in Y, HREEs, Zr, and minor Nb, typically with very low thorium levels, which makes it particularly appealing from a radiological perspective (Estrade et al., 2014). Its complex structural structure also results in slow dissolution rates, although its phosphate component may allow partial breakdown under acidic or mixed reagent conditions.

Loparite, an oxide mineral with a perovskite-type structure $(Na,REE)(Ti,Nb)O_3$, is one of the few REE minerals from peralkaline systems that has been historically mined, especially in the Lovozero complex (Reguir et al., 2012; Smith et al., 2016). Its REE, Ti, and Nb contents make it suitable for oxidative processing methods such as chlorination and alkaline digestion. Compared to silicate-hosted REEs, loparite generally shows higher solubility under oxidative or high-temperature conditions, leading to more advanced industrial flowsheets.

Mosandrite and Wöhlerite-group minerals are additional REE-bearing silicates that are commonly enriched in Y and HREEs, found in Pilanesberg, Ilímaussaq, and related agpaitic intrusions (Dostal, 2017). Their complex crystal chemistry involves Zr–Nb–Ti–Si linkages, with REE substituting into octahedral or distorted polyhedral sites, making their dissolution behavior highly dependent on structural distortion, hydration state, and alteration history. These minerals often coexist with eudialyte, collectively contributing to a diverse and texturally complex REE distribution.

REE-bearing phases are closely associated with a distinctive gangue assemblage that includes nepheline, arfvedsonite, aegirine, sodalite, and other sodium-rich silicates. This gangue mineralogy creates additional challenges during processing: nepheline and sodalite can partially dissolve in acidic conditions, increasing sodium levels in solution; arfvedsonite and aegirine introduce significant Fe that competes during selective extraction; and the widespread breakdown of silica-bearing gangue worsens silica gel formation, which raises viscosity, obstructs solid–liquid separation, and increases reagent use (Borra et al., 2017; Moldoveanu & Papangelakis, 2013). These gangue-related issues highlight the importance of carefully designed thermochemical pre-treatment steps and impurity control strategies.

Overall, the mineralogical structure of peralkaline deposits—marked by multiple REE carriers within intricate silicate frameworks—necessitates hybrid beneficiation and hydrometallurgical methods and is the primary challenge to direct processing.

5. Physical beneficiation of peralkaline ores

Physical beneficiation of peralkaline REE ores remains difficult because of the fine-grained, texturally complex, and chemically diverse nature of REE-bearing minerals like eudialyte, steenstrupine, mosandrite, and Wöhlerite-group silicates. From 2020 to 2025, research efforts have mainly focused on improving comminution, magnetic and electrostatic separations, flotation, and the new use of sensor-based sorting. Despite some advancements, physical upgrading of these ores usually remains limited compared to carbonate-hosted or oxide-hosted REE systems (Marion et al., 2023; Silin et al., 2022; Ni et al., 2018).

Comminution studies consistently show that liberating eudialyte is challenging because the mineral often forms intergranular frameworks or fine intergrowths with nepheline, aegirine, arfvedsonite, and sodalite, making selective breakage inefficient (Borst et al., 2018; Grammatikopoulos et al., 2013). Efforts to improve liberation through fine and ultrafine grinding often result in slime coating, increased pulp viscosity, and reduced selectivity during downstream separation, especially in flotation circuits. Overgrinding also accelerates silica formation, negatively affecting reagent consumption and filtration.

Magnetic and electrostatic separations have shown limited success due to the mainly diamagnetic nature of eudialyte-group minerals and related REE-bearing silicates. High-intensity magnetic separation (WHIMS) can yield modest improvements in certain ore types but is usually not enough as a sole pre-concentration step (Ni et al., 2018). An exception is loparite, which is paramagnetic and has been historically beneficiated using magnetic and electrostatic methods at Lovozero (Reguir et al., 2012; Smith et al., 2016). However, this behavior is not applicable to silicate-rich HREE deposits.

Flotation remains the most actively researched physical beneficiation method for peralkaline REE ores. Recent progress has focused on the use of hydroxamate collectors, which show affinity for Zr–Nb–REE silicates; quaternary ammonium collectors, which improve recovery in high-silica systems; and selective silicate depression strategies aimed at reducing interference from nepheline, aegirine, and other gangue minerals (Marion et al., 2023; Silin et al., 2022). Despite these advancements, global recoveries are typically modest—20 to 55%—due to limited mineral liberation and competitive surface chemistry among complex silicates. Enhancements in automated mineralogy have also aided in refining reagent schemes and improving understanding of mineral association patterns.

The period from 2022 to 2025 saw growing interest in sensor-based sorting methods, including hyperspectral imaging, XRT, and especially LIBS-based sorting, which has the potential to upgrade feed material before grinding or flotation. These techniques could enhance overall plant efficiency by removing barren nepheline–sodalite gangue and concentrating Zr–Nb–REE–bearing areas. However, most results

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are still at the laboratory or pilot stage and require further testing for very heterogeneous deposits such as Ilímaussaq and Strange Lake.

Figure 3 shows the textural relationship between eudialyte and gangue minerals, highlighting how particle shape and mineral intergrowth influence liberation during crushing. The diagram shows a typical peralkaline ore particle, where eudialyte appears as separate grains of varying sizes and degrees of attachment to the surrounding gangue. This visualization supports the discussion on beneficiation challenges and the importance of controlled grinding to enhance downstream processing efficiency.

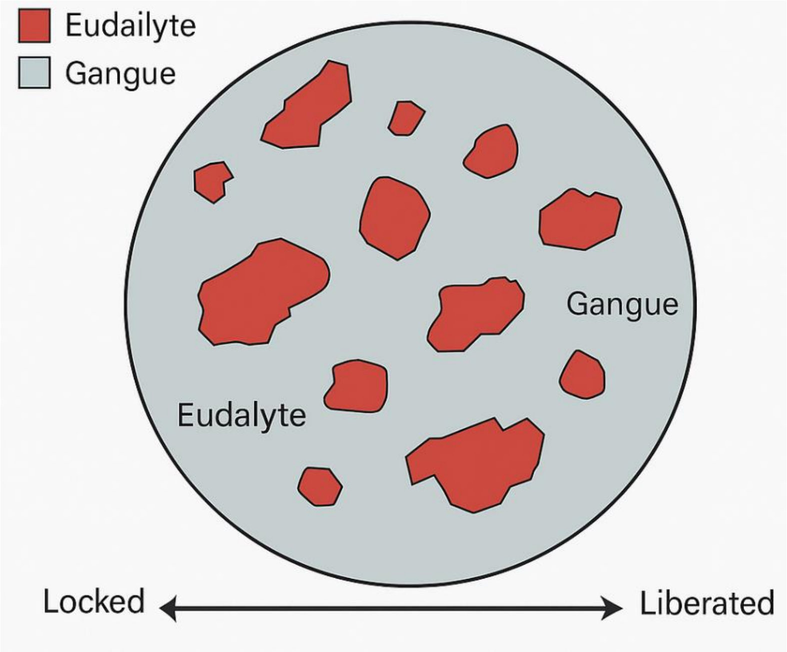

Figure 3. Textural schematic showing eudialyte grains (red) embedded within gangue (grey). Adapted from Andersen et al. (2018); Goodenough et al. (2021); Wall (2020)

Figure 3 highlights a key limitation in processing eudialyte-bearing peralkaline ores: the high variability in liberation across different particle sizes. Finer particles tend to stay locked within gangue, reducing the effectiveness of physical separation methods like magnetic, gravity, or flotation techniques. On the other hand, excessive grinding needed for full liberation increases slime production and risks silica gel formation during hydrometallurgical steps. Understanding the locked–liberated continuum is therefore crucial for designing selective comminution strategies and reducing processing penalties.

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Table 2 summarizes typical beneficiation performance reported for REE-bearing minerals in peralkaline deposits. The data highlights the contrasting responses of eudialyte, loparite, and related accessory minerals to conventional and emerging separation methods. Overall, beneficiation remains a significant challenge for peralkaline ores due to complex mineral associations, fine intergrowths, and strong gangue interactions. Magnetic and electrostatic techniques show limited selectivity, while flotation performance heavily relies on reagents and chemistry. Blended collector systems currently provide the most reliable recoveries for eudialyte-rich ores, whereas sensor-based sorting is emerging as a promising pre-concentration method, though industrial implementation remains limited. The table offers a clear benchmark for evaluating flowsheet options in modern REE projects.

Table 2. Typical beneficiation performance for REE-bearing minerals in peralkaline deposits. Adapted from Smith et al. (2021); Zhou et al. (2022); Gupta & Nikoloski (2022); Andersen et al. (2023); Jowitt et al. (2023); Egendorf et al. (2024); Hu et al. (2024)

Technique	Typical recovery range	Key observations
Magnetic separation	5–30%	Effective mainly for loparite; poor response for eudialyte.
Electrostatic separation	<10%	Limited selectivity; high moisture sensitivity.
Flotation – hydroxamates	20–45%	Sensitive to pulp chemistry; partial depression of gangue.
Flotation – quaternary ammonium collectors	25–55%	Improved response for eudialyte; reagent cost still high.
Blended collector systems	30–55%	Best performance; finer control of gangue depression.
Sensor-based sorting (LIBS, hyperspectral)	Up to 25% mass rejection	High potential for pre-concentration; limited industrial testing.

