

Review

Efficient Exploitation of Lepidolite Resources: A Review on Beneficiation Techniques, Extraction Methods, and Synergistic Optimization

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Abstract: Lithium is a critical mineral resource. With the development of high-end manufacturing industry, the demand for high-performance lithium-containing chemical raw materials continues to grow. At present, lithium needs to be acquired from a large amount of lepidolite ore, constrained by the existing lithium resource supply limitation quandary, and the industry urgently needs to develop more efficient beneficiation and extraction methods for lepidolite. Findings have suggested mixed collectors (e.g., DDA/SDBS) achieve a 4.99% Li₂O grade and 98% recovery at neutral pH, reducing reagent use by 20–30%. Microwave-assisted roasting boosts Li recovery to 95.9% and cuts energy use by 26.9%. Bioleaching with *Acidithiobacillus ferrooxidans* (A.F.) and rhamnolipid releases 6.8 mg/L Li with a lower environmental impact. Sulfuric acid baking recovers Li (97.1%), Rb (96.0%), and Cs (95.1%) efficiently. Despite challenges in fine-particle recovery and reagent costs, integrated strategies like nanobubble flotation, green collectors, and AI optimization offer sustainable, high-efficiency extraction. This work provides insights for advancing lepidolite processing, balancing economics and environmental stewardship.

Keywords: lepidolite; comprehensive utilization; froth flotation; direct leaching method; thermal activation methods



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1. Introduction

Lithium, a critical element widely utilized in rechargeable batteries, ceramics, glass, and other high-tech applications, plays a pivotal role in modern technology [1]. The global lithium resource mining share distribution is shown in Figure 1. For every ton of lithium iron phosphate (LFP), 0.08 to 0.1 tons of lithium carbonate equivalent (LCE) are required; for every smartphone, 2 to 3 g of LCE are consumed; and for every ton of lithium grease, 0.5 to 1 kg of lithium metal is needed. It is estimated that the global lithium demand will reach 1.67 million tons of LCE by 2025 [2–4]. As the cornerstone of energy storage systems, lithium-ion batteries are central to the global transition toward renewable energy and the electrification of transportation [5,6]. Consequently, the exploration and efficient utilization of lithium resources have garnered significant attention. Among the various lithium-bearing minerals, lepidolite has emerged as a promising candidate due to its relatively high lithium content and widespread geological occurrence [7].

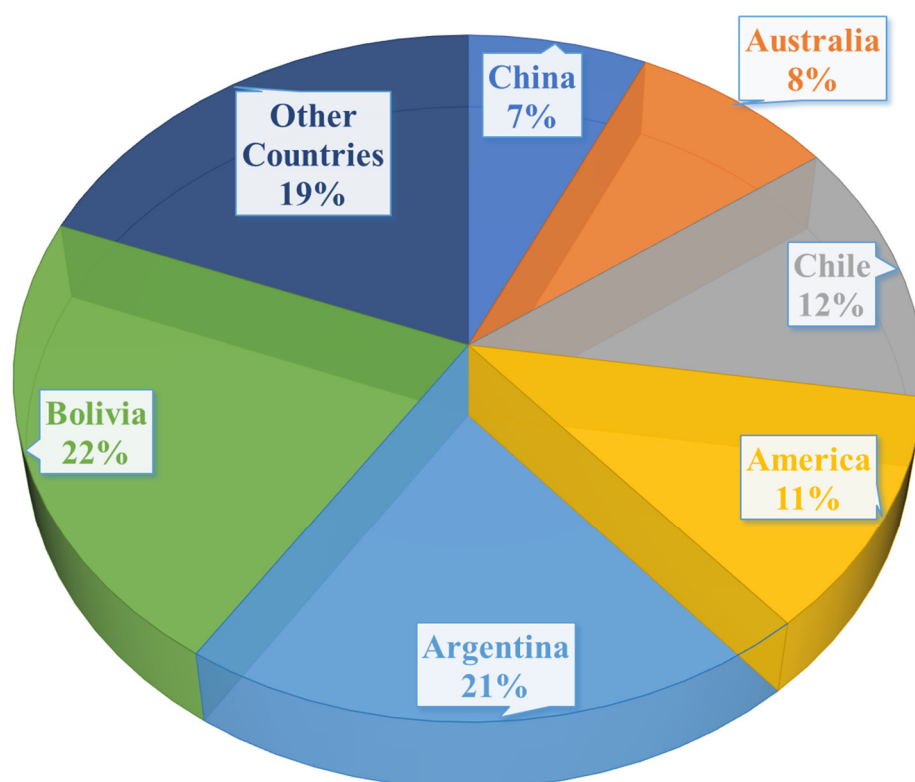


Figure 1. Global lithium resource mining share distribution [1,2].

Lepidolite, a lithium-rich mica, is typically found in pegmatitic rocks and is often associated with minerals such as spodumene, petalite, and feldspar. While its mineralogical properties make it an appealing resource, lepidolite's complex composition and association with gangue minerals pose significant challenges to efficient beneficiation and lithium extraction [8]. These challenges necessitate the development and optimization of mineral processing and extraction technologies tailored to the unique characteristics of lepidolite ores. To address these issues, significant research efforts have been devoted to exploring various beneficiation and extraction techniques [9–11]. Beneficiation methods such as froth flotation [12], magnetic separation, and optical sorting have been investigated to concentrate lithium-bearing phases [13–18]. Concurrently, advances in pyrometallurgical methods, including sulfation, carbonation, and microwave treatment, have enabled the breakdown of lepidolite's crystal structure, facilitating lithium recovery. Additionally, hydrometallurgical processes like acid leaching, alkali leaching, and bioleaching have demonstrated potential for selective lithium extraction under milder conditions [19]. These methods, combined with process flowsheet innovations, aim to achieve high recovery rates while minimizing environmental impact [20,21]. Nevertheless, the lepidolite separation and purification process is complex, high cost, has a low recovery rate, has difficulty synergistically extracting the valuable metals in lepidolite (such as potassium, rubidium, and cesium), and causes greater environmental pollution; the industry is in urgent need of greener and more efficient beneficiation and metallurgy of new technologies.

