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Application of Magnesium Sulfate in In-Situ Leaching of Rare Earth Elements: Mechanisms, Performance and Environmental Implications

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ABSTRACT: Ion-adsorption clay deposits are among the most important sources of heavy rare-earth elements (REEs), particularly in southern China, where extraction is commonly performed by in situ leaching (ISL) using ammonium salts. Although ammonium sulfate and related lixiviants achieve high extraction efficiencies via ion-exchange mechanisms, their large-scale use has raised significant environmental concerns, including ammonium contamination, soil degradation, and groundwater pollution. In recent years, magnesium sulfate ($MgSO_4$) has emerged as a potential alternative lixiviant with lower environmental impact. This review critically analyzes the application of $MgSO_4$ in the in-situ leaching of REE-bearing ion-adsorption clays, focusing on ion-exchange mechanisms, leaching performance, hydrodynamic behavior, and environmental implications. The thermodynamic and geochemical aspects governing Mg^{2+}–REE exchange reactions are examined together with laboratory, column, and pilot-scale studies. Comparative analyses with conventional ammonium-based lixiviants are discussed in terms of extraction efficiency, selectivity, reagent consumption, and environmental footprint. The review also identifies key research gaps related to process optimization, hydrogeological modeling, and large-scale implementation. Overall, $MgSO_4$-based leaching systems represent a promising pathway toward more sustainable rare-earth extraction, although further technological and environmental validation is required before full-scale industrial deployment.

KEYWORDS: Ion-adsorption clays, In-situ leaching, Magnesium sulfate, Ion-exchange leaching, Rare earth elements, Sustainable rare earth mining

Highlights

- Ion-adsorption clay deposits are major sources of heavy rare earth elements extracted via in-situ leaching.
- Conventional ammonium-based lixiviants provide high recovery but cause significant environmental contamination.
- Magnesium sulfate emerges as a promising alternative lixiviant with lower ecological impact.
- Ion-exchange mechanisms, leaching performance, and sustainability implications of $MgSO_4$ systems are critically evaluated.

Graphical abstract

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1. INTRODUCTION

Rare earth elements (REEs) are vital raw materials used in magnets, electric vehicles, wind turbines, catalysts, ceramics, polishing compounds, phosphors, and defense technologies. Their importance grows due to rising demand, supply chain concentration, the complexity of extraction, and the environmental impacts of traditional production (Asubonteng et al., 2026; Bailey et al., 2020; Huang et al., 2015; Vahidi et al., 2016; Yang et al., 2013). Consequently, REE production is now seen as a strategic issue for resource security, technological sovereignty, and sustainability.

From a geological and metallurgical perspective, REE resources are found in several deposit types, including bastnäsite, monazite, xenotime, lateritic monazite, and regolith-hosted ion-adsorption clay deposits. Among these, ion-adsorption clays hold a unique position because they are a major source of medium and heavy REEs and are often extractable through ion-exchange leaching rather than full mineral digestion (Miiro, 2023; Moldoveanu & Papangelakis, 2016, 2025; Nie et al., 2020; Sobri et al., 2024; Xu et al., 2023). This mineralogical and chemical characteristic has made ion-adsorption deposits particularly significant in southern China, where weathered granitic crusts have supplied a large portion of the global supply, particularly of critical heavy rare earths (Huang et al., 2015; Packey & Kingsnorth, 2016; Yang et al., 2013).

The industrial relevance of these deposits is tied to in-situ leaching (ISL), also called in-place or heap/percolation ion-exchange extraction, depending on the setup. Unlike hard-rock REE processing that needs crushing, beneficiation, cracking, and solvent extraction, ion-adsorption clay exploitation typically involves leaching solutions percolating through ore to desorb REE from clay surfaces via weak electrostatic interactions and exchangeable sites (Moldoveanu & Papangelakis, 2016, 2025; Nie et al., 2020; Sobri et al., 2024; Xu et al., 2023). This simplicity has helped ISL expand rapidly in China, but it also masks significant hydrogeochemical, environmental, and process-control challenges.

Ammonium salts, especially ammonium sulfate, have been the main lixiviants for ion-adsorption REE ores due to their effectiveness and low cost, with widespread use owing to operational familiarity and proven industrial success (Huang et al., 2015; Moldoveanu & Papangelakis, 2016; Nie et al., 2020; Xu et al., 2023). However, this model faces criticism as environmental concerns grow, including ammonium buildup, groundwater contamination, soil degradation, reagent persistence, and ecological damage, especially in poorly regulated mining sites (Bailey et al., 2020; Packey & Kingsnorth, 2016; Vahidi et al., 2016; Wang et al., 2025; Yang et al., 2013). Therefore, describing ion-adsorption clay extraction as a “mild” or “low-intensity” process is misleading without assessing the fate of reagents, subsurface transport, and environmental liabilities.

This environmental tension has increased interest in alternative lixiviants, such as magnesium sulfate ($MgSO_4$), to mitigate the drawbacks of ammonium systems while maintaining good recovery. $MgSO_4$ may reduce nitrogen pollution, mitigate secondary environmental impacts, and offer alternative selectivity, impurity co-leaching, and solution management options (Sobri et al., 2024; Wang et al., 2025; Xu et al., 2023). However, research on $MgSO_4$-based systems is scattered across mineralogical, hydrometallurgical, environmental, and process engineering studies, often focusing on isolated aspects such as lab leaching, adsorption–desorption, or solution purification, lacking a comprehensive framework. As a result, it is unclear whether $MgSO_4$ is simply a cleaner alternative to ammonium salts or part of a broader shift in ion-adsorption REE extraction strategies.

This review explores the use of magnesium sulfate in in situ leaching of ion-adsorption rare earth deposits, focusing on deposit characteristics, ion exchange, hydrodynamics, operational factors, environmental impacts, process performance, and downstream effects. It details how $MgSO_4$ alters chemistry, selectivity, environmental profile, and limits of REE extraction from weathered clay systems. The goal is to synthesize current knowledge, highlight advantages and limitations of $MgSO_4$ leaching, and identify research priorities for sustainable, robust ISL operations (Asubonteng et al., 2026; Moldoveanu & Papangelakis, 2025; Sobri et al., 2024; Wang et al., 2025; Xu et al., 2023).

To ensure this critical assessment is transparent and reproducible, the following section describes the review design, literature search strategy, screening criteria, and article selection process used in the present study.

2. METHODOLOGY

This study was a structured literature review that critically evaluated the role of magnesium sulfate in the in situ leaching of ion-adsorption rare-earth deposits. It used a systematic search to find peer-reviewed papers on geology, mineralogy, leaching chemistry, hydrometallurgical mechanisms, environmental effects, and process optimization.

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The survey used databases such as Scopus, Web of Science, ScienceDirect, and Google Scholar covers 2010-2026 publications on rare-earth hydrometallurgy and sustainable extraction. It uses keywords like ion-adsorption deposits, in-situ leaching, magnesium sulfate leaching, ammonium sulfate leaching, ion exchange, rare-earth desorption from clays, and environmental impacts of REE mining.

Only peer-reviewed journal articles, review papers, and authoritative book chapters were included. Conference abstracts, non-technical reports, and sources lacking methodological transparency were excluded. After removing duplicates and screening titles, abstracts, and full texts, the most relevant studies were selected for detailed analysis.

The overall workflow for identifying, screening, and selecting literature sources is summarized in the PRISMA diagram below.

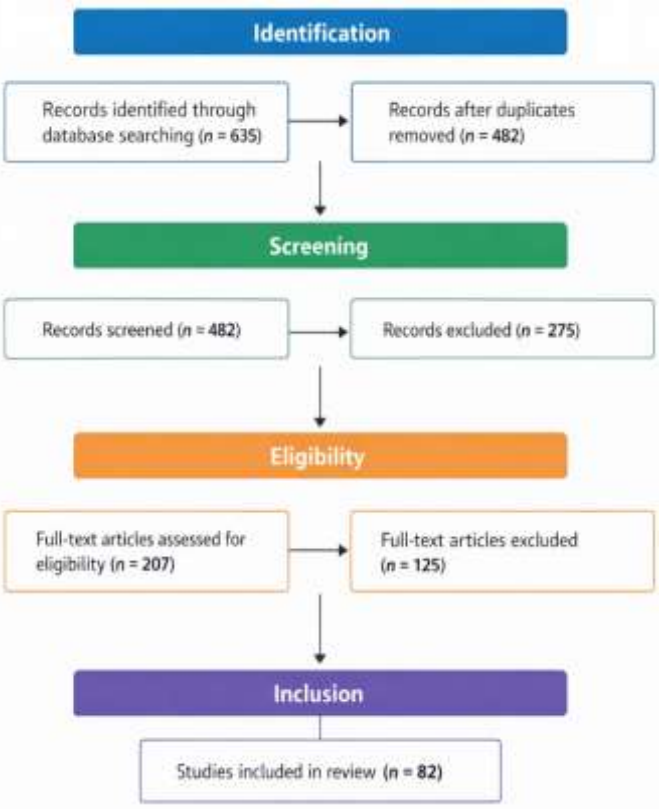

Figure 1. PRISMA flow diagram of the literature selection process used in this review. Adapted from Page et al. (2021).

The diagram shows the filtering process, which resulted in 82 references on the geological, hydrometallurgical, environmental, and process-engineering aspects of ion-adsorption rare-earth deposits and leaching technologies.

The selected publications were subsequently analyzed according to thematic categories, including:

- geological formation and mineralogical characteristics of ion-adsorption deposits
- mechanisms of rare earth adsorption and ion-exchange desorption in clay minerals
- hydrodynamics and operational parameters of in-situ leaching systems
- performance of conventional ammonium-based lixiviants
- emerging alternatives such as magnesium sulfate leaching
- environmental implications and sustainability considerations

This structured classification allowed the integration of results from mineralogy, hydrometallurgy, geochemistry, and environmental engineering studies into a coherent critical framework.

The section offers a geological and mineralogical overview of rare earth ion-adsorption clay deposits, which are key to understanding how rare earths are adsorbed and extracted via ion-exchange leaching.

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3. RARE EARTH ION-ADSORPTION CLAY DEPOSITS

Ion-adsorption clay deposits are among the most distinctive sources of rare earth elements (REEs). Unlike hard-rock deposits, the REEs in these systems are not primarily hosted within discrete mineral lattices. Instead, they are weakly bound to the surfaces of clay minerals via ion exchange and surface complexation (Moldoveanu & Papangelakis, 2016; Wu et al., 2023). This unusual geochemical behavior makes these deposits particularly amenable to extraction using in situ leaching technologies.

These deposits occur predominantly in deeply weathered granitic terrains, where prolonged chemical weathering breaks down primary REE-bearing minerals and redistributes REEs onto secondary clay minerals. As a result, the economic value of these deposits derives less from mineral concentration and more from the chemical accessibility of REEs through ion-exchange processes (Borst et al., 2020; Yang et al., 2013).