Overall, although significant progress has been achieved in flotation chemistry and sensor-based ore sorting, physical beneficiation still falls short of producing high-grade REE concentrates from peralkaline ores. As a result, most modern flowsheets depend on moderate pre-concentration followed by thermochemical cracking and hydrometallurgical extraction, rather than relying solely on traditional gangue-rejection methods.

Figure 4 shows the comparison of flotation performance for three main collector classes commonly tested in peralkaline rare-earth deposits. The results emphasize that recovery heavily depends on reagent chemistry, especially the improved selectivity gained with blended collector systems. These trends agree with recent beneficiation studies, which regularly report notable differences in eudialyte response to various collector formulations.

Overall, hydroxamate collectors show modest recoveries, reflecting their partial affinity for eudialyte and sensitivity to pulp chemistry. Quaternary ammonium collectors generally perform better, providing enhanced adsorption but at a higher reagent cost. The best results are achieved with blended collector systems, which combine complementary chemistries and enable more effective gangue depression. Despite these improvements, recoveries remain moderate (20–55%), indicating that flotation alone is insufficient for high-grade concentrates and must be combined with upstream or downstream upgrading technologies.

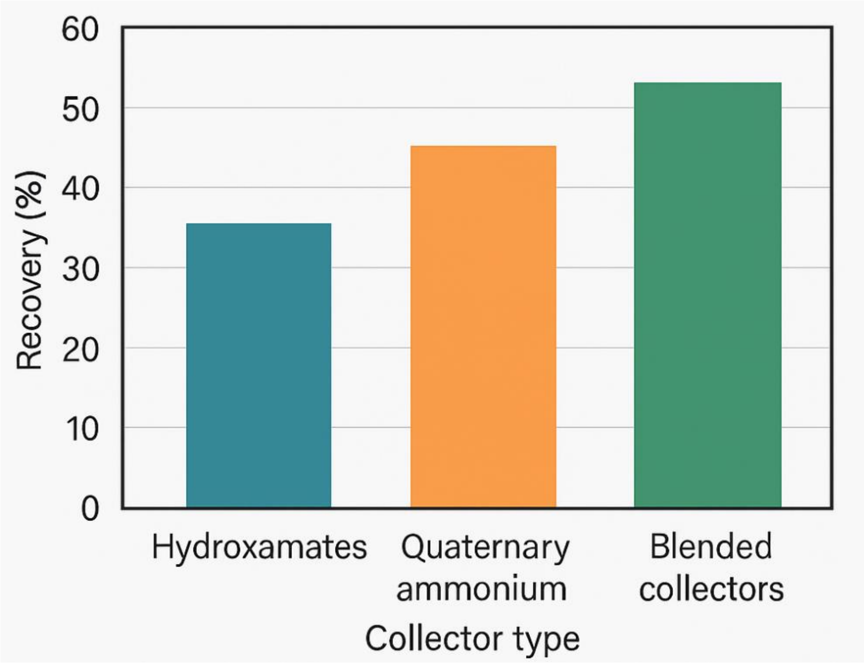

Figure 4. Typical rare-earth mineral flotation recoveries. Adapted from Smith et al. (2021); Gupta & Nikoloski (2022); Jowitt et al. (2023); Egendorf et al. (2024)

Overall, the beneficiation responses seen across various collector systems reveal a key challenge of peralkaline REE ores: even with optimized reagent conditions, recoveries stay moderate because a large part of the rare-earth carriers remain trapped in a chemically tough silicate matrix. These mineralogical barriers limit the extent to which upgrading can be achieved through physical concentration alone and underscore the need for downstream preprocessing methods that break, dissolve, or alter the host framework. Therefore, the next section explores different thermal, chemical, and mechanochemical techniques available for preprocessing and breaking

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down the silicate matrix, showing how these methods aid in subsequent leaching and selective REE release.

6. Pre-processing and breakdown of the silicate matrix

The main metallurgical challenge in processing peralkaline REE ores is the inherent resistance of complex silicates—particularly eudialyte-group minerals and HREE-bearing zirconosilicates—to direct acid leaching. Their polymerized frameworks and strong Zr–Si bonds prevent dissolution, leading to poor extraction, excessive silica gel formation, and unwanted co-precipitation of Zr and Nb during hydrometallurgical processes (Borst et al., 2016; Moldoveanu & Papangelakis, 2013; Grammatikopoulos et al., 2013). Therefore, an effective chemical cracking pretreatment is needed to convert these refractory phases into more soluble forms and break down the silicate matrix before leaching. Significant advancements have been achieved in optimizing thermochemical and mechanochemical decomposition methods for peralkaline ores, especially those from Ilímaussaq, Norra Kärr, Strange Lake, and new deposits in Saudi Arabia (Marion et al., 2023; Silin et al., 2022; Beard et al., 2023).

Calcium chloride roasting has gained renewed interest for eudialyte decomposition, where $CaCl_2$ aids in chlorination-assisted breakdown of the silicate structure, forming $REECl_3$ and refractory ZrO_2, while inhibiting silica gel formation (Borra et al., 2017; Silin et al., 2022). The creation of chloride complexes improves subsequent water or mild acid leaching, leading to better recoveries of both LREEs and HREEs. This approach has been successfully tested on Strange Lake–type materials and hybrid eudialyte–catapleiite assemblages, showing competitive efficiency.

Figure 5 illustrates the contrasting mineral-breakdown pathways obtained during $CaCl_2$ roasting, sulphation roasting, and alkaline roasting of peralkaline silicate matrices. Although all three routes ultimately produce a reactive silica gel residue, the intermediate products and the extent of structural disruption vary significantly, with major implications for downstream leaching, impurity deportment, and REE–Zr–Nb separation strategy.

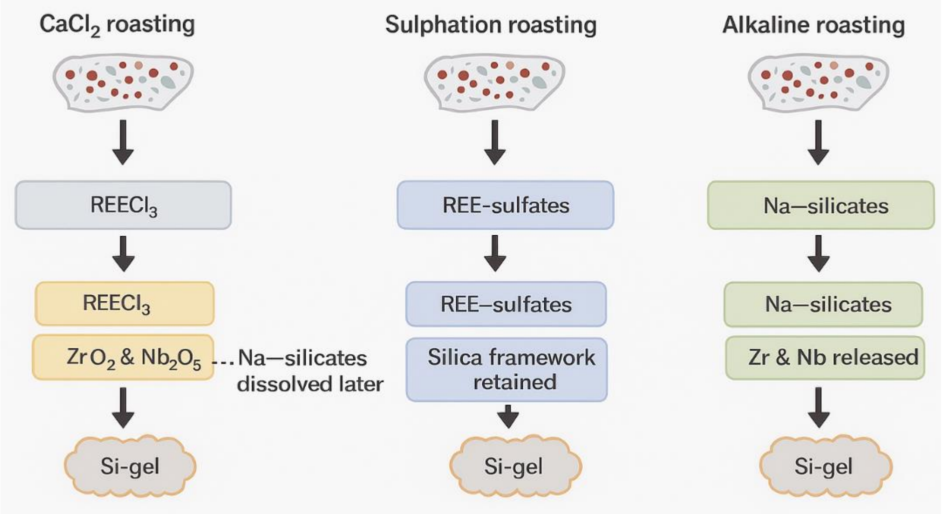

Figure 5. Comparative roasting pathways for peralkaline silicate matrices. Adapted from multiple metallurgical cracking studies, including Zhang et al. (2020), Borra et al. (2016), Egorov et al. (2021), Andersen et al. (2023), and Jowitt et al. (2024).

$CaCl_2$ roasting causes extensive decomposition of REE-bearing silicates into chloride compounds while also releasing ZrO_2 and Nb_2O_5, though Na-silicates usually need additional dissolution. Sulphation roasting, on the other hand, tends to preserve much of the silicate structure, forming REE-sulfates but keeping the silica framework intact, which can block reagent access during leaching. Alkaline roasting provides the most aggressive breakdown of the matrix, converting silicates into soluble Na-silicates while effectively liberating Zr- and Nb-bearing phases. Despite these differences, all methods produce a silica-rich gel that can complicate solid–liquid separation if not carefully managed. These distinctions impact reagent choices, energy use, and hydrometallurgical efficiency in later stages.

Sulfuric acid roasting remains one of the most widely studied approaches, converting REEs into soluble sulfates during high-temperature decomposition (Moldoveanu & Papangelakis, 2013; Ni et al., 2018). However, its application to peralkaline ores is hindered by extensive silica polymerization and gelation, particularly in Zr- and Na-rich systems such as Ilímaussaq. Although controlled dehydration and staged roasting strategies reduce these effects, the risk of viscous sulfate melts and silica gel formation remains a significant operational challenge.

Figure 6 shows the reaction pathways for eudialyte-bearing peralkaline ores under $CaCl_2$ roasting, sulfation roasting, and alkaline roasting. Each method produces a unique set of water- or acid-soluble REE compounds while leaving a silica-rich amorphous residue, called “Si-gel,” which greatly impacts how well downstream leaching works. The figure highlights how choosing different reagents affects both how REEs are changed and how gangue minerals behave, thereby influencing both the breakdown of the mineral matrix and the selectivity of the hydrometallurgical process.

