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SUSTAINABLE RECOVERY OF RARE EARTH ELEMENTS FROM GRANITE: A REVIEW OF MODERN TECHNIQUES

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Abstract

The extraction of Rare Earth Elements (REEs) is important for clean energy, electronics, and high-tech materials. While minerals like monazite and bastnäsite are the main sources, granite is also being studied as a backup source because it contains REE-rich minerals such as apatite, zircon, and allanite. But extracting REEs from granite is difficult due to its hardness, low REE content, and radioactive materials, which make separation and recovery more complex. This paper reviews different extraction methods, including standard physical processes, bio-based techniques, and newer, greener methods like using ionic liquids. Additionally this study also reviews the importance of finding cleaner, more efficient ways to recover REEs from granite, focusing on better results with less harm to the environment. The findings show that pre-treatment with microwaves reduces the strength of the rock, making it easier to process, and acid leaching after this treatment improves the REE extraction rate.

Key words: Rare Earth Elements; Granite Leaching; Microwave Pre-treatment; Sustainable Extraction

Introduction

REEs consist of 17 elements, including 15 lanthanides, Yttrium (Y), and Scandium (Sc), with similar chemical properties (Hoshino *et al.*, 2016; Hu *et al.*, 2004). Although widely distributed in the Earth's crust, Promethium (Pm) is excluded due to its radioactive nature. REEs are critical for modern technologies, particularly in clean energy and electronics, where they are used in permanent magnets for electric vehicles (Dent, 2012), wind turbines (Per Kalvig and Machacek, 2018), and electronics (Daigle and DeCarlo, 2021). REEs also play an essential role in catalysts for petroleum refining (Nieto *et al.*, 2013), pollution control (Patel *et al.*, 2024) , medical imaging (Reddy and Pranav, 2024). The global demand for REEs continues to rise, driven by the shift toward renewable

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energy (Drobniak and Mastalerz, 2022). China dominates the REE market, holding significant reserves and leading in production (Massari and Ruberti, 2013). Due to their low concentrations, REEs are typically obtained as byproducts during the processing of other minerals (Jha *et al.*, 2016), with common minerals such as allanite, bastnaesite, and monazite being the primary sources of REEs (Lashen *et al.*, 2016). However, granite, typically composed of quartz, mica, and feldspar, has emerged as an underutilized source of REEs (Balaram and Sawant, 2022). A-type and S-type granites contain REE-rich minerals like apatite, zircon, allanite, and monazite, and weathering processes can concentrate these elements in regolith-hosted deposits, offering easier extraction options than primary ore bodies (Bucher and Seelig, 2018; Li *et al.*, 2017). Granite extraction presents unique challenges, including the presence of radioactive elements such as thorium (Th) and uranium (U), which complicate the process (Balaram, 2023a). Analytical techniques like ICP-MS, gamma spectrometry, and SEM-EDS are crucial for understanding ore composition and optimizing extraction methods (Pinto *et al.*, 2012). Eco-friendly methods such as ionic liquids and bio-extraction offer sustainable options for recovering rare earth elements (REEs). Ionic liquids allow for selective and low-impact extraction, while bio-extraction uses microorganisms to recover REEs in a cost-effective and environmentally safe way. The results show that using microwave pre-treatment weakens the rock, making it easier to break down, and that acid leaching after this step leads to better REE recovery.

Mineralogical specification of REE in granite

REEs possess unique chemical, physical, magnetic, and luminescent properties, owing to their distinctive atomic structures and electronic configurations (Dushyantha *et al*., 2020). Analyzing REE distribution within granite is essential for developing efficient extraction methods, as highlighted in several studies.

Nature of occurrence of REEs in granite

In granite, REEs are primarily concentrated in accessory minerals like monazite, bastnäsite, and xenotime, which are often part of the igneous mineral assemblage. These minerals are important for the primary extraction of REEs from granite deposits (Ishihara *et al.*, 2008) (Table 1). Demonstrates various granite types along with their concentration of REEs and economic potential, highlighting the correlation between mineral composition and REE concentration.

Table 1. Demonstrates various granite types along with their concentration of REEs and economic potential, highlighting the correlation between mineral composition and REE concentration.