Ion-adsorption deposits are therefore both geologically unique and metallurgically unconventional. Their formation, mineralogical structure, and surface chemistry directly control the efficiency of leaching processes used for REE recovery. Understanding these characteristics is essential for evaluating alternative lixiviants such as magnesium sulfate.

3.1. Geological Formation

Ion-adsorption rare earth deposits form through prolonged tropical to subtropical weathering of granitic rocks. During this process, primary minerals such as feldspar, mica, and REE-bearing phases gradually decompose. The released rare earth elements migrate within the regolith profile and become adsorbed onto newly formed clay minerals (Borst et al., 2020; Liang et al., 2025).

The weathering process typically produces thick lateritic profiles consisting of kaolinite-rich and illite-bearing clay horizons. These clay minerals provide abundant surface sites that can host trivalent REE ions via electrostatic adsorption and outer-sphere complexation (Ding & Azimi, 2024; Wu et al., 2023). As weathering progresses, REEs originally contained in minerals such as monazite, bastnäsite, or allanite are redistributed and become dispersed within the clay matrix rather than remaining in discrete mineral grains (Miiro, 2023).

This redistribution process explains the relatively low REE grades commonly observed in ion-adsorption deposits; their economic viability depends on the facile desorption of REEs via ion exchange with leaching solutions (Moldoveanu & Papangelakis, 2016). These ore bodies often exhibit vertical zonation due to the mobilization and re-adsorption of REEs during weathering (Yang et al., 2013).

Figure 2 summarizes the conceptual evolution of these deposits. The progressive transformation of granite into clay-rich regolith creates a geochemical environment in which REEs are mobilized and subsequently immobilized via adsorption. This mechanism differentiates ion-adsorption deposits from conventional hard-rock REE ores and explains their suitability for ion-exchange leaching.

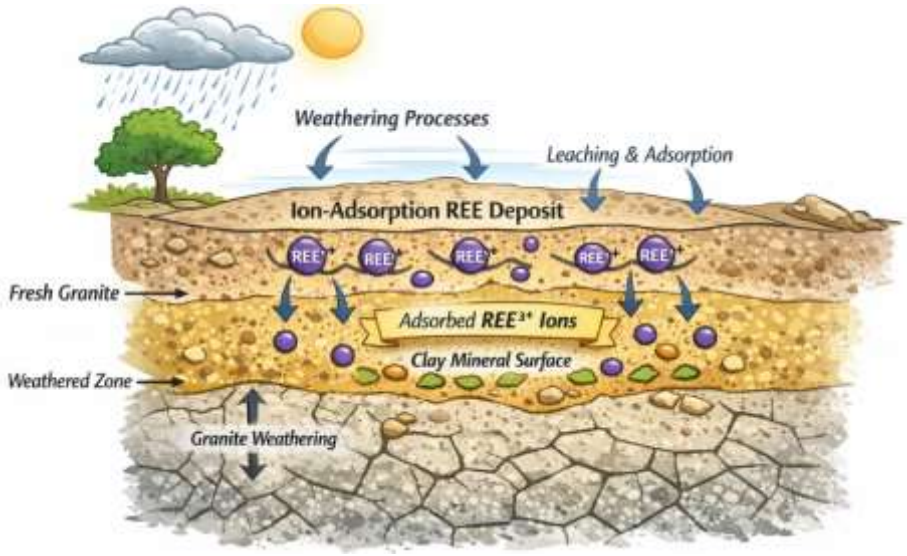

Figure 2. Conceptual formation of ion-adsorption rare earth deposits in weathered granitic regolith profiles. Adapted from Borst et al. (2020) and Liang et al. (2025).

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As weathering progresses, secondary clay minerals like kaolinite, halloysite, and illite form from altered feldspars and silicates. They develop negatively charged sites that can adsorb trivalent rare earth ions from soil solutions (Liang et al., 2025).

Unlike conventional hard-rock deposits, ion-adsorption deposits contain rare earth elements primarily as exchangeable ions loosely bound to clay surfaces, rather than within mineral structures. This allows recovery via ion-exchange leaching.

3.2. Mineralogical Characteristics

Ion-adsorption deposits mainly consist of secondary clay minerals from granite weathering, including kaolinite, halloysite, illite, and smectite, which host adsorbed REEs (Borst et al., 2020; Liang et al., 2025).

These minerals have large surface areas and functional groups that interact with rare-earth ions, mainly adsorbing onto negatively charged silanol and aluminol sites on clay surfaces (Bishop et al., 2024). Iron oxyhydroxides may also aid REE retention through adsorption or co-precipitation (Cristiani et al., 2020).

The distribution of REEs in regolith depends on mineralogy and surface chemistry. Clay minerals, grain size, and iron oxides affect REE adsorption and mobility (Ding & Azimi, 2024; Wu et al., 2023).

Table 1 shows mineral phases involved in REE adsorption in weathered clay deposits. Their abundance varies, explaining differences in leaching and recovery.

Table 1. Typical mineralogical components of ion-adsorption rare earth deposits and their role in REE adsorption. Adapted from Borst et al. (2020), Bishop et al. (2024), and Liang et al. (2025).

Mineral phase	Typical role in REE retention
Kaolinite	Major adsorption surface
Illite	Ion-exchange capacity
Smectite	High surface charge
Fe oxyhydroxides	Surface adsorption and co-precipitation

3.3. Speciation of REE in Clays

Rare earth elements in ion-adsorption deposits occur primarily as adsorbed or exchangeable ions rather than as structurally bound mineral phases. Three principal forms of REE occurrence are generally recognized: adsorbed REEs, exchangeable REEs, and surface-complexed species (Moldoveanu & Papangelakis, 2012, 2013).

Adsorbed REEs are weakly bound to negatively charged clay surfaces through electrostatic interactions. These ions are typically associated with the electrical double layer surrounding clay particles and can be readily displaced by competing cations in solution (Bishop et al., 2024; Wu et al., 2023).

Exchangeable REEs represent the fraction most directly involved in ion-exchange leaching processes. In this case, REE^{3+} ions are replaced by other cations introduced in the leaching solution, such as NH_4^+ or Mg^{2+}, allowing them to enter the aqueous phase (Moldoveanu & Papangelakis, 2013).

A third fraction involves surface-complexed REEs, which are associated with stronger chemical interactions at clay mineral surfaces or iron oxide interfaces. These species may require more aggressive chemical conditions or complexing agents to be mobilized (Cristiani et al., 2020; Moldoveanu & Papangelakis, 2021).

The relative proportions of these REE species vary depending on mineralogy, weathering intensity, and local geochemical conditions. Consequently, the efficiency of leaching processes depends not only on the lixiviant chemistry but also on the speciation of REEs within the clay matrix.

The adsorption mechanisms form the basis of ion-exchange leaching for the recovery of rare earth elements. The next section reviews in situ leaching principles, including ion-exchange reactions, transport processes, and operational parameters that affect REE recovery.

4. PRINCIPLES OF IN-SITU LEACHING OF RARE EARTHS

In situ leaching (ISL) is the dominant extraction method for ion-adsorption rare-earth deposits. Unlike conventional mining and mineral processing routes, ISL relies on the chemical desorption of rare earth elements (REEs) directly from clay minerals

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within the ore body. The method exploits the weak electrostatic binding of REE^{3+} ions to clay surfaces, allowing their displacement by competing cations introduced in the leaching solution (Moldoveanu & Papangelakis, 2012, 2013, 2016).

The process involves injecting a leaching solution into weathered ore, allowing it to percolate through the regolith, and collecting the leachate. This reduces the need for comminution and beneficiation but introduces complex hydrogeochemical interactions, such as adsorption, fluid transport, and geotechnical changes (Guo & Zhuang, 2023; Wang et al., 2024).

Understanding the ion-exchange mechanism, the hydrodynamics of fluid transport, and the operational variables controlling the leaching process is essential for evaluating both conventional and alternative lixiviants.

4.1. Ion-Exchange Mechanism

The extraction of rare earth elements from ion-adsorption clays is primarily governed by ion-exchange reactions occurring at clay mineral surfaces. In these systems, REE^{3+} ions are weakly adsorbed within the electrical double layer surrounding clay particles. When a solution containing competing cations is introduced, these ions can replace REE^{3+} at the adsorption sites, releasing the rare earths into solution (Moldoveanu & Papangelakis, 2012, 2013).

A simplified representation of the classical ammonium-based leaching mechanism can be expressed as:

$$\text{REE–Clay} + 3\,NH_4^+ \rightarrow REE^{3+} + NH_4\text{–Clay}$$

This exchange reaction reflects the relatively weak binding of REEs to clay surfaces. The efficiency of the process depends on the ionic strength of the solution, the valence and hydration properties of the competing cation, and the surface chemistry of the clay minerals involved (He et al., 2023; Wu et al., 2023).

Early mechanistic studies demonstrated that ammonium salts can effectively displace REE ions from adsorption sites through electrostatic exchange processes (Moldoveanu & Papangelakis, 2012, 2013). Later work expanded this framework by incorporating concepts such as electrical double-layer interactions, surface complexation, and ligand-assisted desorption mechanisms (Moldoveanu & Papangelakis, 2021; Xiao et al., 2018; Zou & Zhao, 2025).

Recent studies show that adsorption and desorption are dynamic and may involve partial readsorption of REEs within the leaching column. Sequential chemical extraction experiments suggest that desorption can involve multiple steps depending on mineralogy and chemical conditions (He et al., 2023; Pan et al., 2025).

Figure 3 summarizes the conceptual ion-exchange mechanism underlying the leaching process. The diagram emphasizes the role of surface adsorption sites and illustrates how competing cations disrupt the equilibrium between adsorbed and dissolved REE species.

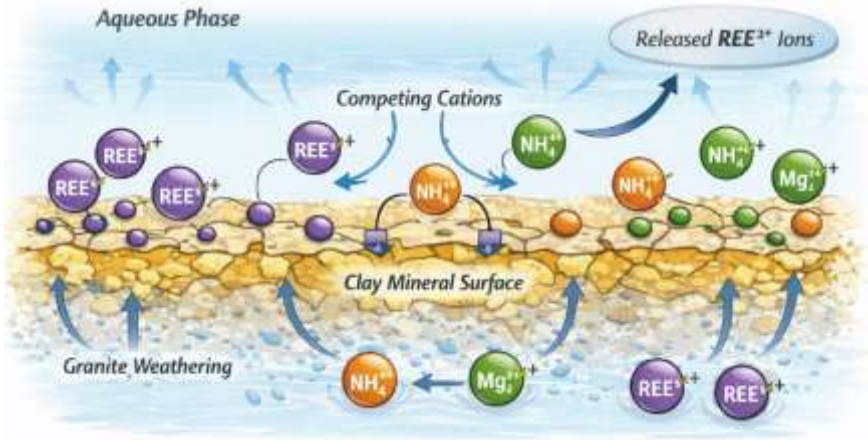

Figure 3. Conceptual mechanism of ion-exchange leaching of rare earth elements from clay minerals. Adapted from Moldoveanu and Papangelakis (2013), Wu et al. (2023), and Xiao et al. (2018).