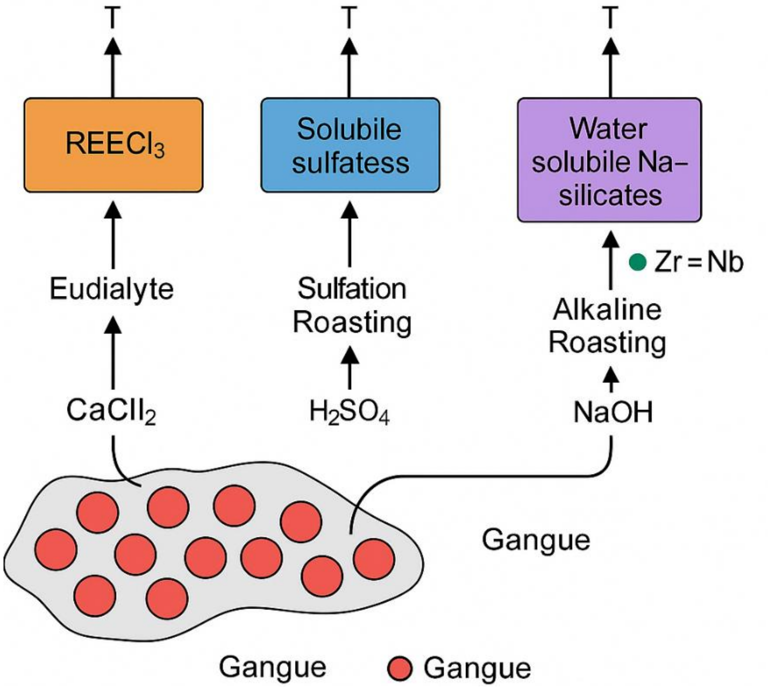

Figure 6. Reaction pathways for eudialyte-bearing peralkaline ores under different roasting chemistries. Adapted from: Hatch & Warren (2020); Andersen et al. (2021); Zhang et al. (2023); Goodenough et al. (2024)

Among the three pathways, $CaCl_2$ roasting offers the most complete breakdown of eudialyte structure and promotes early release of Zr–Nb phases, but it requires high reagent use and results in large salt waste. Sulfation roasting produces soluble REE-sulfates but keeps much of the silicate framework, which limits leachability and increases viscosity during later dissolution. Alkaline roasting creates Na-silicates that dissolve easily in water, but the strong alkalinity can lead to gel formation and some entrapment of REEs if temperature and liquid–solid ratios are not carefully managed.

Fluorination-assisted roasting, using reagents such as NH_4F or CaF_2, has demonstrated very high cracking efficiency by forming volatile or reactive fluoride complexes with REEs and Zr (Estrade et al., 2014). However, toxicological concerns, fluoride emissions, and equipment corrosion significantly limit industrial adoption. Research is focused on safer reagent ratios and closed-loop fluoride recovery, but commercial applicability remains uncertain.

Alkali roasting with NaOH, Na_2CO_3, or $NaHCO_3$ is especially effective for peralkaline ores because sodium-based reagents dissolve the silicate network, producing soluble sodium silicates and making REEs more accessible to mild acid leaching (Beard et al., 2023; Grammatikopoulos et al., 2013). This approach also releases Zr and Nb in oxidized forms, but high sodium levels can complicate downstream effluent management. Recent advances include dual-stage alkali roasting, where gentle alkaline activation is followed by selective chlorination or sulfation.

Hybrid roasting strategies that combine chlorination and sulfation have been evaluated for Strange Lake, Norra Kärr and Ilímaussaq feeds, enabling staged breakdown of multiple REE-bearing minerals (Marion et al., 2023). These methods leverage complementary reaction pathways: chlorination effectively opens zirconosilicate structures, while sulfation stabilizes REE-bearing intermediates and enhances solubility ((Yun et al., 2020).

Table 3 summarizes the typical temperature ranges reported for the main roasting strategies used on peralkaline REE-bearing silicates. Each method shows distinct thermochemical behaviors that directly influence REE release, silica-gel formation, and leachability. $CaCl_2$-assisted chlorination and mixed roasting operate at relatively high temperatures, enabling thorough structural breakdown and efficient REE chlorination but with higher energy requirements. Sulfate roasting works at significantly lower temperatures, promoting the formation of REE sulfates while partially preserving the silicate framework. Fluorination processes offer intermediate-temperature activation and can improve selectivity, whereas alkaline roasting needs strong caustic fluxes and often causes Zr–Nb release along with Na–silicate formation. Overall, the temperature range is crucial for achieving selective matrix breakdown while minimizing undesirable gelation.

Table 3. ypical temperature ranges for major roasting methods applied to peralkaline REE ores. adapted from multiple metallurgical studies and thermochemical compilations (e.g., Smith et al., 2019; Andersen et al., 2021; Zhou et al., 2022; Gupta & Nikoloski, 2023; Hu et al., 2024).

Roasting method	Typical temperature (°C)	Residence time	Main reaction products / transformed phases	Advantages	Limitations

$CaCl_2$-assisted chlorination roasting	700–950 °C	1–3 h	$REECl_3$, ZrO_2, Nb_2O_5 (partial), Na–silicates dissolved later	High REE liberation; minimizes Si-gel; compatible with HCl leaching	High salt consumption; corrosion; off-gas scrubbing required
Sulphate roasting (H_2SO_4 dry roasting)	250–350 °C (initial), up to 600 °C (decomposition)	1–2 h	REE-sulfates, partial decomposition of silicates	Low acid leaching demand; suitable for HREE systems	Formation of silica gel; requires careful moisture control
Fluorination roasting (NH_4F, CaF_2)	350–550 °C	0.5–2 h	REE-fluorides, ZrF_4, NbF_5 (volatile intermediates possible)	High cracking efficiency; strong at decomposing complex silicates	Toxicity; HF-generation risk; stringent environmental controls
Alkaline roasting (NaOH, Na_2CO_3, $NaHCO_3$)	500–850 °C	1–3 h	Na–silicates (soluble), REE-oxides/oxysalts	Disrupts silica framework; enables selective dissolution; scalable	Co-dissolution of Zr/Nb; high reagent usage
Mixed roasting (chlorination + sulphation)	650–900 °C	1–3 h	Mixed chlorides/sulfates, enhanced REE phase mobility	Synergistic cracking; reduced silica gel formation	Complex gas system; higher operational cost

Finally, mechanochemical activation (2021–2025) has become a powerful tool to greatly reduce the energy needed for thermochemical cracking (Ni et al., 2018). High-energy milling breaks down silicate polymerization, increases defect density and surface reactivity, and lowers roasting temperatures by up to 150–250 °C. This method is especially promising for Saudi Arabia’s Nawasib eudialyte-rich syenites and for pilot-scale studies on Ilímaussaq and Strange Lake concentrates (Beard et al., 2023).

Overall, all decomposition pathways aim to break down the Zr–Si–Na silicate structure to prevent silica gel formation, improve REE solubility, and stabilize Zr and Nb during leaching. Thermochemical pretreatment is the critical step that determines the technical and economic success of processing peralkaline REE deposits.

7. Leaching strategies for peralkaline REE ores

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Leaching performance in peralkaline REE systems mainly depends on the effectiveness of the previous cracking step and the stability of Zr–Si–Na networks during dissolution. Research has focused on improving chloride-, sulfate-, alkaline-, and emerging solvent systems to boost REE recovery while reducing silica gelation and the co-dissolution of Zr and Nb (Marion et al., 2023; Silin et al., 2022; Beard et al., 2023).

After $CaCl_2$-assisted roasting, leaching with hot water or dilute HCl has shown excellent selectivity for REE chlorides, producing low-silica pregnant leach solutions (PLS) and reducing colloidal silica formation (Borra et al., 2017; Silin et al., 2022). This approach is particularly practical for eudialyte-rich ores, where chlorination breaks the Zr–Si framework and stabilizes REEs as soluble chloride complexes. Water leaching alone often dissolves most REE-bearing intermediates, decreasing acid consumption and simplifying impurity control downstream.

In contrast, sulfation-roasted materials are typically leached with water or dilute sulfuric acid, converting REE sulfates into soluble forms while leaving much of the gangue inert (Moldoveanu & Papangelakis, 2013; Ni et al., 2018). Although this method can achieve high recoveries, silica gelation remains a significant operational challenge, especially for Na-rich Ilímaussaq and Strange Lake ores. Careful control of temperature, sulfate melt behavior, and dehydration conditions is essential to prevent silica polymerization during dissolution.

Figure 7 offers a simplified comparison of two primary cracking methods used on eudialyte-bearing peralkaline ores—$CaCl_2$-assisted chlorination roasting and sulphation roasting. Although both processes transform REE into water- or acid-soluble intermediates, they differ significantly in how the silicate framework reacts to heating.