Country names	Types/classification of Granite	Concentration of REE(ppm)	Mineral composition	Reference
USA (New Mexico)	Granites (Various Types) / Peralkaline Granite	Tajo Granite: 174.9 (avg.), Sevilleta Granite: 107.1 (avg.), Gallinas Granite: 264.5 (avg.)	Monazite, zircon, apatite,feldspars,fluorite, xenotime,thorite, allanite, samarskite	(Dietz and McLemore)
China (Jiangxi Province)	Peralkaline Granites /HREE-enriched Granites	Dingnan Biotite Granite: 358, 429 ppm, Wuliting Mafic Biotite Granite: 344 ppm	Alkali feldspars, quartz, biotite, zircon, aegirine, fluorite,allanite, samarskite, xenotime	(Zhao *et al.*, 2022)
Cameroon (Biou Area)	Granites (S-type, Peraluminous) / Weathered Granites	Weathered materials: 200 to 1,400 ppm	Quartz, alkali feldspars, biotite,muscovite, plagioclase,zircon, monazite,apatite, fluorite	(Sababa *et al.*, 2021)
Egypt (W. Hawashia, North Eastern Desert)	Monzogranites / Intrusive Granites	43 ppm (average)	Plagioclase, quartz, alkali feldspars, biotite Accessory minerals: apatite, zircon	(Saleh *et al.*, 2019)
Indonesia (Sijunjung, West Sumatra)	A-type Unggan Granite	Average REE = 860 ppm, with La and Nd as the major REE	Quartz, feldspar, mica (dark red coarse-grained granite) with significant presence of Ga, Nb, and Y, indicating A-type affinity	(Irzon *et al.*, 2018)

Major and minor mineral constituents

REEs occur in various mineral classes such as oxides, phosphates, silicates, carbonates, and halides (Balaram and Sawant, 2022), but current production is primarily sourced from fewer than ten key minerals, notably bastnäsite, xenotime, and monazite (Jordens *et al.*, 2013). In granite systems, important REE-bearing minerals include apatite, allanite, xenotime, and zircon (Zhang *et al.*, 2021; Ishihara *et al.*, 2008; Anitha *et al.*, 2020b). Studies from southern Jiangxi Province (China) and Skye (UK) show significant LREE enrichment in allanite and apatite (Ishihara *et al.*, 2008; Anitha *et al.*, 2020a). Additionally, ion-exchangeable clays formed from the weathering of minerals such as allanite, titanite, and fluorocarbonates are major hosts for secondary REEs (Kanazawa and Kamitani, 2006; Sanematsu *et al.*, 2015). Less commonly, minerals like britholite and thorite also contribute to REE distribution in some granite complexes (Zozulya *et al*., 2019; Santana and Botelho, 2022).

Spectroscopic and mineralogical analysis: Characterization Method

Accurate identification and quantification of REEs require a combination of elemental, isotopic, and mineralogical techniques. ICP-MS is widely used due to its sensitivity and ability to detect low REE concentrations in rock and mineral samples (Alnour *et al.*, 2015; Navarro *et al.*, 2008). For in-situ measurements, LA-ICP-MS allows REE mapping within individual minerals without full digestion (Sindern, 2017; Jarvis and Williams, 1993). XRD and SEM-EDS are used to identify REE-hosting minerals and determine their textural relationships within the rock (Balaram, 2023b). INAA is also effective for multi-element analysis, offering high sensitivity without the need for chemical separation (El-Taher, 2007; Silachyov, 2020). For rapid, non-destructive elemental assessment, XRF is used, though with lower sensitivity for trace REEs; it performs better when combined with pre-concentration or calibration methods (Srivastava and Premadas, 1999; Sitko *et al.*, 2005). Raman spectroscopy can support the identification of REE-bearing phosphates, especially in lateritic or weathered granites (Zhukova *et al*., 2022).

Processing techniques for rare earth element recovery from granite

REEs, due to their similar ionic sizes and stable trivalent states, are challenging and costly to separate. Efficient isolation methods have been the focus of extensive research, with fractional crystallization being an early technique that exploits slight solubility differences in REE salts.

Beneficiation techniques: Physical approaches: (Gravity and Froth flotation)

Physical separation techniques are often used as a pre-concentration step in REE extraction from granite-hosted ores, where REEs are found in minerals like monazite, xenotime, and allanite. These methods help remove gangue before applying hydrometallurgical processes. Gravity separation exploits the density contrast between REE minerals (specific gravity ~2.9–7.2) and lighter gangue (2.5–3.5) (Somani *et al.*, 2017). Devices like shaking tables, spiral concentrators, and centrifugal separators (e.g., Falcon, Knelson) are used to concentrate REE-rich particles. The Wilfley shaking table has shown effectiveness in processing granite-derived ores, as demonstrated in studies from Wadi Abu Dob, and combined use of spirals and centrifugal methods has enhanced recovery in Eastern Siberia (Hassan, 2023; Khokhulya *et al.*, 2021). Froth flotation is widely used to separate REE-bearing minerals, particularly when associated with gangue minerals like ilmenite, rutile, quartz, and zircon. Successful separation depends on tailoring flotation parameters reagents, pH, and surface chemistry to the ore's mineralogy (Abaka-Wood *et al.*, 2016). Avazpour *et al.*, (2021) demonstrated that using a Maxblend impeller significantly improves recovery and enrichment (65% and 3.85×, respectively), while minimizing environmental impact.