The schematic shows REE^{3+} ions adsorbing onto clay surfaces, being displaced by cations such as NH_4^+ or Mg^{2+}, thereby releasing rare earth ions into water during leaching.

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4.2. Leaching Hydrodynamics

Ion exchange drives REE extraction, but in situ leaching efficiency depends on hydrodynamics such as fluid infiltration, solution flow, and recovery, which control the contact between the lixiviant and the ore (Guo et al., 2020; He et al., 2017).

Infiltration begins by injecting or applying the leaching solution, which percolates downward through the weathered ore under gravity and capillary forces. Ion-exchange reactions happen as the lixiviant interacts with clay minerals (Guo & Zhuang, 2023).

Subsurface flow conditions are crucial to recovery efficiency and are influenced by heterogeneity in pore structure, clay swelling, and permeability. These factors affect the distribution of the leaching solution and the transport of rare earths (Rao et al., 2025; Zhang et al., 2024; Zhou et al., 2021). Soil properties that change during leaching can also alter flow pathways and hydraulic conductivity (Wang et al., 2024).

Column experiments and reactive transport models simulate ISL hydrodynamics, showing that leaching depends on chemical factors, flow-channel distribution, and lixiviant residence time in the ore (He et al., 2016; Shi et al., 2022).

Recent studies explore electrokinetic transport to improve solution migration and recover rare earth ions in low-permeability deposits (Xu et al., 2024). However, industrial-scale feasibility remains uncertain.

4.3. Operational Parameters

The performance of in-situ leaching operations is highly sensitive to several operational parameters, including lixiviant concentration, pH, contact time, and the permeability of the ore body. These factors influence both the kinetics of ion exchange and the hydrodynamic behavior of the leaching system.

Lixiviant concentration is one of the most critical variables controlling REE recovery. Higher concentrations generally increase ion-exchange efficiency, although excessive ionic strength may also promote impurity dissolution or mineral alteration (Al Wafi et al., 2025; Chai et al., 2020).

The pH of the leaching solution also plays a significant role. Acidic conditions may enhance desorption by destabilizing surface complexes, while neutral or slightly alkaline conditions tend to favor selective ion exchange without excessive dissolution of gangue minerals (Feng et al., 2023; Gao et al., 2023).

Leaching time and reaction kinetics further influence extraction efficiency. Kinetic studies show that the desorption process typically follows diffusion-controlled or mixed kinetic regimes, depending on mineralogy and reagent concentration (Long et al., 2020; Tian et al., 2010a, 2010b).

Finally, the permeability of the soil matrix controls the distribution of the lixiviant within the ore body. Low permeability may limit solution penetration and reduce recovery, while excessive permeability can lead to poor contact between the lixiviant and the ore (Han et al., 2023; Yang et al., 2024).

Table 2 summarizes the main operational parameters that control ISL performance. Their interactions often determine the practical recovery efficiency of rare earths in industrial operations.

Table 2. Key operational parameters influencing in situ leaching efficiency in ion-adsorption rare-earth deposits. Adapted from Long et al. (2020), Gao et al. (2023), and Zhou et al. (2024).

Parameter	Influence on leaching
Lixiviant concentration	Controls ion-exchange capacity
pH	Influences surface complexation and selectivity
Leaching time	Determines desorption kinetics
Soil permeability	Controls solution distribution
Additives / surfactants	May enhance leaching efficiency

The ion-exchange mechanism, fluid transport, and operational parameters form the basis for evaluating the performance of the lixiviant system. The next section examines conventional leaching agents in ion-adsorption rare-earth mining, focusing on ammonium-based reagents and their environmental and technological impacts.

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5. CONVENTIONAL LEACHING AGENTS FOR REE ISL

Ion-exchange leaching with ammonium salts has been the dominant extraction technology for ion-adsorption rare-earth deposits for several decades. These reagents can displace rare earth ions adsorbed on clay mineral surfaces via cation exchange, allowing REE^{3+} ions to enter the aqueous phase (Moldoveanu & Papangelakis, 2013; Nie et al., 2020).

Several ammonium salts have been investigated or applied in industrial practice. Among them, ammonium sulfate has historically been the most widely used lixiviant. Ammonium chloride and ammonium bicarbonate have also been explored in various operational contexts, often as alternatives to improve leaching efficiency or control solution chemistry (Xu et al., 2023; Sobri et al., 2024).

Although these reagents are effective in promoting ion exchange, their use has raised increasing environmental concerns. Ammonium-based systems may generate nitrogen contamination in soils and groundwater, and the management of residual ammonium in leachates remains a significant challenge in rare earth mining districts (Packey & Kingsnorth, 2016; Liu et al., 2022).

5.1. Ammonium Sulfate

Ammonium sulfate ($(NH_4)_2SO_4$) is the standard lixiviant for ion-adsorption rare earth deposits. It supplies ammonium ions that compete with REE^{3+} ions for clay exchange sites. As monovalent and mobile in water, ammonium ions can displace trivalent rare earth ions from clay (Moldoveanu & Papangelakis, 2013).

Industrial use of ammonium sulfate leaching is favored due to its low cost and high efficiency. Early studies showed it could recover significant rare earths from weathered crust deposits under mild conditions (Tian et al., 2010a, 2010b). Further research confirmed its effectiveness across different reagent concentrations and leaching times (He et al., 2016; He et al., 2017).

More recent studies have focused on understanding the hydrodynamic and geochemical behavior of ammonium sulfate during in-situ leaching. Reactive transport modeling indicates that the infiltration of ammonium solutions through the regolith profile strongly influences the distribution of REE desorption and the migration of residual reagents (Guo & Zhuang, 2023). Column leaching experiments further show that ammonium concentration gradients and solution residence time can significantly affect recovery efficiency (Shi et al., 2022).

Ammonium sulfate may alter soil properties, thereby impacting pore structure and permeability during leaching and affecting fluid flow and leaching consistency (Yang et al., 2024). It can also persist in regolith, raising long-term environmental concerns (Huang et al., 2021; Zhang et al., 2023).

Figure 4 summarizes the ion-exchange mechanism involved in ammonium sulfate leaching. The displacement of REE ions occurs through electrostatic exchange reactions within the clay mineral surface layer.

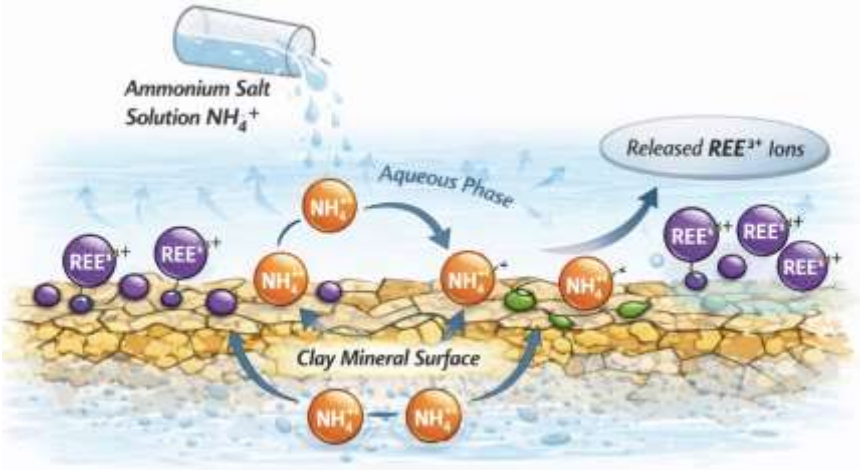

Figure 4. Conceptual mechanism of ammonium-salt ion exchange during in-situ leaching of ion-adsorption rare earth deposits. Adapted from Moldoveanu and Papangelakis (2013) and Nie et al. (2020).

The schematic shows how NH_4^+ ions displace adsorbed REE^{3+} ions from clay mineral surfaces during leaching with ammonium salts.

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5.2. Ammonium Chloride

Ammonium chloride (NH_4Cl) has also been investigated as an alternative ammonium-based lixiviant. The mechanism of REE extraction is similar to that observed with ammonium sulfate, as the ammonium ion remains the active species responsible for ion exchange (Moldoveanu & Papangelakis, 2016).

Some studies suggest that ammonium chloride solutions may provide improved control over solution chemistry and ionic strength during leaching operations. However, the overall extraction efficiency is often comparable to that obtained using ammonium sulfate under similar conditions (Nie et al., 2020).

Reviews of ion-exchange leaching technologies indicate that ammonium chloride has mainly been considered for laboratory-scale or pilot-scale investigations rather than large-scale industrial operations (Sobri et al., 2024). The selection between ammonium sulfate and ammonium chloride typically depends on operational constraints such as reagent availability, cost, and environmental management strategies (Xu et al., 2023).

5.3. Ammonium Bicarbonate and Alternative Ammonium Systems

Other ammonium-based lixiviants have also been proposed, including ammonium bicarbonate and various compound ammonium salts. These systems are sometimes investigated to improve selectivity or to control the dissolution of gangue minerals during leaching.

Experimental studies show that mixed ammonium salts or modified ammonium systems influence leaching kinetics and solution chemistry. Compound ammonium carboxylate systems enhance rare earth extraction by altering the ionic environment around clay surfaces (Chai et al., 2020). Additives and inhibitors may control aluminum dissolution and improve leaching selectivity (Feng et al., 2023; Gao et al., 2023).

Biologically derived organic acids have been explored as auxiliaries in ammonium systems, potentially improving desorption by forming soluble complexes with rare earth ions (Shen et al., 2023). However, most remain experimental and not yet widely used industrially.

5.4. Environmental Limitations of Ammonium-Based Lixiviants

Despite their effectiveness, ammonium salts present significant environmental challenges. One of the most widely reported concerns is the accumulation of ammonium nitrogen in soils and groundwater during in-situ leaching operations. Residual ammonium may migrate through the regolith profile and contaminate surrounding ecosystems (Liu et al., 2022).

In addition, nitrification can convert ammonium into nitrate, which may contribute to eutrophication in nearby aquatic systems. The environmental consequences of uncontrolled ammonium discharge have been documented in several rare earth mining regions, particularly in southern China (Packey & Kingsnorth, 2016; Yang et al., 2013).

Ammonium-based leaching can affect soil stability by altering mechanical properties and pore structure, as reported during long-term operations (Hamka et al., 2024; Wang et al., 2024). It also mobilizes contaminants, such as heavy metals, from the regolith (Qi et al., 2024).