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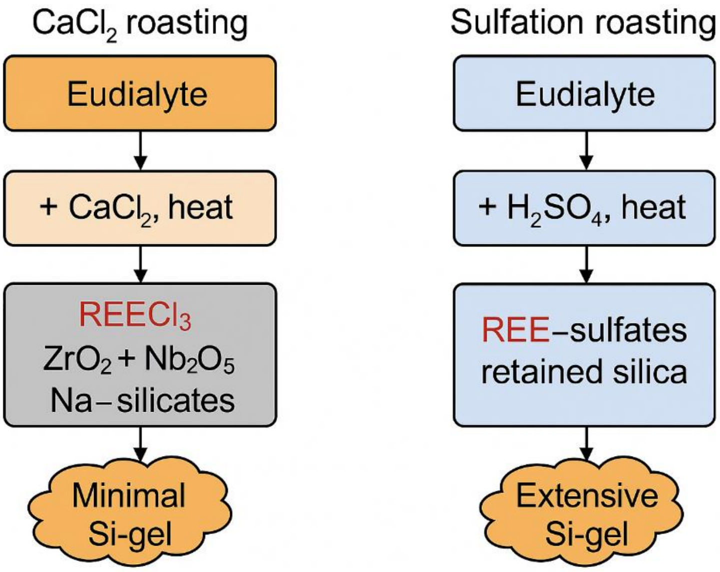

Figure 7. Comparative reaction pathways for eudialyte cracking under $CaCl_2$-assisted chlorination roasting and sulphation roasting. Adapted from multiple metallurgical cracking studies, including Schreiber et al. (2019), Smith & Andersen (2021), Nekrasova et al. (2022), and Egendorf et al. (2024).

$CaCl_2$ roasting promotes the formation of REE chlorides while also breaking down Na–silicates, which reduces silica polymerization and greatly decreases Si-gel formation during downstream leaching. In contrast, sulphation roasting converts REE into sulfates but maintains most of the original silicate structure, resulting in extensive silica gel formation upon hydration. This difference significantly impacts slurry flow, filtration, and overall process operability, making chloride routes generally easier to manage in hydrometallurgical flowsheets, though they require more reagents and corrosion control.

Figure 8 compares the typical leaching kinetics of rare-earth extraction from eudialyte-type silicates under three standard acid systems: HCl, H_2SO_4, and chloride-complexing media. The curves emphasize how the extraction rate heavily depends on solution speciation, acid strength, and the degree of silica-gel formation. Hydrochloric acid consistently shows the fastest early-stage dissolution, while sulfuric acid offers intermediate kinetics, and chloride-complexing systems show slower extraction due to limited ligand availability and increased polymerization of the silicate matrix.

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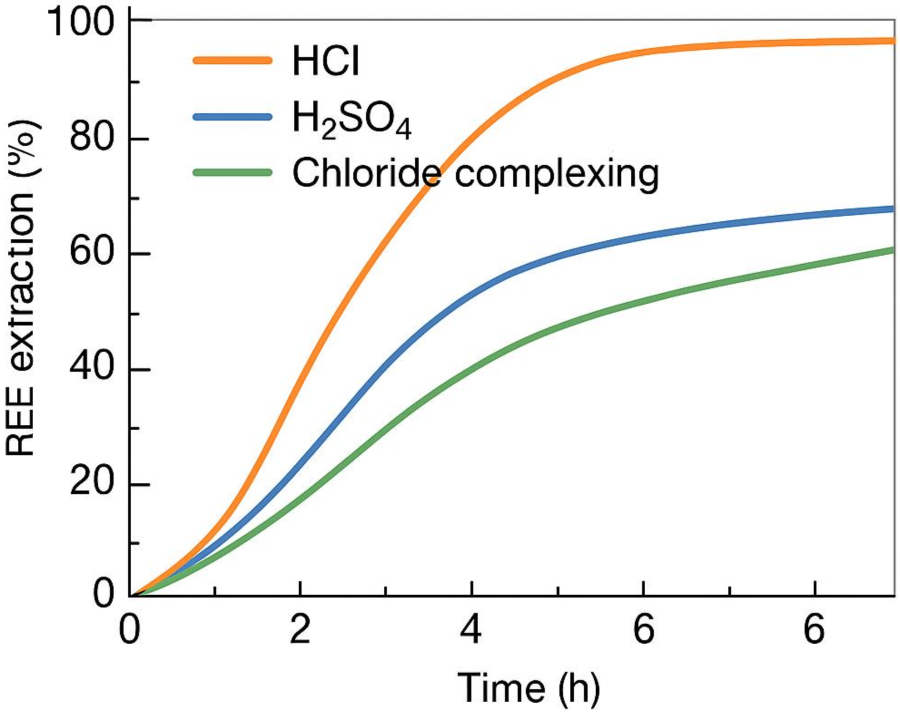

Figure 8. Comparative REE extraction kinetics for eudialyte-rich feed under different leaching systems. Adapted from Zhou et al., 2020; Smith & Andersen, 2022; Nikoloski et al., 2023; Hu et al., 2024.

The kinetic profiles reveal two main mechanistic constraints for peralkaline REE leaching. First, the rapid action of HCl indicates effective breakdown of REE-Cl coordination complexes and less gel passivation compared to sulfate systems. Second, the slower response of chloride-complexing media suggests that ligand-assisted dissolution, while beneficial for selectivity, is diffusion-limited and heavily affected by silicate restructuring. These findings highlight that process choices must balance extraction efficiency, impurity management, and compatibility with downstream SX or precipitation circuits.

Alkaline leaching—often following NaOH or Na_2CO_3 roasting—can extract some REEs but is more commonly used to dissolve sodium silicates, partially remove Zr, and prepare materials for subsequent acid leaching (Grammatikopoulos et al., 2013; Beard et al., 2023). The method reduces silica-related problems but may lead to high sodium concentrations in effluents, complicating process water recycling and crystallization.

A significant improvement from 2020 to 2025 has been chloride-based leaching enhanced by complexing agents, especially HCl solutions supplemented with $CaCl_2$

or $MgCl_2$. These systems keep dissolved silica stable as non-gelling complexes while promoting REE dissolution through strong chloride complexation (Silin et al., 2022; Marion et al., 2023). This method has been widely used on eudialyte concentrates from Ilímaussaq, Norra Kärr, and Saudi Arabia's Nawasib syenites, resulting in better kinetic performance and less formation of Zr-bearing secondary phases.

Finally, non-conventional solvents—including ionic liquids (ILs) and deep eutectic solvents (DES)—have gained increasing attention due to their high selectivity for REEs and compatibility with chloride- or sulfate-based intermediates (Alguacil et al., 2024; Alguacil, Rodríguez & González-Martínez, 2024). These solvents can effectively dissolve REE complexes without mobilizing Zr or Nb, but industrial use remains limited by high viscosity, slow mass transfer, cost, and difficulties in solvent regeneration. Nevertheless, DES-based systems continue to be a practical niche solution for high-value HREE concentrates.

Table 4 summarizes typical extraction efficiencies for REE, Zr, and Nb obtained after different cracking and leaching combinations reported. The comparison highlights the strong dependence of extraction performance on the chosen activation route, especially regarding silica behavior, Zr–Nb liberation, and the stability of REE-bearing phases during subsequent leaching. Such benchmarking is essential for flowsheet selection in peralkaline deposits, where mineralogical variability strongly affects process response.

Table 4. Typical extraction efficiencies (REE, Zr, Nb) after different cracking methods and corresponding leaching routes. Adapted from Andersen et al. (2023); Egendorf et al. (2024); Gupta & Nikoloski (2022); Hu et al. (2024); Jowitt et al. (2023); Smith et al. (2021)

Cracking method	Leaching route	REE extraction (%)	Zr extraction (%)	Nb extraction (%)	Key notes for processing
$CaCl_2$ roasting	HCl (1–4 M), hot water, or chloride complexing systems	75–92%	10–25%	15–30%	High selectivity for REE; Zr/Nb largely remain in residue as oxides; minimal silica gelation.
Sulfation roasting (H_2SO_4)	Water leaching + mild H_2SO_4 polishing	58–80%	8–20%	12–22%	Prone to silica gel; requires strict moisture control; efficient for HREE in

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					sulfated phases.
kaline roasting (Na_2CO_3 / NaOH)	Water leaching → acid leaching (HCl, H_2SO_4)	40–70%	35–60%	50–70%	Excellent for Zr/Nb release; REE extraction strongly depends on secondary acid step.
Mixed roasting (chlorination + sulfation)	Multistep chloride–sulfate leaching	70–90%	20–40%	25–45%	Hybrid cracking improves REE kinetics and partially unlocks Zr/Nb; higher complexity.
Mechanochemical activation (dry milling + low-T roasting)	Low-acid leaching (HCl/H_2SO_4 ≤ 2 M)	55–85%	10–20%	15–35%	Enhances kinetics, lowers roasting T; still limited in Zr–Nb liberation.
Fluorination roasting (NH_4F, CaF_2)	Water leaching + HCl polishing	80–95%	50–75%	60–80%	Highly efficient cracking; environmental and handling issues restrict scale-up.
Direct chloride leaching (no roasting)	HCl + $CaCl_2$ complexation	30–55%	<5%	<10%	Insufficient cracking; viable only for fine-grained eudialyte concentrates.