Integrated metallurgical extraction methodology for REE separation

An integrated metallurgical extraction approach for the separation of REEs involves the combination of various techniques. This comprehensive methodology enhances the efficiency of REE recovery by addressing the complexities of mineral matrices, optimizing the purification process.

Pre-Treatment (Thermal)

Granite’s hardness requires high energy for comminution. Pre-treatment methods like microwave heating, thermal breakage, and ultrasonic reduce energy use by weakening its structure. Microwave heating is the most energy-efficient, causing localized damage and reducing compressive strength (Somani *et al.*, 2017; Pressacco *et al.*, 2023). Ji and Zhang (2021a) showed that thermal treatment at 600 °C improved REE recovery from kaolinite to 92%, compared to <20% with mechanical grinding. In further studies, thermal pre-treatment followed by acid leaching significantly boosted REE recovery from both kaolinite and phosphatic clay to over 80% (Ji and Zhang, 2021b; Ji and Zhang, 2021a).

Hydrometallurgy: Methods and Application

Physical beneficiation methods are often ineffective for REE recovery due to mineral complexity, making chemical leaching essential (Liu and Chen, 2021). Table 2 shows the summary of Hydrometallurgical REE Extraction Methods: Reagents, Advantages, and Limitations.

Enhance recovery and purification of REEs

The purification of REEs requires removal of impurities often present in processing streams. Gupta and Krishnamurthy (1992) reported methods such as vacuum melting, electrorefining, zone refining, and solid-state electrotransport to eliminate volatile,

Table 2. Summary of Hydrometallurgical REE Extraction Methods: Reagents, Advantages, and Limitations (W. Liu *et al.*, 2024) (Hazan *et al.*, 2022) (Prasastia *et al.*, 2015) (Merroune *et al.*, 2024; Xie *et al.*, 2014).

Method	Target REE Host Mineral(s)	Typical Reagent(s)/Process	Advantages	Limitations
Acid leaching	Granite-associated silicate minerals (e.g., allanite, apatite)	H_2SO_4, HCl, HNO_3 – commonly used mineral acids for silicate REE dissolution .	High LREE recovery (~85%), well-suited for granite silicates.	Less effective for monazite; acid waste generation.
Alkaline Leaching	Phosphate-rich minerals (e.g., monazite in granite)	NaOH.	Efficient breakdown of phosphate matrix; selective REE liberation.	High temperature; caustic waste handling.
Sequential Leaching	Mixed mineral phases in weathered granite	Stepwise acids/bases (e.g., acetic acid, HNO_3, NaOH) depending on mineral matrix.	Phase-specific REE targeting; improved overall recovery.	Lab-scale complexity; slower and reagent-intensive.
Solvent Extraction (SX)	Leachate from previous leaching steps (acidic or alkaline)	D2EHPA, TBP, HEHEHP, Versatic 10, Aliquat 336 – organic solvents for REE separation.	High selectivity and purity; widely used at industrial scale.	Multistage; uses hazardous organic solvents.

metallic, and interstitial impurities. SX is commonly used to purify REEs from pregnant leach solutions (PLS), utilizing kerosene as diluent and P507 as extractant, with scrubbing and stripping stages. Due to similar REE behaviors, some SX systems exceed 1500 stages (McNulty *et al.*, 2022). Precipitation methods using hydroxides, carbonates, sulfates, and oxalates are also widely applied (Han, 2020). U and Th, common in monazite and xenotime, are removed via selective precipitation, leaching, or solvent extraction (Garcia *et al.*, 2020). Combined approaches precipitation, sorption, and extraction efficiently separate radioactive impurities (Mukhachev *et al.*, 2021), while selective Th precipitation is used industrially, And ion exchange with dual resins enables >99% recovery of REEs and U [96]. Impurities such as Co, Zn, Cu, Pb, Cr, Fe, Mn, Ni, and others are typically removed via ion exchange, SX, adsorption or precipitation (Altaş *et al*., 2018). Judge and Azimi (2020) provide a detailed review on recent impurity removal advancements. Cerium purification via ceric hydroxide and manganese dioxide achieves >98% recovery and 99–99.5% purity (Abreu and Morais, 2010). REE processing involves roasting, leaching (acid/alkali), and subsequent purification by techniques such as ion exchange, SX, precipitation, bioleaching and membrane separation (Judge and Azimi, 2020).