Table 3 summarizes environmental concerns associated with ammonium-based lixiviants, prompting a search for alternatives that sustain rare-earth extraction while reducing environmental risks.

Table 3. Environmental and operational limitations of ammonium-based lixiviants in rare-earth in situ leaching. Adapted from Liu et al. (2022), Wang et al. (2024), and Qi et al. (2024).

Issue	Description
Ammonium accumulation	Residual NH_4^+ remaining in regolith
Groundwater contamination	Migration of ammonium and nitrogen species
Eutrophication risk	Nitrate formation in aquatic systems
Soil structure alteration	Changes in permeability and geotechnical stability
Secondary element mobilization	Release of associated metals during leaching

The next section, therefore, explores magnesium sulfate as a potential alternative lixiviant, emphasizing its chemical properties, ion-exchange mechanisms, and potential benefits for sustainable rare-earth extraction.

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6. MAGNESIUM SULFATE AS AN ALTERNATIVE LEACHING AGENT

Growing environmental concerns associated with ammonium-based lixiviants have spurred research into alternative reagents for rare-earth extraction from ion-adsorption clays. Among these alternatives, magnesium sulfate ($MgSO_4$) has attracted growing attention for its potential to reduce nitrogen pollution while maintaining effective ion-exchange performance.

Magnesium salts provide divalent cations that can displace adsorbed rare-earth ions from clay surfaces. Unlike ammonium-based reagents, magnesium sulfate does not introduce nitrogen species into the environment. This characteristic is often cited as an important advantage for environmental management and groundwater protection.

However, substituting ammonium ions with magnesium ions also modifies the chemical behavior of the leaching system. Ion valence, hydration energy, ionic radius, and adsorption strength may affect both the efficiency and selectivity of the desorption process. For this reason, the role of $MgSO_4$ in ion-exchange leaching must be evaluated not only in terms of recovery efficiency but also in terms of reaction mechanisms and thermodynamic constraints.

6.1. Chemical Characteristics of $MgSO_4$

Magnesium sulfate is a highly soluble salt that dissociates readily in aqueous solutions, producing Mg^{2+} and SO_4^{2-} ions. The high solubility of $MgSO_4$ facilitates the preparation of lixiviant solutions with controlled ionic strength, which is important for maintaining stable leaching conditions during in-situ operations (Xiao et al., 2015a, 2015b).

The behavior of Mg^{2+} in aqueous systems is influenced by its relatively strong hydration shell. Compared with monovalent cations such as NH_4^+, magnesium ions exhibit stronger electrostatic interactions with surrounding water molecules. This property may influence their mobility in porous media and their interaction with negatively charged clay surfaces (Chen et al., 2020; He et al., 2021).

Several experimental studies have shown that magnesium ions can effectively interact with clay mineral surfaces, promoting ion exchange with adsorbed rare earth elements. The adsorption of Mg^{2+} onto clay minerals may alter the electrostatic balance of the electrical double layer surrounding clay particles, thereby facilitating REE desorption (Bo et al., 2021; Gao et al., 2023).

Recent research also suggests that $MgSO_4$ solutions can influence the pore structure and physicochemical properties of ion-adsorption ores during leaching. Changes in clay swelling behavior and mineral surface charge have been reported, potentially affecting both fluid flow and ion-exchange efficiency (Hu et al., 2025; Cai et al., 2024).

Studies on rare earth sulfates show that sulfate ions can form complexes that affect rare earth mobility in leachates (Sun et al., 2026). Both cationic and anionic species are crucial for evaluating the behavior of $MgSO_4$ in leaching systems (Pan et al., 2025).

Figure 5 shows how magnesium ions interact with clay mineral surfaces, competing with adsorbed REE species for exchange sites.

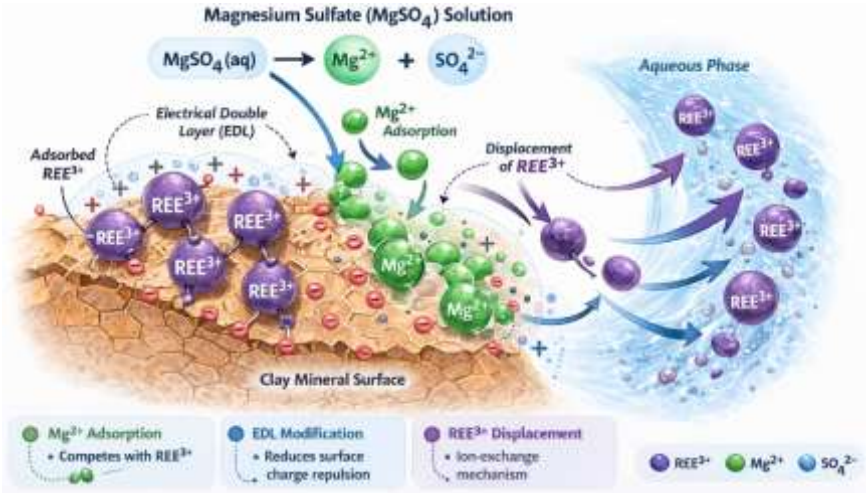

Figure 5. Conceptual representation of magnesium sulfate interaction with clay minerals during rare earth leaching. Adapted from Xiao et al. (2015a), He et al. (2021), and Pan et al. (2025).

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The schematic illustrates Mg^{2+} adsorption on clay surfaces, modification of the electrical double layer, and displacement of adsorbed REE^{3+} ions during ion-exchange leaching.

6.2. Ion-Exchange Mechanism with Rare Earth Elements

The ion-exchange mechanism associated with magnesium sulfate leaching follows the same general principle as ammonium-based systems. Magnesium ions introduced in the leaching solution compete with adsorbed REE^{3+} ions for exchange sites on clay mineral surfaces.

A simplified representation of this reaction can be written as:

$$REE\text{–}Clay + Mg^{2+} \rightarrow REE^{3+} + Mg\text{–}Clay$$

In practice, the process is more complex due to multiple exchange sites and surface interactions. Experiments show that magnesium ions can displace adsorbed rare-earth ions under suitable conditions (Xiao et al., 2015a, 2015b).

Column leaching experiments show Mg^{2+} influences aluminum dissolution and rare earth redistribution (Guo et al., 2023; Han et al., 2025). Sometimes, rare earth ions may readorb during leaching, especially with concentration gradients in the ore (He et al., 2023).

Sequential extraction experiments further demonstrate that magnesium ions interact with clay mineral surfaces through a combination of electrostatic adsorption and surface complexation mechanisms (Pan et al., 2025). These processes are influenced by the mineralogical composition of the ore and by the ionic strength of the leaching solution.

Comparative studies suggest that Mg^{2+} ions may provide different selectivity characteristics compared with NH_4^+ ions. While ammonium ions tend to promote rapid ion exchange, magnesium ions may lead to slower but potentially more controlled desorption processes depending on the mineralogical context (Hu et al., 2025; Xiao et al., 2018).

6.3. Thermodynamic Considerations

The performance of magnesium sulfate as a lixiviant is strongly influenced by thermodynamic factors governing ion exchange and adsorption equilibria. These include ionic strength, adsorption energy, and the relative affinity of competing cations for clay mineral surfaces.

Ion-exchange reactions in clay minerals are commonly described using surface complexation and electrical double-layer models. These models indicate that adsorption energy varies according to the charge and hydration properties of the exchanging ions (Moldoveanu & Papangelakis, 2012).

Magnesium ions possess a higher charge density than ammonium ions, which may lead to stronger electrostatic interactions with clay mineral surfaces. This property can influence both the equilibrium position of ion-exchange reactions and the kinetics of rare earth desorption (Moldoveanu & Papangelakis, 2021).

Experimental studies have also shown that the thermodynamic stability of rare earth sulfate species may affect their solubility and mobility during leaching processes (Sun et al., 2026). In addition, ligand interactions and surface coordination effects may modify rare earth adsorption behavior in complex mineral systems (Zou & Zhao, 2025).

Table 4 summarizes the main physicochemical variables that influence $MgSO_4$-based leaching systems. These factors determine the balance between adsorption, ion exchange, and dissolution processes that ultimately control rare earth recovery

Table 4. Key physicochemical factors influencing $MgSO_4$ leaching performance in ion-adsorption rare earth deposits. Adapted from Moldoveanu and Papangelakis (2012), He et al. (2021), and Pan et al. (2025).

Factor	Influence on leaching
Ionic strength	Controls ion-exchange equilibrium
Hydration energy of Mg^{2+}	Affects adsorption and mobility
Clay mineral surface charge	Determines adsorption capacity
Sulfate complexation	Influences REE solubility
Surface coordination reactions	Controls adsorption–desorption equilibria

The next section assesses $MgSO_4$ leaching experiments, column tests, and comparisons with traditional ammonium lixiviants.s.

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7. LEACHING PERFORMANCE OF $MgSO_4$ SYSTEMS

Experimental investigations on magnesium sulfate leaching have expanded significantly in recent years. These studies aim to evaluate whether $MgSO_4$ can achieve recovery efficiencies comparable to those obtained with ammonium-based lixiviants while reducing environmental impacts.

Research on $MgSO_4$ systems typically focuses on three experimental scales. Laboratory experiments are used to evaluate fundamental leaching parameters and reaction mechanisms. Column experiments simulate in-situ leaching conditions under controlled hydraulic gradients. Pilot-scale investigations aim to reproduce field-scale hydrodynamic conditions and assess process feasibility.

Together, these studies provide insight into the chemical and operational factors controlling the performance of magnesium sulfate leaching systems.

7.1. Laboratory Experiments

Laboratory-scale experiments are the first stage in evaluating $MgSO_4$ as a lixiviant for ion-adsorption rare-earth ores. These studies typically investigate the effects of lixiviant concentration, solid-to-liquid ratio, temperature, and pH on the efficiency of rare earth desorption.

Experimental results indicate that magnesium sulfate solutions can effectively promote the desorption of rare earths from clay minerals under suitable conditions. Batch leaching tests have demonstrated that increasing the $MgSO_4$ concentration generally enhances ion-exchange efficiency by increasing the availability of Mg^{2+} ions for competition at adsorption sites (Xiao et al., 2015a, 2015b).

The solid-to-liquid ratio is another critical variable influencing rare earth extraction. Lower ratios often improve contact between the lixiviant and the clay surface, thereby enhancing the desorption process (Bo et al., 2021; Gao et al., 2023).

Temperature effects appear to be less pronounced compared with strongly acidic hydrometallurgical systems. However, moderate increases in temperature may still accelerate ion-exchange kinetics and improve extraction efficiency (He et al., 2021; Han et al., 2023).

The pH of the leaching solution also influences rare earth recovery. Experimental studies suggest that near-neutral conditions favor selective ion exchange while minimizing the dissolution of gangue minerals such as aluminum-bearing phases (Hu et al., 2025; He et al., 2023).