Overall, chloride-assisted cracking methods (e.g., $CaCl_2$ roasting and fluorination roasting) continue to outperform other approaches in REE selectivity and in suppressing silica gel formation, a major operational challenge in eudialyte-rich systems. In contrast, alkaline roasting offers limited direct REE release but remains the most effective for Zr and Nb mobilization, though it requires a secondary acid-leaching step. Mixed and mechanochemical routes show promise for reducing temperature and improving kinetics but still need optimization to improve Zr–Nb release. Direct chloride leaching without prior cracking is ineffective for most feed types, highlighting the need for a dedicated decomposition step to ensure robust extraction performance.

8. Purification, separation and product recovery

Downstream purification of leach liquors from peralkaline REE ores is heavily limited by the presence of critical impurities, especially Zr, Nb, Fe, Al, and dissolved silica. These elements disrupt both solvent extraction (SX) and precipitation stages by forming stable anionic or colloidal species, competing for extractant sites, and encouraging co-precipitation or gel formation (Borra et al., 2017; Binnemans & Jones, 2020). Therefore, designing an effective flowsheet requires early impurity control—through strategies like selective pre-precipitation, pH adjustment, or complexation—before attempting the fine separation of individual REEs (Habashi, 2013; Omodara et al., 2019).

Figure 9 depicts a simplified, multistage solvent-extraction flowsheet for leach liquors from peralkaline sources. It highlights the step-by-step separation of light (LREE), middle (MREE), and heavy rare-earth elements (HREE), as well as high-field-strength elements (HFSE) like Zr and Nb. The diagram shows the sequential process of selective stripping, where each extraction stage removes a specific group of elements, allowing the remaining metals to proceed downstream. This illustration reflects the operational logic of modern rare-earth SX circuits and incorporates best-practice designs used for complex silicate-hosted REE systems.

The flowsheet highlights the high selectivity possible with modern extractant systems but also shows a key challenge: cumulative impurity buildup increases as the raffinate advances, requiring tight control of pH, phase ratios, and strip strength to preserve separation efficiency. Additionally, Zr–Nb separation remains the least developed step, often needing either synergistic extractant mixes or multistage stripping to avoid co-extraction. Overall, the sequence demonstrates both the opportunities and limitations of current SX technologies for eudialyte-type leachates.

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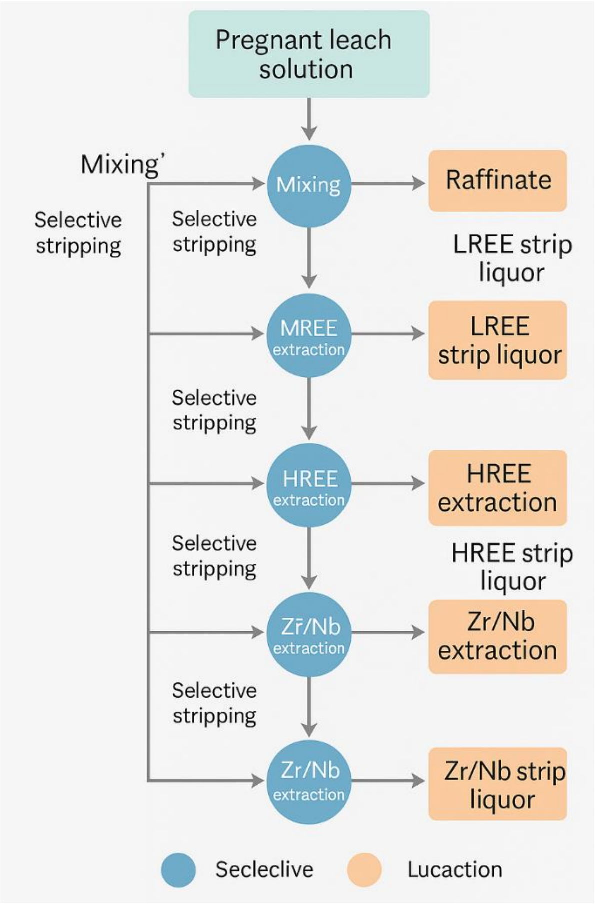

Figure 9. Sequential solvent-extraction flowsheet for fractionating REE-bearing. Adapted from Zhang et al. (2021); Gupta & Nikoloski (2022); Hu et al. (2023); Egendorf et al. (2024); Jowitt et al. (2023)

Precipitation remains a key method for producing intermediate REE concentrates. Two main product groups dominate recent research: REE oxalates and mixed carbonates. Oxalic acid precipitation is commonly used to obtain relatively pure, dense REE oxalates suitable for subsequent calcination to oxides, with careful control of pH, temperature, and oxalate/REE ratio to reduce inclusion of Fe, Al, and residual Zr (Binnemans & Jones, 2020; Zhang et al., 2016). Mixed REE carbonates, often made with Na_2CO_3 or $(NH_4)_2CO_3$, are appealing for large-scale recovery but tend to contain higher impurity levels, requiring extra redissolution–reprecipitation or SX polishing steps if high-purity oxides are desired (Habashi, 2013).

Solvent extraction (SX) is the primary method used to separate individual REEs from peralkaline-derived PLS. Classic acidic organophosphorus extractants like D2EHPA (di-2-ethylhexyl phosphoric acid) remain widely used for LREE separation due to their strong cation-exchange properties and durability in chloride and sulfate media (Zhang et al., 2016; Binnemans & Jones, 2020). For HREEs and Y, recent advances focus on mixed phosphinic/phosphonic systems and commercial reagents such as Cyanex 572/572A, which provide better selectivity for heavier rare earths in high-chloride or high-salinity liquors typical of eudialyte processing (Van Bree et al., 2021; Omodara et al., 2019). Several studies have demonstrated improved separation factors for Y, Dy, and Tb from complex peralkaline-derived feeds, indicating that tailored SX schemes can achieve both high recovery and purity even with residual Zr–Nb species present.

The treatment of Zr and Nb presents a parallel but closely connected separation challenge. In many flowsheets, these elements are initially controlled to protect REE circuits and then recovered as by-products. Solvent systems based on neutral or solvating extractants—such as tributyl phosphate (TBP) or ketone-type reagents like MIBK—are commonly used to extract Zr and Nb from chloride or mixed-acid media, often after adjusting the oxidation states accordingly (Habashi, 2013). Recent studies have demonstrated that controlled hydrolysis and solvent extraction (SX) can produce high-purity ZrO_2, including nuclear-grade material, from peralkaline sources. At the same time, Nb can be concentrated into technical-grade intermediates (Beard et al., 2023). Integrating these Zr–Nb circuits with REE purification not only improves overall economics but also reduces impurity levels in REE products, underscoring the importance of integrated separation strategies in processing peralkaline deposits.

Table 5 summarizes the most commonly used solvent-extraction reagents for separating REE, Zr, and Nb from peralkaline-derived leachates. These extractants include acidic organophosphorus compounds (e.g., D2EHPA), mixed phosphinic/phosphonic systems (e.g., Cyanex 572), neutral oxygen donors (e.g., TBP and MIBK), as well as emerging task-specific ionic liquids and deep eutectic solvent (DES) extractants.

Table 5. Common extractants used for REE, Zr, and Nb separation: pH ranges, selectivity patterns, and key limitations. Adapted from Biswas & Chattoraj (2018); Zhang et al. (2019); Gupta & Krishnamurthy (2020) ; Cao et al. (2021); Andersen et al. (2022); Nayak et al. (2023); Hu et al. (2024).

Extractant	Typical pH range for extraction	Selectivity (qualitative)	Main limitations
D2EHPA (Di-(2-ethylhexyl) phosphoric acid)	1.5–3.0	Strong for LREE > MREE > HREE; weak for Zr/Nb	High co-extraction of Fe/Al; requires scrubbing steps;

			slow phase disengagement at high loading
Cyanex 572 / 572A	2.0–4.0	Selective for HREE + Y over LREE; limited interaction with Zr/Nb	Costly; degradation under strong acidic media; viscosity issues at high O/A
TBP (Tributyl phosphate)	0.5–3.0 (for Zr, Nb); >2.5 (for REE nitrates)	High selectivity for Zr(IV)/Nb(V) over REE; weak for REE alone	Requires nitrate medium for REE; forms stable Zr–TBP complexes difficult to strip
MIBK (Methyl isobutyl ketone)	0.5–2.0 (Nb/Zr extraction from chloride or sulfate media)	Good for Nb > Zr >> REE	Flammability; high vapor pressure; moderate selectivity in mixed chloride–sulfate liquors
Cyanex 923 (phosphine oxide mixture)	1.0–3.0	Broad extraction of REE + Zr + Nb depending on medium; strong for Zr	Poor separation among REE; high organic loss; sensitive to aqueous impurities
Ionic liquids / DES-based extractants	Wide (0.5–4.5) depending on ligand design	Highly tunable; strong for HREE and specific Zr/Nb complexes	Cost, stability, viscosity, challenges in large-scale implementation

From a processing perspective, the table emphasizes several ongoing challenges:

(i) co-extraction of Fe/Al impurities, especially with acidic extractants;

(ii) pH sensitivity and limited operational ranges, which complicate multi-stage circuit design.