Recent developments and innovations in REE extraction and purification

REE recovery from ores is limited to 50–80% due to process constraints (McNulty *et al.*, 2022). Table 3 shows the. Comparison of Advanced Methods for REE Extraction: Biohydrometallurgy, Ionic Liquids, Polymer-Based Materials, and Membrane Separation. With rising demand, focus is shifting to alternative resources and eco-friendly methods. Clay in weathered granite shows potential for HREE extraction, though traditional methods are ineffective. Greener alternatives like in-situ leaching with ammonium salts are being explored (Azimi, 2025). Fig. 1 shows the schematic diagram depicts the bioleaching mechanisms and ionic-liquid mechanisms.

Complications in the extraction of REEs and recommendation

REE extraction from granite is challenging due to uneven distribution across ore minerals and alteration processes, such as K-silicate, sericitic, and tourmalinization, which can result in the loss of specific REEs (Alderton *et al.*, 1980). Alterations can form REE-rich minerals like cerite and bastnäsite but also cause unpredictable changes in composition. Granite's hardness complicates physical separation, requiring energy-intensive grinding. Extracting REEs from complex mixtures is time-consuming and energy-demanding, especially for high purity. The presence of radioactive elements, such as uranium and thorium, further complicates extraction and raises environmental and health concerns (Taalab *et al*., 2024). A multi-method approach is proposed for REE extraction from granite to overcome challenges related to its hardness, low REE concentrations, and environmental impact.1. Microwave-Assisted Acid Leaching**.** The use of microwave heating weakens the granite’s dense structure, reducing the energy needed for grinding and improving the efficiency of subsequent acid leaching. Advantages: High recovery rates (up to 92%), cost effective by reducing grinding energy and chemical usage, environmentally sustainable, minimizing energy consumption and chemical waste, Scalable for industrial applications. 2. Ionic Liquid-Based Extraction**.** It can be customized for high selectivity of lanthanides, improving the purity of extracted materials while being environmentally friendly and recyclable. Advantages: High selectivity for REEs, improving purity, Eco-friendly due to low toxicity and recyclability, Sustainable with minimal chemical waste. Disadvantages**:** High cost and limited scalability for large-scale applications, currently in the early stages.