More recent work has explored the influence of sequential leaching processes and chemical extraction methods to understand better the mechanisms controlling rare earth desorption in $MgSO_4$ systems (Pan et al., 2025; Pan et al., 2025b).

Table 5 summarizes the principal experimental variables investigated in laboratory studies. These parameters strongly influence the desorption behavior of rare earth elements from clay minerals.

Table 5. Key parameters investigated in laboratory-scale $MgSO_4$ leaching experiments. Adapted from Xiao et al. (2015), Gao et al. (2023), and Hu et al. (2025).

Parameter	Influence on leaching
$MgSO_4$ concentration	Controls ion-exchange capacity
Solid-to-liquid ratio	Influences contact efficiency
Temperature	Affects reaction kinetics
pH	Controls selectivity and mineral dissolution

7.2. Column and Pilot-Scale Studies

Column experiments are widely used to simulate the hydrodynamic conditions encountered in in-situ leaching operations. These studies allow researchers to evaluate fluid flow through porous media, solution residence time, and rare earth recovery under conditions closer to field operations.

Column leaching tests with magnesium sulfate solutions have shown that fluid infiltration and pore-structure evolution can strongly influence extraction performance. Changes in clay particle migration and pore connectivity may affect the distribution of the leaching solution within the ore column (Zhou et al., 2021; Zhang et al., 2024).

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Reactive transport experiments also demonstrate that rare-earth desorption can occur progressively along the lixiviant's flow path. This behavior may lead to concentration gradients within the leaching column and partial reabsorption of rare earth ions in downstream regions (Guo et al., 2023; Han et al., 2025).

Studies examining the evolution of permeability during leaching show that clay swelling and particle redistribution may modify hydraulic conductivity over long-term operations (Rao et al., 2025). These changes can influence solution flow patterns and ultimately affect the efficiency of rare earth recovery.

Emerging research has also explored electrokinetic approaches to enhance fluid transport in low-permeability deposits. Electrokinetic leaching may improve the migration of magnesium ions through the clay matrix, although its industrial applicability remains uncertain (Xu et al., 2024).

7.3. Recovery Efficiencies

One of the most important questions regarding magnesium sulfate leaching is whether it can achieve rare-earth recovery efficiencies comparable to those of conventional ammonium-based systems.

Experimental comparisons indicate that $MgSO_4$ can achieve moderate to high recovery rates depending on ore characteristics and operating conditions. In many laboratory studies, rare earth recoveries obtained with $MgSO_4$ are slightly lower than those achieved with ammonium sulfate but remain within a range that may still be acceptable for industrial application (Xiao et al., 2015a, 2015b).

More recent studies report improved recovery efficiencies when operational parameters are optimized. For example, controlled $MgSO_4$ concentrations and optimized solid–liquid ratios can enhance rare earth extraction and reduce impurity dissolution (Han et al., 2023; Hu et al., 2025).

Comparative studies involving different rare earth ores suggest that mineralogical composition and clay surface chemistry strongly influence the relative performance of $MgSO_4$ systems (Anawati & Azimi, 2023; Al Wafi et al., 2025).

Process optimization strategies, including sequential leaching and improved solution management, have further increased recovery efficiency in some experimental systems (Pan et al., 2025; Wang et al., 2025).

Figure 6 highlights the general trend reported in the literature. Ammonium sulfate typically provides high recovery efficiency, whereas magnesium sulfate often achieves moderate to high recoveries depending on operating conditions.

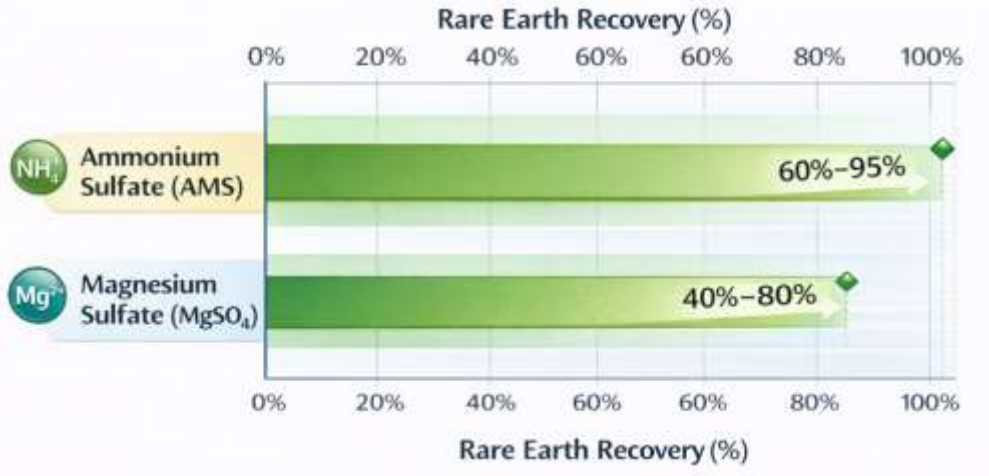

Figure 6. Comparative rare earth recovery efficiencies obtained using ammonium sulfate and magnesium sulfate lixiviants. Adapted from Xiao et al. (2015), Han et al. (2023), and Hu et al. (2025).

The figure illustrates typical recovery ranges reported in experimental studies on ion-adsorption rare-earth ores.

These findings indicate magnesium sulfate could be a viable, environmentally friendly alternative for rare earth extraction.

The next section discusses environmental and sustainability aspects of rare earth in-situ leaching, emphasizing magnesium sulfate's potential benefits over ammonium-based reagents.

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8. ENVIRONMENTAL AND SUSTAINABILITY ASPECTS

Environmental performance has become a central issue in the evaluation of rare earth extraction technologies. Although ion-adsorption clay deposits can be processed through relatively mild hydrometallurgical routes, the environmental consequences of in-situ leaching operations remain significant. The use of ammonium-based lixiviants has raised concerns regarding nitrogen contamination, groundwater quality, and long-term soil degradation.

These environmental challenges have spurred the search for alternative lixiviants that reduce ecological risks while maintaining acceptable recovery performance. In this context, magnesium sulfate has been proposed as a potentially more sustainable reagent for rare earth extraction from ion-adsorption deposits.

8.1. Ammonium Pollution Problems

The most widely reported environmental issue associated with conventional in situ leaching of rare earths is the accumulation of ammonium species in soils and groundwater. During ammonium-based leaching, significant quantities of residual NH_4^+ may remain within the regolith profile after extraction operations (Huang et al., 2021).

Once introduced into the subsurface environment, ammonium ions may undergo nitrification, producing nitrate, which is more mobile in groundwater systems. This transformation can lead to the migration of nitrogen compounds into surrounding ecosystems (Liu et al., 2022; Qi et al., 2024).

Elevated nitrate concentrations in aquatic systems may contribute to eutrophication processes, which can degrade water quality and disrupt local ecosystems. Such impacts have been documented in rare earth mining regions where ammonium-based leaching has been practiced extensively (Packey & Kingsnorth, 2016; Yang et al., 2013).

In addition to water contamination, ammonium-based leaching may also alter the geotechnical properties of the soil matrix. Changes in pore structure and mechanical stability have been reported during leaching operations, potentially affecting slope stability and subsurface flow pathways (Hamka et al., 2024; Wang et al., 2024).

Furthermore, ammonium salts may influence element mobilization in the regolith. Some studies indicate secondary leaching of metals or contaminants under certain conditions (Geng et al., 2024; Mao et al., 2025). Geotechnical analyses suggest that long-term operations could affect the mechanical stability of leached slopes (Yuan et al., 2025).

Figure 7 summarizes the main environmental pathways through which ammonium-based leaching may affect surrounding ecosystems. These processes highlight the importance of improving reagent selection and environmental management practices in rare earth mining.

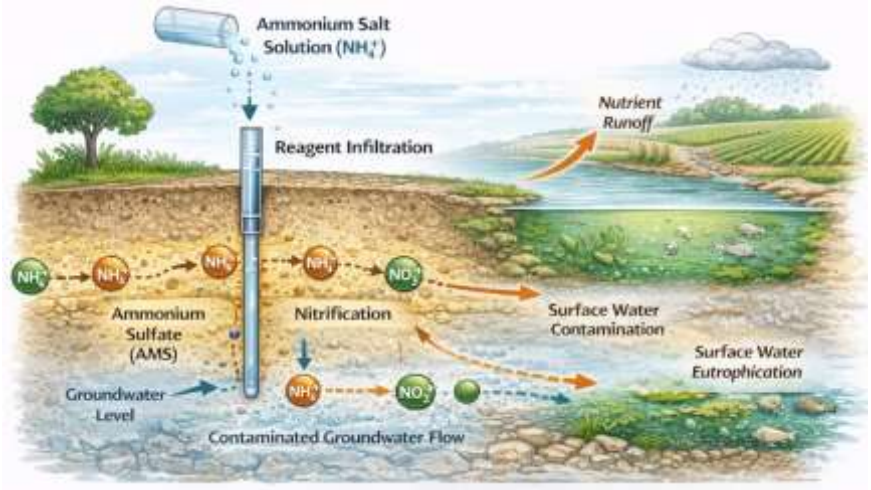

Figure 7. Environmental pathways associated with ammonium-based in-situ leaching of rare earth deposits. Adapted from Packey and Kingsnorth (2016), Liu et al. (2022), and Qi et al. (2024).

The diagram illustrates ammonium infiltration into the regolith, nitrification processes, groundwater contamination, and potential eutrophication of surface waters.

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8.2. Environmental Advantages of $MgSO_4$

Magnesium sulfate is a promising alternative lixiviant because it avoids introducing nitrogen species into the environment. Unlike ammonium salts, $MgSO_4$ does not produce nitrate or ammonium residues that can cause eutrophication (Xiao et al., 2015).

Life cycle assessments of rare earth extraction processes suggest that replacing ammonium-based lixiviants with magnesium salts may reduce the environmental footprint of ion-adsorption clay mining operations (Bailey et al., 2020; Vahidi et al., 2016).

In addition, magnesium ions tend to exhibit lower environmental mobility compared with ammonium ions. This property may reduce the risk of long-distance migration of residual reagents within groundwater systems (Huang et al., 2015).

Several studies also report that magnesium sulfate leaching can reduce the dissolution of certain impurity elements, thereby improving downstream purification processes and potentially decreasing waste generation (Li et al., 2022; Ni et al., 2022).

More recent environmental assessments indicate that $MgSO_4$-based systems may provide a better balance between extraction efficiency and environmental protection, particularly when integrated with improved leachate management strategies (Wang et al., 2025).

Table 6 highlights the main environmental differences between conventional ammonium salts and magnesium sulfate lixiviants. Although $MgSO_4$ does not eliminate all environmental concerns, its use may reduce several of the most critical risks associated with ammonium-based systems.