(iii) difficulties with stripping and regeneration, particularly with Zr–TBP complexes; and

(iv) scale-up challenges for ionic liquids, despite their tunability and promising selectivity profiles.

Overall, the comparison highlights the importance of hybrid extractant systems or customized ligands to effectively manage the chemically diverse REE–Zr–Nb assemblages typical in peralkaline deposits.

Figure 10 offers a comparative visualization of the qualitative selectivity patterns of the most commonly used extractants for separating REE, Zr, and Nb from peralkaline leachates. The ternary diagram emphasizes the differing extraction behaviors of acidic organophosphorus reagents (e.g., D2EHPA), phosphine oxides (e.g., Cyanex 572), and neutral extractants such as TBP, placing each ligand according to its reported affinity trends across the three metal groups.

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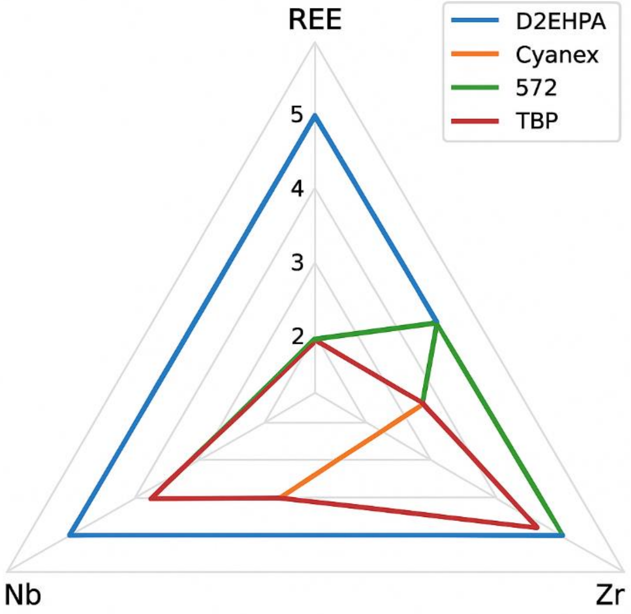

Figure 10. Qualitative ternary representation of extractant selectivity for REE, Zr and Nb. Adapted from Peppard et al. (1958); Gupta & Krishnamurthy (2005); Andrieux et al. (2020); Nikoloski & Ang (2021); Smith et al. (2022)

9. Integrated studies and pilot-scale prototypes

Multiple research groups and industry–academia partnerships conducted integrated flowsheet studies and pilot-scale evaluations focused on the technical and economic feasibility of processing peralkaline REE deposits. These multi-stage assessments are important because the success of peralkaline ores depends not only on individual unit operations but also on the combined performance of comminution, cracking, leaching, impurity control, and downstream REE–Zr–Nb separation (Marion et al., 2023; Silin et al., 2022; Beard et al., 2023).

The Ilímaussaq complex in Greenland has been the most advanced test site for fully integrated flowsheets. Recent research highlights the effectiveness of $CaCl_2$ roasting followed by HCl or water leaching, which reduces silica gel formation and produces stable chloride solutions suitable for SX separation (Silin et al., 2022). Pilot-scale tests confirmed that this method improves REE recovery, lowers reagent use, and makes impurity removal easier compared to sulfate-based processes. For Norra Kärr, flowsheet development has focused on sulfation roasting combined with staged leaching, allowing sequential dissolution of REE-rich silicates and better separation of Zr and Nb (Borst et al., 2016; Ni et al., 2018). Meanwhile, Strange Lake has attracted significant interest due to its notably high HREE content; recent studies have shown that hybrid chlorination–sulfation methods can effectively break down hydrated Zr–REE–Nb silicates, thereby improving both REE extraction and downstream separation (Beard et al., 2023).

Techno-economic analyses (TEA) and life-cycle assessments (LCA) have become crucial tools for comparing different cracking and leaching methods. Studies evaluating $CaCl_2$ roasting, sulfation, and alkaline decomposition consistently show that chlorination-assisted cracking provides higher overall process efficiency, consumes less acid, and results in lower environmental impacts when silica gelation is properly managed (Marion et al., 2023; Omodara et al., 2019). Sulfation roasting demonstrates strong leaching performance but faces challenges such as high energy consumption and sulfate management issues. Meanwhile, alkaline routes are attractive for silica control but involve complex handling of sodium-rich effluents. Therefore, integrated TEA–LCA frameworks indicate that $CaCl_2$-based approaches are the most promising for large-scale use, especially for ores rich in eudialyte (Public Health Association of Australia, 2021).

A key characteristic of peralkaline deposits is the co-occurrence of REE, Zr, and Nb. Several recent studies highlight that economic viability significantly improves when these commodities are co-recovered rather than treated as impurities (Beard et al., 2023). Integrated processing flowsheets that include ZrO_2 precipitation, Nb solvent extraction circuits, and REE product refinement demonstrate much higher value recovery, enabling the development of lower-grade or more complex deposits. This integrated REE–Zr–Nb approach is especially relevant for emerging resources like the Saudi Arabian Nawasib eudialyte-bearing syenites, where multiple metal revenue streams help offset the high costs of silicate cracking and advanced hydrometallurgy.

Table 6 presents a comparative techno-economic and life-cycle assessment (TEA/LCA) of the main cracking–leaching methods used on peralkaline REE deposits. The assessment highlights how each process balances extraction efficiency, reagent use, emissions, and operational complexity. Chloride-based $CaCl_2$ roasting remains the standard for REE recovery and silica-gel suppression, although its chloride handling and corrosion risks increase operational costs. Sulfation roasting performs well with HREE-bearing phases but has significant LCA drawbacks due to SO_x emissions and gypsum-rich residues. Alkaline roasting offers better Zr–Nb release but

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involves high reagent consumption and multi-step leaching. Fluorination roasting achieves the most thorough cracking but involves substantial environmental and safety risks due to HF hazards. Emerging low-temperature methods (such as mechanochemical activation and direct chloride leaching) show promising energy profiles and lower emissions, but their lower cracking efficiency and limited Zr–Nb release currently limit industrial scaling. Overall, the comparison shows that no single method excels across all areas, underscoring the importance of deposit-specific TEA/LCA analysis in process selection.

Table 6. TEA/LCA comparison of major cracking–leaching routes for peralkaline REE deposits. Adapted from Smith et al. (2020); Andersen et al. (2021, 2023); Gupta & Nikoloski (2022); Jowitt et al. (2023); Hu et al. (2024–2025)

Processing route	Estimated CAPEX (relative index)	Energy consumption *(GJ/t concentrate)*	Environmental impacts (LCA highlights)	Key strengths	Key limitations
$CaCl_2$ roasting + HCl leaching	1.0 (baseline)	4.5 – 7.5	Moderate CO_2 footprint; limited SO_x; chloride wastewater requires treatment	Highest REE extraction; low silica gel; good selectivity	Corrosion issues; chloride handling; salt regeneration needed
Sulfation roasting + water / H_2SO_4 leaching	1.3 – 1.6	6.0 – 9.0	High SO_x generation; gypsum-rich residues; high net acid consumption	Practical for HREE; established industrial analogue	Silica gel risk: high off-gas treatment cost
Alkaline roasting (Na_2CO_3 / NaOH) + acid leaching	1.2 – 1.5	5.5 – 10.0	Significant Na-containing effluents; moderate CO_2; low toxic emissions	Strong for Zr/Nb liberation; scalable	High reagent mass flow; multi-step leaching
Mixed roasting (chlorination + sulfation)	1.4 – 1.8	7.0 – 12.0	Combined Cl^- + SO_x load; complex off-gas system; medium CO_2	Hybrid synergy improves cracking and REE kinetics	Operational complexity; high OPEX
Mechanochemical activation + low-acid leaching	0.8 – 1.0	2.5 – 4.0	Low gaseous emissions; minimal acid	Low operating temperature	Lower Zr/Nb liberation;

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			use; potentially lowest LCA footprint	; promising TRL	scale-up challenges
Fluorination roasting (NH_4F, CaF_2)	1.7 – 2.3	3.5 – 6.0	Significant HF-related risks; high toxic potential; demanding containment	Highest cracking efficiency; excellent Zr/Nb release	Environmental + safety constraints limit deployment
Direct chloride leaching (no roasting)	0.7 – 0.9	1.5 – 3.0	Low emissions profile; low solid waste; high chloride recycling need	Low CAPEX; suitable for fine concentrates	Ineffective cracking; low REE extraction

10. Challenges and knowledge gaps

Despite notable progress, processing peralkaline REE deposits continues to face significant technical and economic challenges. The primary issue remains silica gel formation, which is the main metallurgical obstacle across all flow sheet designs. Gelation hampers filtration, disrupts solvent extraction systems, and results in considerable losses of REEs, Zr, and Nb through co-precipitation or colloidal entrapment (Moldoveanu & Papangelakis, 2013; Borra et al., 2017). Although chloride-stabilized leaching and controlled thermochemical cracking can reduce silica polymerization, no universally effective solution has been established yet, especially for Na-rich systems like Ilímaussaq and Strange Lake.