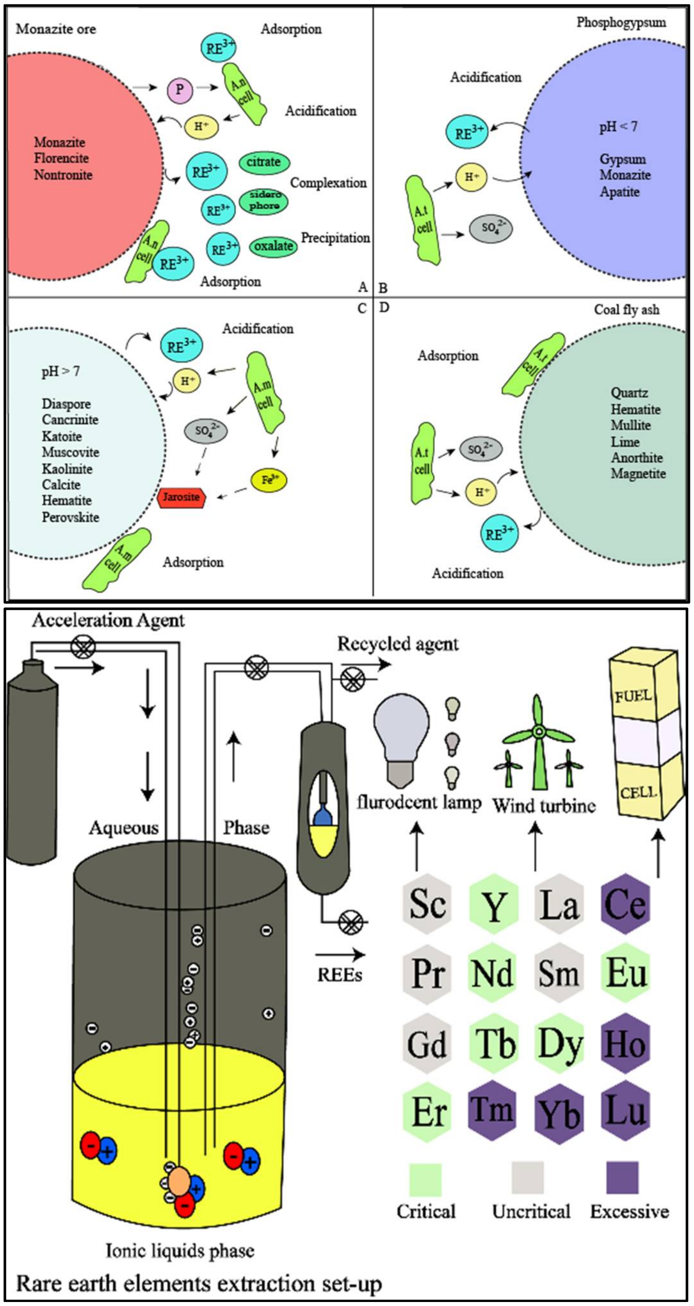

Fig. 1. The schematic diagram depicts the bioleaching mechanisms and ionic-liquid mechanisms (Arrachart *et al.*, 2021; Shi *et al.*, 2023).

Table 3. Comparison of Advanced Methods for REE Extraction: Biohydrometallurgy, Ionic Liquids, Polymer-Based Materials, and Membrane Separation (Fathollahzadeh *et al.*, 2019; Kumar and P. R, 2020) (Y. Liu *et al.*, 2011) (Quijada-Maldonado and Romero, 2020) (Almeida *et al.*, 2012; H. Zhang and Gao, 2023) (Bashiri *et al.*, 2022; Chen *et al.*, 2017).

Method	Sub-methods	Description	Advantages	Limitations
Biohydrometallurgy	1. Bioleaching 2. Microbial Leaching 3. Bioprecipitation	Biohydrometallurgy uses microorganisms to extract REEs. Bioleaching, with microbes like Aspergillus niger and Acidithiobacillus ferrooxidans, releases REEs from ores like monazite. Biosorption concentrates REEs using microbial biomass, while bioprecipitation induces REE precipitation through microbial metabolites.	Environmentally friendly, sustainable, cost-effective, low energy consumption, can be applied to low-grade ores and waste streams.	Slow process, requires careful control of parameters (e.g., pH, temperature, microbial population), low recovery rates for some REEs.
Ionic Liquids (IL)		ILs are green solvents known for their thermal stability, low flammability, and minimal vapor pressure. They offer a sustainable, selective method for REE extraction, especially from complex mixtures. Imidazolium-based ILs are commonly used and can be tailored for specific REEs. ILs are non-volatile, customizable, and offer high selectivity for REE separation.	Environmentally friendly, high selectivity for REE separation, non-volatile, low toxicity.	Expensive, limited scalability, potential toxicity.
Polymer-based Materials	1. Ion-Imprinted Polymers (IIPs) 2. Solvent Impregnated Resins (SIRs) 3. Polymer Composite Nanoparticles	Polymer-based materials like IIPs, SIRs, and polymer composite nanoparticles provide selective REE extraction, working similarly to traditional SX methods but in a more sustainable manner. These materials are particularly useful for REE extraction from granite, as they target specific ions and provide higher selectivity.	Eco-friendly, selective for REEs, sustainable, scalable, and chemical similarity to SX methods.	Limited large-scale industrial research, complexity in fabrication, and higher cost for advanced polymer materials.
Membrane Separation	1. Hollow Fiber Supported Liquid Membrane (HFSLM) 2. Bulk Liquid Membrane (BLM) 3. Supported Liquid Membrane (SLM) 4. Emulsification Liquid Membrane (ELM)	Membrane technologies like HFSLM, BLM, and SLM offer eco-friendly, non-thermal solutions for REE separation, integrating stripping and extraction without relying on thermal processes. PIMs are a promising development for REE separation in complex systems.	Non-thermal, rapid separation, selective, scalable, no reliance on high-energy methods.	Membrane fouling, cost, limited lifetime of membranes, and requirement for pre-leaching of ores like granite.

Conclusion

Granite contains REEs, but traditional extraction methods are energy-intensive and environmentally challenging. Microwave-Assisted Acid Leaching is recommended for its ability to enhance ore reactivity, reduce energy use, and improve recovery rates, offering a cost-effective and environmentally friendly solution. Additionally, Ionic Liquid-Based Extraction provides a selective, sustainable alternative to traditional solvents, with high potential for purity and minimal waste, though it remains in the early stages of industrial use. Combining these methods optimizes REE recovery from granite, ensuring better efficiency, sustainability, and reduced environmental impact.

Declaration of competing interest

The authors 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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