Table 6. Comparison of environmental characteristics of ammonium-based and magnesium sulfate lixiviants. Adapted from Bailey et al. (2020), Xiao et al. (2015), and Wang et al. (2025).

Aspect	Ammonium salts	Magnesium sulfate
Nitrogen pollution	High risk	None
Eutrophication potential	Significant	Minimal
Reagent mobility	High	Moderate
Environmental footprint	Higher	Lower

8.3. Groundwater Protection and Environmental Monitoring

Effective groundwater protection is essential for sustainable in-situ leaching operations. Because the leaching process occurs directly within the ore body, careful monitoring of subsurface fluid flow and chemical transport is required to prevent uncontrolled migration of leaching solutions.

Hydrogeological monitoring systems are commonly used to track groundwater quality and detect potential leakage of leaching solutions. These systems typically include monitoring wells, geochemical sampling programs, and hydraulic modeling tools (Guo & Zhuang, 2023).

Reactive transport models have been developed to simulate the movement of leaching solutions and dissolved elements through porous media. Such models help identify potential contamination pathways and support the design of effective containment strategies (Liu et al., 2022).

Geotechnical monitoring may also be necessary to evaluate the structural stability of the leached ore body. Changes in pore structure and hydraulic conductivity during leaching operations can influence slope stability and groundwater flow patterns (Wang et al., 2024; Yuan et al., 2025).

Engineering solutions such as controlled injection systems and optimized solution recovery methods can further reduce the risk of uncontrolled lixiviant migration (Zhang et al., 2016). In combination with continuous environmental monitoring, these approaches are essential for minimizing environmental impacts during rare-earth in situ leaching operations.

Environmental considerations focus on evaluating alternative lixiviants for efficiency, sustainability, and risk. Next, the comparison of ammonium-based and magnesium sulfate leaching systems highlights their advantages and limitations in rare earth extraction.

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9. COMPARATIVE ASSESSMENT OF LEACHING SYSTEMS

The comparison between ammonium-based lixiviants and magnesium sulfate systems has become a central topic in recent research on rare earth extraction from ion-adsorption clay deposits. The two approaches differ not only in extraction efficiency but also in environmental impact, operational behavior, and long-term sustainability.

Ammonium sulfate has been the primary lixiviant due to its high ion-exchange efficiency and low cost (Moldoveanu & Papangelakis, 2013). However, environmental concerns about nitrogen contamination have spurred research into alternatives like magnesium sulfate.

Recent experimental and environmental studies suggest that the evaluation of these leaching systems must consider multiple criteria simultaneously, including recovery efficiency, environmental footprint, reagent consumption, hydrodynamic behavior, and process controllability (Bailey et al., 2020; Vahidi et al., 2016).

9.1. Process Efficiency

Ammonium sulfate remains one of the most efficient lixiviants for ion-exchange leaching of rare earth elements. Numerous experimental studies have reported high recovery rates under controlled conditions using ammonium-based solutions (Moldoveanu & Papangelakis, 2013).

Magnesium sulfate systems typically produce slightly lower extraction efficiencies under comparable experimental conditions. However, optimized operational parameters can significantly improve $MgSO_4$ leaching performance. Several studies report moderate-to-high recovery levels when parameters such as reagent concentration, solution flow, and contact time are carefully controlled (Han et al., 2023; Pan et al., 2025).

Experimental comparisons indicate that ore mineralogy and clay surface chemistry strongly influence the relative performance of the two lixiviants. In some deposits, magnesium sulfate may achieve recovery efficiencies close to those obtained with ammonium sulfate (Xiao et al., 2015a, 2015b).

9.2. Environmental Impact

Environmental performance represents one of the most significant differences between the two leaching systems. Ammonium-based lixiviants may introduce substantial quantities of nitrogen into the subsurface environment during in-situ leaching operations.

Residual ammonium ions may accumulate in soils and groundwater, where they can undergo nitrification and contribute to eutrophication processes (Packey & Kingsnorth, 2016; Huang et al., 2021). The mobilization of nitrogen compounds in groundwater systems has been widely reported in rare earth mining regions (Qi et al., 2024).

In contrast, magnesium sulfate does not introduce nitrogen species into the environment. This property reduces the risk of eutrophication and improves the overall environmental profile of the extraction process (Bailey et al., 2020; Vahidi et al., 2016).

Environmental studies also suggest that magnesium sulfate systems may reduce the dissolution of certain impurity elements during leaching, thereby simplifying downstream solution treatment (Li et al., 2022; Ni et al., 2022). Life cycle assessments indicate that these factors may contribute to lower overall environmental impacts compared with ammonium-based systems (Wang et al., 2025).

9.3. Hydrodynamic and Geochemical Behavior

Hydrodynamic behavior also differs between ammonium and magnesium-based leaching systems. Ammonium ions exhibit high mobility in aqueous systems and can migrate rapidly through porous media. While this property promotes rapid ion exchange, it also increases the risk of reagent dispersion beyond the intended leaching zone (Huang et al., 2021).

Magnesium ions, in contrast, tend to exhibit stronger interactions with clay mineral surfaces. These interactions may reduce their mobility in the regolith and potentially allow better control of the leaching front (Pan et al., 2025).

Experimental observations suggest that Mg^{2+} ions can influence clay swelling and the evolution of pore structure during leaching. These effects may alter hydraulic conductivity and fluid distribution within the ore body (Geng et al., 2024).

Understanding these hydrodynamic differences is essential for evaluating the practical feasibility of large-scale $MgSO_4$-based leaching systems.

Table 7 summarizes the principal differences between the two leaching systems. The comparison highlights the trade-off between extraction efficiency and environmental performance.

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Table 7. Comparative characteristics of ammonium sulfate and magnesium sulfate lixiviants in rare earth in-situ leaching. Adapted from Bailey et al. (2020), Moldoveanu and Papangelakis (2013), and Wang et al. (2025).

Parameter	Ammonium sulfate	Magnesium sulfate
Extraction efficiency	High	Moderate to high
Environmental impact	High (nitrogen pollution risk)	Lower
Reagent cost	Low	Moderate
Reagent mobility	High	Moderate
Process controllability	Moderate	Potentially higher
Regeneration potential	Limited	Possible

Different lixiviant systems in ion-adsorption rare earth deposits exhibit unique geochemical behaviors and environmental effects. Ammonium sulfate, historically the main choice due to its high ion-exchange efficiency, raises increasing environmental concerns. This has led to greater interest in alternatives like magnesium sulfate. Figure 8 compares the ion-exchange performance, reagent mobility, and environmental impacts of ammonium- and magnesium-based leaching systems.

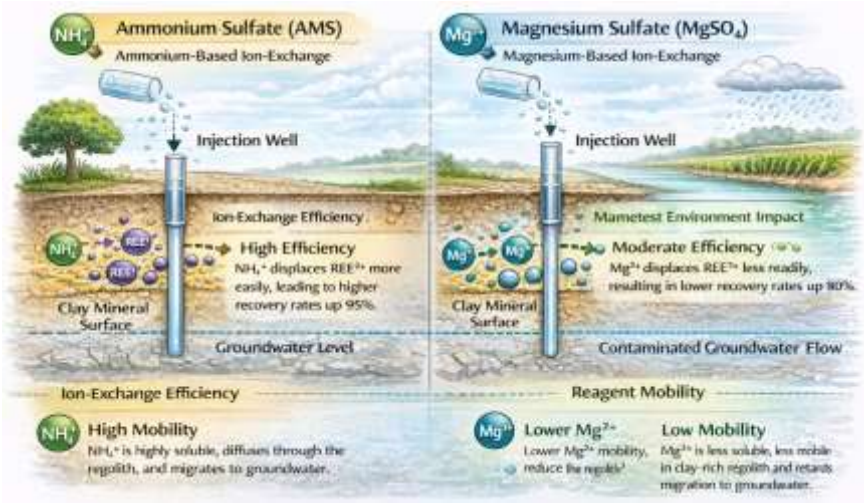

Figure 8. Conceptual comparison between ammonium sulfate and magnesium sulfate leaching systems in ion-adsorption rare earth deposits. Adapted from Bailey et al. (2020), Xiao et al. (2015), and Wang et al. (2025).

Figure 8 provides a conceptual overview of the relative advantages and limitations of each lixiviant system. While ammonium sulfate offers high extraction efficiency, magnesium sulfate may provide a more balanced solution when environmental considerations are included in process evaluation.

These findings suggest lixiviant selection must balance metallurgical performance and environmental sustainability. The next section discusses process optimization strategies, such as mixed lixiviants, ionic strength control, and operational improvements to improve rare earth recovery and reduce environmental impacts.

10. PROCESS OPTIMIZATION STRATEGIES

Although magnesium sulfate shows promise as an alternative lixiviant for rare earth extraction from ion-adsorption clay deposits, several operational limitations remain. These include moderate extraction efficiencies under certain conditions, sensitivity to mineralogical variability, and hydrodynamic constraints during in situ leaching operations.

Recent studies have therefore focused on optimization strategies designed to improve extraction performance while preserving the environmental advantages of magnesium-based systems. These strategies typically involve modifying the chemical composition of the lixiviant, adjusting solution chemistry, and using multi-stage leaching approaches.

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Four optimization approaches have been widely discussed in the literature: mixed lixiviant systems, controlled ionic strength, pH adjustment, and sequential or enhanced leaching strategies.

10.1. Mixed Lixiviant Systems

Mixed lixiviant systems combine magnesium sulfate with ammonium salts in order to balance extraction efficiency and environmental performance. The presence of ammonium ions can accelerate ion exchange, while magnesium ions can help reduce the total nitrogen load introduced into the regolith.

Experimental studies suggest that mixed systems can improve rare earth recovery compared with pure $MgSO_4$ solutions while maintaining lower ammonium consumption than conventional ammonium-based leaching (Chen et al., 2023).

Hybrid lixiviant systems can modify clay interactions and enhance the desorption of strongly bound rare earth ions, with experiments indicating they may more effectively displace REE^{3+} from clay exchange sites (Meng et al., 2022).

Recent work has also explored the use of controlled ratios of Mg^{2+} and NH_4^+ to optimize extraction efficiency and minimize reagent consumption (Shen et al., 2023; Wang et al., 2025). In some cases, hybrid systems have shown improved recovery kinetics and more stable hydrodynamic behavior during column experiments (Zou & Zhao, 2025).

10.2. Controlled Ionic Strength

The ionic strength of the leaching solution strongly influences ion-exchange reactions in clay minerals. Higher ionic strength can increase the electrostatic interactions between the lixiviant ions and the negatively charged clay surfaces.

Experimental research indicates that increasing ionic strength may enhance rare earth desorption from clay mineral surfaces. This effect is attributed to the compression of the electrical double layer surrounding clay particles (Xiao et al., 2015).