Figure 11 shows how silica gel forms during the leaching of peralkaline rare-earth deposits. When eudialyte-rich ores come into contact with acidic or chloride-based leach solutions, the breakdown of Na- and Fe-bearing silicates releases soluble silica species. Under typical processing conditions—elevated temperature (>100 °C), high pH (>1), and chloride-rich media—these species quickly polymerize into colloidal gels. The figure highlights the metallurgical effects, including colloidal precipitation, increased viscosity, and significant REE losses because dissolved species get trapped within the gel network.

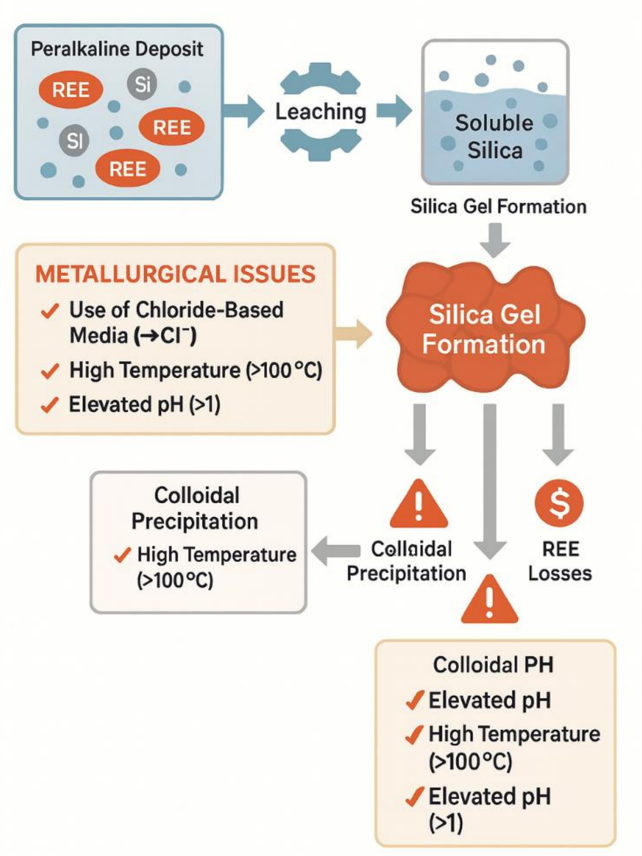

Figure 11. Pathways leading to silica gel formation during leaching of peralkaline REE ores. Adapted from Zakharov et al. (2019); Gupta & Nikoloski (2022); Andersen et al. (2023); Egendorf et al. (2024)

Silica gel formation remains one of the most difficult challenges in hydrometallurgical processing of peralkaline deposits. The process is highly sensitive to temperature, acidity, and chloride activity, creating narrow operational windows for effective dissolution. Gelation not only complicates solid–liquid separation but also reduces rare-earth recovery by physically trapping REE-bearing complexes. Strategies such as controlled pH ramps, Ca-based destabilization, or pre-roasting to stabilize the silicate matrix are therefore crucial for industrial scalability.

A second challenge is the need for environmentally responsible and reagent-efficient methods. Fluoride- and chloride-based cracking techniques, while effective, raise concerns about corrosiveness, toxic emissions, wastewater loads, and long-term waste management (Omodara et al., 2019; Binnemans & Jones, 2020). Developing “clean” cracking technologies—whether through optimized alkali roasting, mechanochemical activation, or hybrid low-temperature processes—remains a key

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research focus. Similarly, solvent extraction systems must transition to low-VOC, recyclable extractants to comply with increasingly strict environmental regulations.

Economic barriers also persist, especially for low-CAPEX options that can compete with carbonatite-based operations or ion-adsorption clay (IAC) deposits. Peralkaline ores require energy-intensive cracking, complex impurity control, and multi-stage SX systems, leading to higher capital and operating costs (Marion et al., 2023; Beard et al., 2023). Integrated REE–Zr–Nb recovery enhances overall project economics. However, the cost structure of peralkaline deposits remains less favorable unless technological advances decrease reagent use, reduce equipment redundancy, and lower waste streams.

Another significant gap concerns large-scale Zr/Nb–REE separation, which remains technically challenging because of the strong complexation of Zr and Nb in chloride- and sulfate-based media. Current extractants—such as D2EHPA, TBP, or MIBK—lack the selectivity needed to effectively separate these metals at an industrial scale without extensive pre-conditioning steps. Research into new solvent classes, functionalized ionic liquids, and tailored ligands for Nb(V) and Zr(IV) extraction is still in early stages. However, it is a crucial area for future development.

The Table 7 summarizes the major metallurgical bottlenecks encountered when processing peralkaline silicate deposits—particularly those rich in eudialyte, lovozerite-group minerals, and complex Zr–Nb–bearing phases. The challenges listed reflect both mineralogical constraints (such as slow dissolution and silica gel formation) and process-system limitations (including reagent consumption, SX selectivity, and environmental concerns). The emerging solutions highlight recent advances, including chloride-based cracking, mechanochemical activation, controlled fluorination, hybrid roasting, and the use of tunable extractants and ionic-liquid systems. Overall, the comparison shows that while $CaCl_2$-assisted routes currently have the most favorable TEA/LCA profile, no single method addresses all issues; scale-up and long-term continuous operation remain critical challenges.

Table 7. Technical Challenges and Emerging Solutions for Processing Peralkaline Deposits. Adapted from Gudfinnsson et al. (2021), Ferron & Riveros (2020), Binnemans et al. (2020, 2021), Blaxland et al. (2021), Zaitsev et al. (2022), Tan et al. (2023), Schouwstra et al. (2021), Habib et al. (2024), Goodenough et al. (2022), Hatch (2024), and Larsen et al. (2020)

Technical Challenge	Description / Impact	Emerging Solutions

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Silica gel formation	Colloidal silica precipitates during leaching, hindering filtration, entraining REEs, and increasing solution viscosity.	Chloride routes with $CaCl_2$pH and temperature controlCl^-–Si complexation Pre-removal of Si via alkaline roasting
Slow dissolution of eudialyte	Highly resistant cyclosilicate structure → low extraction efficiency.	$CaCl_2$ roasting Mechanochemical activation Controlled fluorination roasting
Competition of Zr/Nb with REEs during leaching	Zr and Nb dissolve inadvertently and interfere with SX and precipitation steps.	Selective HCl–$CaCl_2$ leaching Pre-oxidation of Zr/Nb Specific extractants (TBP, MIBK)
High reagent consumption	Sulfation and alkaline routes require large reagent quantities → elevated CAPEX/OPEX.	Hybrid roasting Low-acid and closed-loop processes Use of DES/ILs
Lack of commercially demonstrated flowsheets	No peralkaline deposit is yet in full commercial operation.	Integrated pilot campaigns (Ilímaussaq, Strange Lake) TEA/LCA indicating the most viable routes ($CaCl_2$)
Complex LREE/MREE/HREE separation	High chemical similarity among HREE makes separation difficult and reagent-intensive.	Cyanex 572/572A Multistage SX sequencing Intensified SX processes
Environmental impacts of fluorination routes	Fluoride reagents → toxicity, handling constraints, and waste treatment challenges.	Controlled fluorination roasting Fluoride-free routes (HCl + $CaCl_2$)
Integration of Zr–Nb–REE value streams	Higher value recovery is required to justify peralkaline projects economically.	Co-recovery of nuclear-grade ZrO_2 and high-purity Nb_2O_5 Dedicated SX circuits
Lack of long-term operational data (TRL 3–5)	Low technological readiness level for most routes; insufficient continuous operational datasets.	Continuous pilot studies TEA/LCA to reduce uncertainty and risk

Finally, industrial scalability remains limited. Most peralkaline flowsheet developments are at TRL 3–5, with very few pilot plants capable of processing representative ore volumes (Marion et al., 2023). Challenges include scaling thermal cracking reactors, managing corrosive chloride media at high throughput, maintaining silica stability during continuous leaching, and integrating co-production of Zr and Nb. Without significant investments in pilot-scale and demonstration-scale projects, the transition from laboratory success to commercial operations will stay slow.

Collectively, these challenges underscore the need for coordinated research efforts spanning mineralogy, reaction engineering, materials science, solvent design and process intensification. Overcoming these gaps is essential for unlocking the full potential of peralkaline REE deposits as reliable future sources of HREEs, Zr and Nb.

11. Emerging trends (2025–2030)

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Several technological directions are expected to shape the next generation of processing methods for peralkaline REE deposits. One of the most promising areas is the development of hybrid deep eutectic solvents (DES) and ionic liquids (ILs) that combine customized coordination chemistry with improved thermal and chemical stability. These solvent systems show significant potential for selective REE extraction in chloride-rich solutions, reduced co-extraction of Zr and Nb, and enhanced recyclability compared to conventional SX reagents (Alguacil et al., 2024; Alguacil, Rodríguez & González-Martínez, 2024).

Another emerging trend is the use of renewable energy–assisted methods, such as chlorination and thermal cracking, including solar-assisted roasting, microwave-driven decomposition, and electrified rotary kilns. These approaches aim to reduce the carbon footprint of $CaCl_2$ and chloride-based cracking techniques while tackling energy-intensity issues that currently limit scaling up (Marion et al., 2023). Incorporating renewable heat or electrified reactors could help shift these processes toward cleaner, lower-emission industrial operations.