Several studies report that $MgSO_4$ solutions with optimized ionic strength can significantly improve extraction performance compared with dilute systems (Hu et al., 2025; Pan et al., 2025). However, excessively high ionic strength may increase reagent consumption and affect fluid transport in the porous medium.

More recent modeling approaches suggest that the relationship between ionic strength and rare earth recovery is non-linear and strongly influenced by mineralogical factors (Sun et al., 2026; Xiao et al., 2018).

10.3. pH Adjustment

The pH of the leaching solution plays a critical role in the stability of rare earth complexes and the behavior of clay mineral surfaces. Slightly acidic conditions are generally favorable for the release of rare earth ions from exchange sites.

Laboratory experiments show that moderate pH adjustments can improve rare earth desorption without causing significant dissolution of the clay matrix (Bo/Fan et al., 2021). However, overly acidic conditions may mobilize impurity elements or alter the mineralogical structure of the regolith.

Several studies have demonstrated that optimized pH conditions can increase extraction efficiency in $MgSO_4$ systems by improving ion-exchange kinetics (He et al., 2021; Pan et al., 2025).

Environmental assessments also indicate that careful pH control can reduce the mobilization of unwanted metals and minimize secondary contamination during in-situ leaching (Mao et al., 2025; Wang et al., 2025).

10.4. Sequential and Enhanced Leaching

Sequential leaching approaches involve multiple stages of lixiviant injection in order to maximize rare earth recovery. These methods typically use different lixiviant compositions or operating conditions during successive stages.

Several studies have proposed sequential leaching systems in which ammonium salts are applied in early stages followed by magnesium-based solutions to reduce residual ammonium concentrations (Chen et al., 2020; Chen et al., 2023).

Enhanced leaching strategies may also include additives, surfactants, or complexing agents to improve rare-earth desorption from clay surfaces (Feng et al., 2023; Gao et al., 2023).

Column and pilot-scale experiments suggest that sequential injection strategies may improve overall recovery while reducing reagent consumption (Meng et al., 2022; Shen et al., 2023).

More advanced approaches incorporate electrochemical enhancement or surfactant-assisted transport mechanisms to improve ion mobility within the porous ore body (Zhou et al., 2024; Zhou et al., 2026; Zou & Zhao, 2025).

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Figure 9 summarizes the main operational strategies proposed to enhance the performance of magnesium-based leaching systems. These approaches aim to improve recovery efficiency while maintaining the environmental benefits associated with $MgSO_4$ lixiviants.

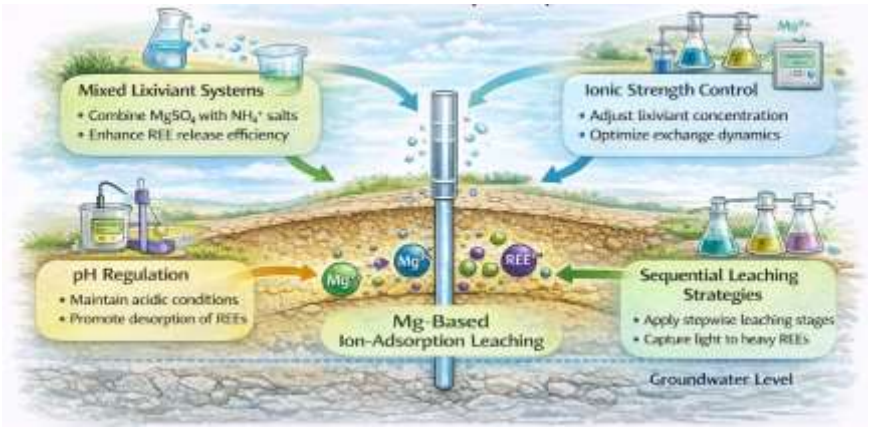

Figure 9. Process optimization strategies for magnesium-based in-situ leaching of rare earth ion-adsorption deposits. Adapted from Meng et al. (2022), Shen et al. (2023), and Wang et al. (2025).

Mixed lixiviant systems combine $MgSO_4$ with ammonium salts to boost ion exchange and reduce ammonium use, aiming for high extraction efficiency and lower environmental risks.

Control of ionic strength is another key parameter. Adjusting lixiviant concentration modifies the electrical double layer around clay particles and influences the competition between Mg^{2+} and REE^{3+} ions at adsorption sites. Proper ionic strength can therefore improve exchange kinetics and overall recovery.

pH regulation affects REE desorption by enhancing ion mobility under slightly acidic conditions, which reduces electrostatic attraction between clay and rare earth ions. Excessive acidity, however, can destabilize clay minerals and cause dissolution of gangue elements.

Sequential leaching strategies involve staged lixiviant injection or alternating reagent compositions. This approach can improve recovery across different REE groups and compensate for the lower exchange strength of Mg^{2+} compared with ammonium ions.

Together, these optimization pathways highlight how geochemical control, reagent engineering, and hydrological management can significantly improve the performance of magnesium-based in-situ leaching systems.

Table 8 highlights the principal strategies currently investigated to improve the performance of magnesium-based leaching systems. Although several promising approaches have been identified, additional pilot-scale validation is still required.

Table 8. Main process optimization strategies for magnesium sulfate leaching systems. Adapted from Chen et al. (2023), Pan et al. (2025), and Zhou et al. (2024).

Optimization strategy	Main objective	Key effects
Mixed lixiviants	Improve recovery	Enhanced ion exchange
Ionic strength control	Increase desorption	Electrical double layer compression
pH adjustment	Improve ion-exchange kinetics	Stabilization of REE complexes
Sequential leaching	Maximize recovery	Multi-stage extraction

These strategies show $MgSO_4$ systems can be improved with proper design and control. The next section explores industrial and economic factors affecting the implementation of these leaching methods in rare earth mining.

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11. INDUSTRIAL AND ECONOMIC CONSIDERATIONS

The industrial implementation of rare earth extraction from ion-adsorption clay deposits requires evaluating both technical feasibility and economic viability. In situ leaching (ISL) operations are generally considered less capital-intensive than conventional mining methods because they avoid extensive ore excavation, crushing, and grinding (Huang et al., 2015).

However, the economic performance of ISL operations depends strongly on reagent consumption, solution management, and downstream processing costs. These factors influence both capital expenditure (CAPEX) and operational expenditure (OPEX) throughout the life cycle of the mining project (Bailey et al., 2020).

Recent analyses suggest that the transition from ammonium-based lixiviants to alternative reagents, such as magnesium sulfate, should be evaluated within a broader techno-economic framework that encompasses environmental management and long-term sustainability (Asubonteng et al., 2026).

11.1. Reagent Cost and Consumption

Reagent cost is a major factor in rare-earth in situ leaching. Ammonium sulfate is preferred for its low price and high ion-exchange efficiency (Moldoveanu & Papangelakis, 2025).

Magnesium sulfate costs more per unit than ammonium salts but may lower environmental remediation and wastewater treatment costs due to its environmental benefits (Bailey et al., 2020).

The total reagent consumption also depends on deposit characteristics, permeability, clay mineralogy, and solution recovery efficiency. In poorly permeable deposits, lixiviant losses may increase reagent demand significantly (Huang et al., 2015).

Operational optimization strategies, such as controlled injection systems and improved solution recovery, can substantially reduce reagent consumption during ISL operations (Wang et al., 2025).

11.2. Logistics and Infrastructure

Logistics play an important role in the industrial deployment of ISL operations. Large volumes of lixiviant solutions must be transported, stored, and injected into the ore body.

Infrastructure requirements typically include reagent storage tanks, injection wells, recovery wells, solution pipelines, and surface processing facilities. These elements represent an important component of initial capital investment (Asubonteng et al., 2026).

The selection of lixiviants may influence logistics requirements. For example, magnesium sulfate may require different storage and solution-preparation systems than ammonium-based reagents.

Furthermore, ISL operations often require continuous monitoring systems to ensure environmental safety and operational efficiency (Bailey et al., 2020).

11.3. Downstream Processing and Solution Purification

After leaching, rare earth ions must be recovered from the pregnant leach solution through hydrometallurgical separation processes. These typically include solvent extraction, precipitation, and purification stages.

Impurity elements dissolved during leaching may complicate downstream processing and increase operational costs. Studies indicate that magnesium-based systems may reduce the dissolution of certain contaminants, potentially simplifying purification stages (Li et al., 2022).

Advanced purification strategies have been proposed to improve rare earth enrichment in leach solutions. These approaches include selective precipitation, ion-exchange resins, and solvent extraction circuits optimized for rare earth separation (Li et al., 2025; Ni et al., 2022).

Recent studies emphasize integrated treatment systems that maximize rare earth recovery and reduce chemical use (Su et al., 2023; Xie et al., 2025).025).

11.4. Wastewater Treatment and Recycling

Wastewater management represents another critical aspect of industrial ISL operations. Residual leaching solutions must be treated before discharge or recycling.

Ammonium-based systems can produce nitrogen-rich effluents needing extensive treatment, such as biological nitrification–denitrification or chemical removal, to prevent environmental contamination (Geng et al., 2024).

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In contrast, magnesium-based lixiviants may simplify wastewater treatment due to the absence of nitrogen species. Recycling of magnesium sulfate solutions has also been proposed as a strategy to reduce reagent consumption and operating costs (Wang et al., 2025).

Figure 10 summarizes the main industrial stages involved in rare earth ISL operations. The flowsheet highlights the integration between leaching operations, solution purification, and environmental management systems.

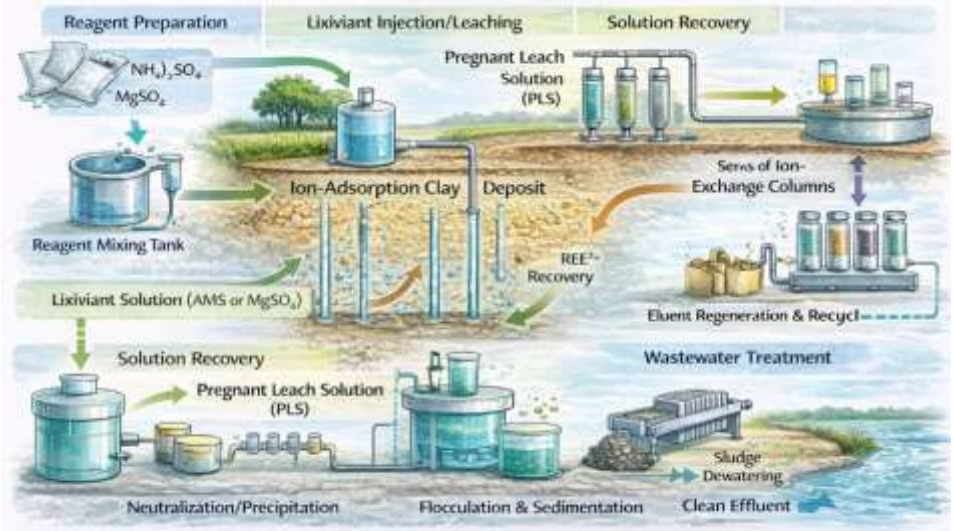

Figure 10. Industrial flowsheet for rare-earth extraction from ion-adsorption clay deposits via in situ leaching. Adapted from Huang et al. (2015), Bailey et al. (2020), and Asubonteng et al. (2026).

The diagram shows stages of reagent prep, lixiviant injection, solution recovery, pregnant leach solution purification, and wastewater treatment.

Table 9 summarizes key economic factors affecting the viability of in-situ leaching. While magnesium sulfate may increase reagent costs, its environmental advantages and potential for solution recycling could offset these expenses.

Table 9. Key economic considerations for in-situ leaching of ion-adsorption rare earth deposits. Adapted from Bailey et al. (2020), Wang et al. (2025), and Asubonteng et al. (2026).

Economic factor	Main cost drivers
Reagent consumption	Lixiviant dosage, recovery efficiency
Infrastructure	Injection wells, pipelines, storage tanks
Solution purification	Solvent extraction, precipitation
Wastewater treatment	Nitrogen removal, recycling systems
Environmental compliance	Monitoring and remediation systems

These considerations show that choosing lixiviants requires balancing metallurgical performance, environmental impact, and costs. The next section discusses future research, including emerging technologies and gaps in rare-earth in-situ leaching systems.

12. FUTURE RESEARCH DIRECTIONS

Despite significant progress in understanding the extraction of rare earth elements from ion-adsorption clay deposits, several scientific and technological challenges remain unresolved. Current research has improved the understanding of ion-exchange mechanisms, lixiviant chemistry, and environmental implications. However, the transition toward more sustainable leaching systems requires additional advances in geochemical modeling, mineral–fluid interaction studies, hydrological optimization, and pilot-scale validation.

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Recent reviews emphasize that the complexity of clay-hosted rare earth systems requires integrated approaches combining mineralogy, hydrology, geochemistry, and process engineering (Miiro, 2023; Sobri et al., 2024). Addressing these research gaps is essential for improving the reliability and sustainability of in-situ leaching technologies.

12.1. Geochemical Modeling of Leaching Systems

Geochemical modeling has become an increasingly important tool for understanding rare-earth mobilization during in situ leaching. Models that incorporate ion exchange, surface complexation, and solution chemistry can help predict the behavior of rare earth ions in clay-rich environments.

However, current models often rely on simplified assumptions about mineral surfaces and ion-exchange reactions. Many models treat clay minerals as homogeneous exchange media, whereas natural deposits exhibit complex mineralogical heterogeneity (Wu et al., 2023).

Future research should focus on integrating surface complexation models with reactive transport simulations to better describe rare earth behavior in natural porous media (Guo & Zhuang, 2023; Xu et al., 2024). Such models may also improve predictions of reagent migration and rare earth recovery efficiency.

12.2. Mineral–Fluid Interaction Mechanisms

The interaction between lixiviant solutions and clay minerals remains one of the least understood aspects of rare earth extraction from ion-adsorption deposits. Rare earth ions may be bound to clay surfaces through a combination of electrostatic adsorption, surface complexation, and structural incorporation.

Experimental studies suggest that different clay minerals exhibit distinct affinities for rare earth ions. Kaolinite, illite, and smectite may display different adsorption capacities and exchange kinetics (Moldoveanu & Papangelakis, 2016).

Further research is required to clarify the roles of clay mineral structure, surface charge distribution, and pore-scale processes in controlling rare-earth mobility (Xu et al., 2023; Wu et al., 2023). Advanced analytical techniques, including synchrotron-based spectroscopy and micro-scale imaging, may provide new insights into these mechanisms.

12.3. Hydrological Optimization of In-Situ Leaching

Hydrological behavior strongly influences the effectiveness of in-situ leaching operations. Fluid flow patterns determine the distribution of lixiviants, the progression of the leaching front, and the efficiency of rare earth recovery.

Reactive transport modeling combined with field-scale hydrological monitoring may help optimize injection strategies and minimize lixiviant losses (Guo & Zhuang, 2023).

Future research should also investigate the influence of pore structure evolution during leaching. Changes in hydraulic conductivity and soil permeability may significantly affect the long-term performance of ISL operations (Yuan et al., 2025).

Electrokinetic transport and controlled injection technologies have also been proposed as potential methods for improving lixiviant distribution in low-permeability deposits (Xu et al., 2024).

12.4. Pilot-Scale Demonstration Studies

Although numerous laboratory studies have investigated magnesium-based lixiviants and alternative extraction strategies, relatively few pilot-scale demonstrations have been reported.

Scaling laboratory results to field-scale operations remains challenging due to the heterogeneity of natural deposits and the complexity of subsurface hydrology (Nie et al., 2020).

Pilot-scale studies are therefore essential for evaluating reagent consumption, solution recovery efficiency, and environmental performance under realistic conditions (Asubonteng et al., 2026; Wang et al., 2025).

More comprehensive pilot experiments may also help validate geochemical models and improve the design of industrial ISL operations.

12.5. Lixiviant Regeneration and Recycling

Another important research direction involves the regeneration and recycling of lixiviants used in rare earth leaching. Reagent recovery may significantly reduce operating costs and environmental impacts.

Several studies have proposed chemical and electrochemical methods to regenerate leaching solutions and recover rare earth ions from pregnant leach solutions (Zhou et al., 2026).

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Closed-loop lixiviant recycling systems could improve process sustainability by reducing reagent consumption and minimizing waste generation (Wang et al., 2025).

Further research is needed to develop cost-effective regeneration technologies suitable for large-scale industrial deployment.

Figure 11 summarizes the main scientific and technological directions that may shape future developments in in situ leaching of rare earths. Addressing these research gaps will be essential for improving both extraction efficiency and environmental performance.

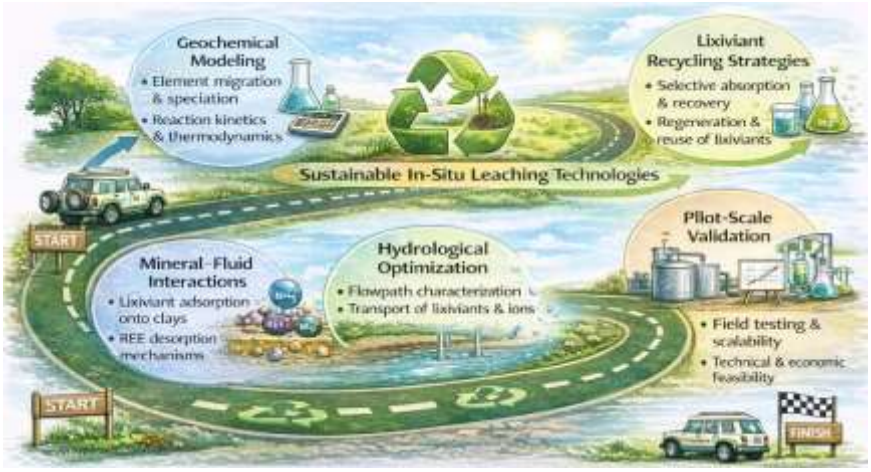

Figure 11. Research roadmap for the development of sustainable in-situ leaching technologies for rare earth ion-adsorption deposits. Adapted from Moldoveanu and Papangelakis (2016), Miiro (2023), and Wang et al. (2025).

The diagram highlights key research areas including geochemical modeling, mineral–fluid interactions, hydrological optimization, pilot-scale validation, and lixiviant recycling strategies.

Table 10 highlights the key research priorities for advancing sustainable rare-earth extraction technologies.

Table 10. Major research gaps and future research priorities in rare earth in-situ leaching technologies. Adapted from Miiro (2023), Sobri et al. (2024), and Wang et al. (2025).

Research area	Key challenges	Suggested research focus
Geochemical modeling	Limited surface complexation data	Integrated reactive transport models
Mineral–fluid interactions	Poor understanding of adsorption mechanisms	Advanced mineralogical characterization
Hydrological optimization	Complex flow patterns	Improved injection strategies
Pilot-scale studies	Limited field validation	Demonstration-scale projects
Lixiviant regeneration	Reagent losses	Closed-loop leaching systems

Future progress in rare-earth extraction from ion-adsorption clay deposits will depend on multidisciplinary approaches that integrate geochemistry, hydrology, and process engineering.

This review's conclusions summarize key findings and implications for future rare earth extraction methods.

13. CONCLUSIONS

This review examined rare-earth extraction from ion-adsorption clays, with a focus on magnesium sulfate as an alternative lixiviant for in situ leaching. It integrated geological, mineralogical, hydrometallurgical, environmental, and process engineering insights.

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Ion-adsorption clay deposits are key sources of heavy rare-earth elements, formed by the weathering of granitic rocks, which produce clay minerals such as kaolinite and illite that hold exchangeable rare-earth ions. Since rare earths primarily adsorb onto clay surfaces, ion-exchange leaching is the primary extraction method.

Conventional ISL operations primarily use ammonium-based lixiviants such as ammonium sulfate and chloride, which are effective and inexpensive but also pose environmental risks by contaminating soils and groundwater.

Magnesium sulfate is a promising alternative lixiviant for rare earth extraction from ion-adsorption deposits. Its low nitrogen content reduces the risks of eutrophication and groundwater contamination, as well as environmental challenges associated with ammonium leaching.

Experimental studies show $MgSO_4$ can recover significant rare earths when optimized but depend on deposit mineralogy, clay chemistry, hydrodynamic conditions, and operational factors like reagent concentration, pH, and ionic strength.

Process optimization strategies such as mixed lixiviant systems, ionic strength control, pH regulation, and sequential leaching improve magnesium-based systems by balancing efficiency and environmental sustainability.

From an industrial perspective, the viability of magnesium sulfate systems depends on reagent use, recycling, and downstream purification. Despite higher reagent costs than those of ammonium salts, their environmental benefits and recyclability may offset the extra expenses.

Future research should improve understanding of mineral–fluid interactions, develop advanced geochemical models for ion exchange, optimize hydrological control during in situ leaching, and conduct pilot-scale tests of magnesium-based systems.

Magnesium sulfate is a promising route for the sustainable extraction of rare earths from ion-adsorption clay deposits. Ongoing research and development are vital to assess its industrial potential.

Author Contributions

Antonio Clareti Pereira conceived the study, reviewed literature, analyzed data, and wrote the manuscript. All interpretations and conclusions were developed by the author based on the reviewed literature.

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No new datasets were generated or analyzed in this study. The article is based exclusively on previously published literature sources cited in the reference list.

Conflict of Interest

The author declares that there are no conflicts of interest regarding the publication of this paper.

Ethical Approval

This article does not contain any studies involving human participants or animals performed by the author.

Consent for Publication

The author consents to the publication of this manuscript.

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