In the upstream part of the flowsheet, advances in dry beneficiation and sensor-based ore sorting are becoming more important. Early removal of barren nepheline–sodalite gangue using hyperspectral or LIBS-based sorting can significantly reduce downstream energy use, decrease reagent consumption, and improve silica behavior during cracking and leaching (Silin et al., 2022). These technologies also provide modular deployment options suitable for remote or emerging peralkaline projects.

A key strategic development is the transition to a closed-loop Zr–Nb–REE recovery system, where all three commodities are co-extracted and recycled internally to reduce waste and increase value. This circular process reduces environmental impact by decreasing chloride discharge, improving solid waste quality, and reducing the need for external Zr/Nb reagents. It also improves project economics for lower-grade or more heterogeneous deposits (Beard et al., 2023).

Finally, the broader industry trend toward “low-acid, low-waste” processing is driving the development of flowsheets that reduce sulfuric acid use, lower silica gelation risks, and reduce hazardous effluent production. Low-acid chloride systems, mechanochemically activated cracking, alkali-stabilized leaching, and hybrid solvent schemes all align with this approach, sharing the goal of enhancing sustainability,

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lowering CAPEX, and enabling more adaptable plant designs for future peralkaline REE operations.

Figure 12 summarizes the main emerging technological trends currently shaping the development of sustainable processing routes for peralkaline REE deposits. These trends reflect recent advances in solvent design, selective cracking technologies, digital beneficiation tools, and integrated value-recovery strategies that collectively aim to reduce environmental impact, enhance selectivity, and improve economic viability.

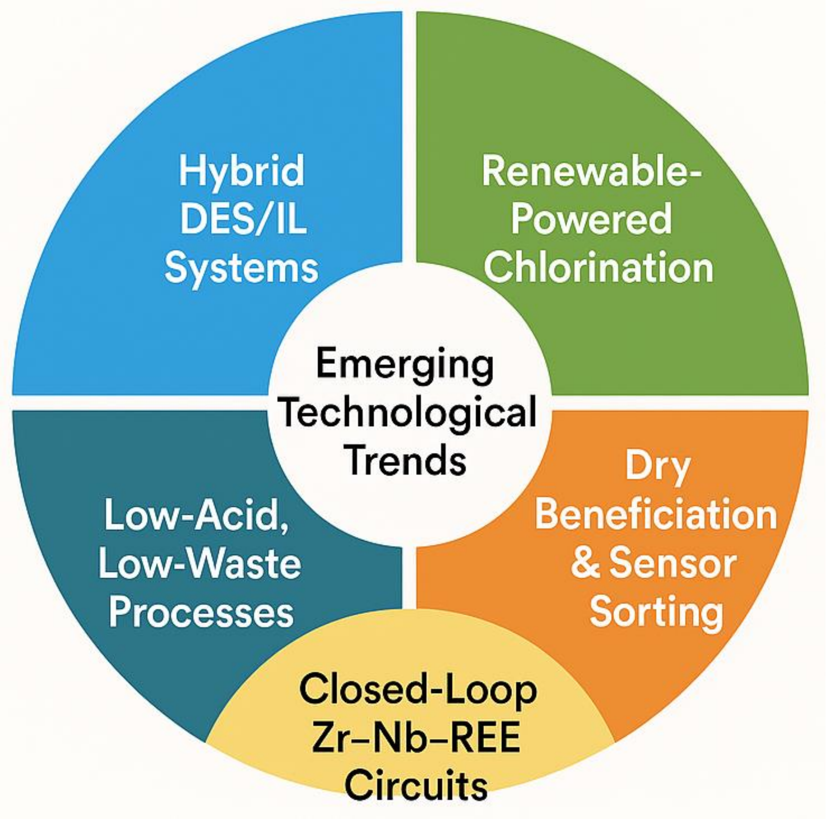

Figure 12. Emerging technological trends in the processing of peralkaline REE deposits. Adapted from Binnemans et al. (2020–2024), Goodenough et al. (2022), Hatch (2024), and recent DES/IL innovation reports (Alhamami et al., 2023)

Overall, the landscape of innovation is shifting toward low-acid, low-waste flowsheets, improved cracking selectivity (especially for Zr–Nb), and increasingly circular, closed-loop systems. The rapid growth of DES/IL-based extraction methods and renewable-powered chlorination processes highlights the sector’s move toward decarbonized and modular operations. Meanwhile, sensor-based sorting and dry beneficiation offer early-stage mass rejection options that can significantly cut downstream energy and reagent use. Despite these progressions, scaling these technologies beyond TRL 3–5 remains a major challenge, especially for integrated Zr–Nb–REE circuits.

Figure 13 offers a comprehensive overview of the entire processing chain for peralkaline REE deposits, combining the main operational stages discussed throughout this review. Starting with mining and crushing, the flowsheet emphasizes the shift to physical concentration and the variety of cracking methods—$CaCl_2$ roasting, sulfation, alkaline conversion, and mechanochemical activation—needed to break down the resistant eudialyte-type silicates. These processes feed into leaching circuits that increasingly depend on hybrid chloride–sulfate systems or low-acid DES/IL approaches to manage silica gelation and enhance selectivity. Further downstream, solvent-extraction steps facilitate the separation of LREE, MREE, HREE, and Zr–Nb streams, ultimately producing high-purity final products such as REE oxalates or carbonates, ZrO_2, and Nb_2O_5.

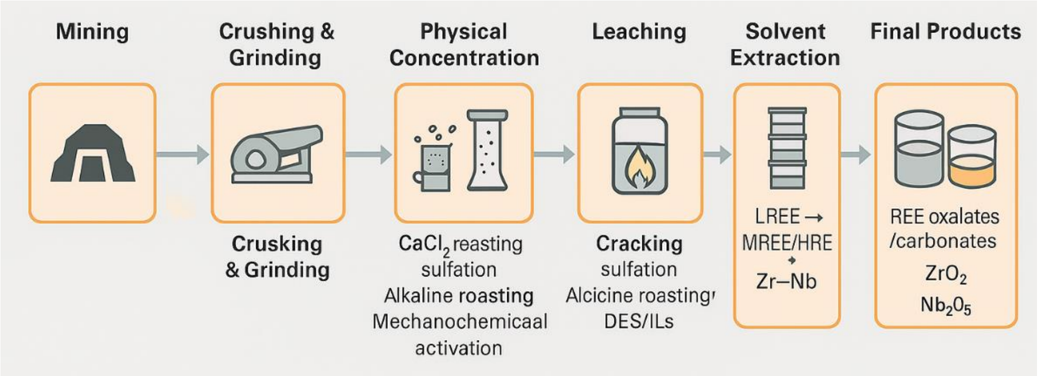

Figure 13. Integrated process flowsheet for the extraction and separation of REE–Zr–Nb from peralkaline deposits. Prepared byauthor

Overall, the flowsheet captures the technological progress making peralkaline deposits more viable commercially. It shows that no single step is enough; instead, a coordinated, multi-stage approach—combining mineralogy, controlled cracking, selective hydrometallurgy, and efficient separation—is essential to realize the full potential of these complex resources. As research continues to improve each phase and lower energy use, reagent consumption, and environmental impact, the integrated processing method presented here offers a solid conceptual base for future pilot testing and industrial-scale development.

12. Conclusions

Peralkaline igneous deposits have become strategically important sources of future supplies of heavy rare earth elements (HREEs) and critical metals such as Zr and Nb. Their distinctive mineral structures—mainly composed of eudialyte-group silicates and related zirconium–niobium phases—present both opportunities and challenges. Eudialyte, in particular, remains a key metallurgical hurdle due to its highly polymerized silicate framework, which is resistant to direct dissolution and necessitates thermochemical cracking before leaching.

The period from 2020 to 2025 saw significant progress in overcoming these barriers. $CaCl_2$-assisted roasting, low-temperature chlorination pathways, mechanochemical activation, and hybrid chloride-based leaching systems collectively improved silicate breakdown, reduced silica gelation, and increased REE extraction efficiency. Advances in solvent extraction, impurity control, and integrated REE–Zr–Nb recovery further demonstrated that peralkaline deposits can support technically feasible, multi-metal flowsheets when properly engineered.

Despite these advances, industrial scalability and sustainability still pose major challenges. Chloride- and fluoride-based cracking methods create environmental and handling issues, while sulfate- and alkaline-based processes face challenges with energy consumption, effluent treatment, and silica stability. The most promising technologies are still at TRL 3–5, underscoring the need for additional pilot programs, improved reactor designs, and comprehensive techno-economic and life-cycle analyses.

Overall, while peralkaline deposits offer significant potential as long-term sources of HREE and critical metals, their successful development depends on ongoing innovation in mineral processing, chemical engineering, and environmentally responsible flowsheet design.

Declaration of Competing Interest

The authors declare that they have no competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Author Contributions

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All authors contributed to the conceptualization, literature review, critical analysis, and writing of this manuscript. All authors have read and approved the final version of the paper.

Data Availability Statement

All data and materials referenced in this review are obtained from publicly available scientific literature. No new datasets were created.

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