This paper aims to provide a comprehensive review of the mineralogical features of lepidolite, the advancements in beneficiation techniques, and the progress in pyrometallurgical and hydrometallurgical extraction methods. By analyzing the physical and chemical properties of lepidolite and the mechanisms underlying various processes, this study seeks to identify promising strategies for lithium recovery. Furthermore, a typical process flowsheet for producing marketable lithium salts is summarized, providing a practical framework for industrial applications.

2. Mineralogical Characteristics

2.1. Chemical Composition and Crystal Structure

Lepidolite is chemically represented by the general formula $K(Li,Al,Rb)_3(Al,Si)_4O_{10}(F,OH)_2$, with lithium often substituting for aluminum in its octahedral sites [22]. Lepidolite is the most abundant lithium-bearing mineral and is a secondary source of this metal with a lithium content typically ranging from 1.5% to 4.5% by weight, making it a viable source of this critical element [23]. In addition to lithium, lepidolite commonly contains rubidium (Rb), cesium (Cs), fluorine (F), and other trace elements such as manganese (Mn) and iron (Fe). Lepidolite is usually found in pegmatites and is a layered aluminosilicate mineral with a TOT (tetrahedral–octahedral–tetrahedral) structure. As shown in Figure 2 [24,25]. The structure consists of aluminum–oxygen octahedra and silica–oxygen tetrahedra, in which the interlayer charge imbalance is caused by the substitution of some Si^{4+} by Al^{3+} like homozygotes, and the interlayer deficit charge needs to be supplemented by alkali-metal cations, such as Li^+ , so that Al^{3+} and Li^+ fill the octahedral positions in the crystal structure [26,27].

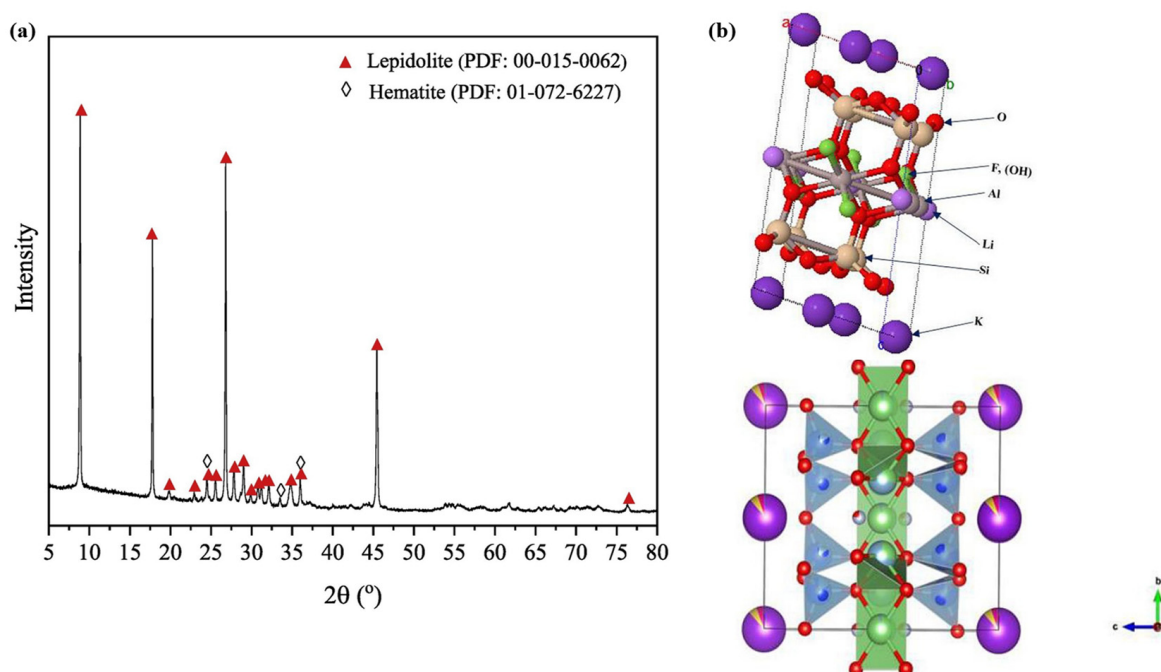


Figure 2. (a) X-ray diffraction patterns of lepidolite. (b) Crystal structure of lepidolite modified from Guggenheim [25].

It has a Mohs hardness of 2–3, is easily over-ground into fine particles, has a density of about 2.8–2.9 g/cm³, and has a perfect cleavage on the (001) plane. After single-crystal dissociation, lepidolite mainly presents a flaky or scaly structure and has a certain natural floatability [28].

2.2. Gangue Mineral Associations

Lepidolite exhibits various textures, ranging from fine-grained disseminations to coarse-grained aggregates, depending on its geological setting. Key textural features include the following: (1) Intergrowth with other minerals—lepidolite is often intergrown with quartz, feldspar, and spodumene, as shown in Figure 3, making physical separation processes more complex [29]. (2) Coarser lepidolite grains are easier to concentrate through flotation or optical sorting, while fine-grained lepidolite requires more advanced processing techniques.

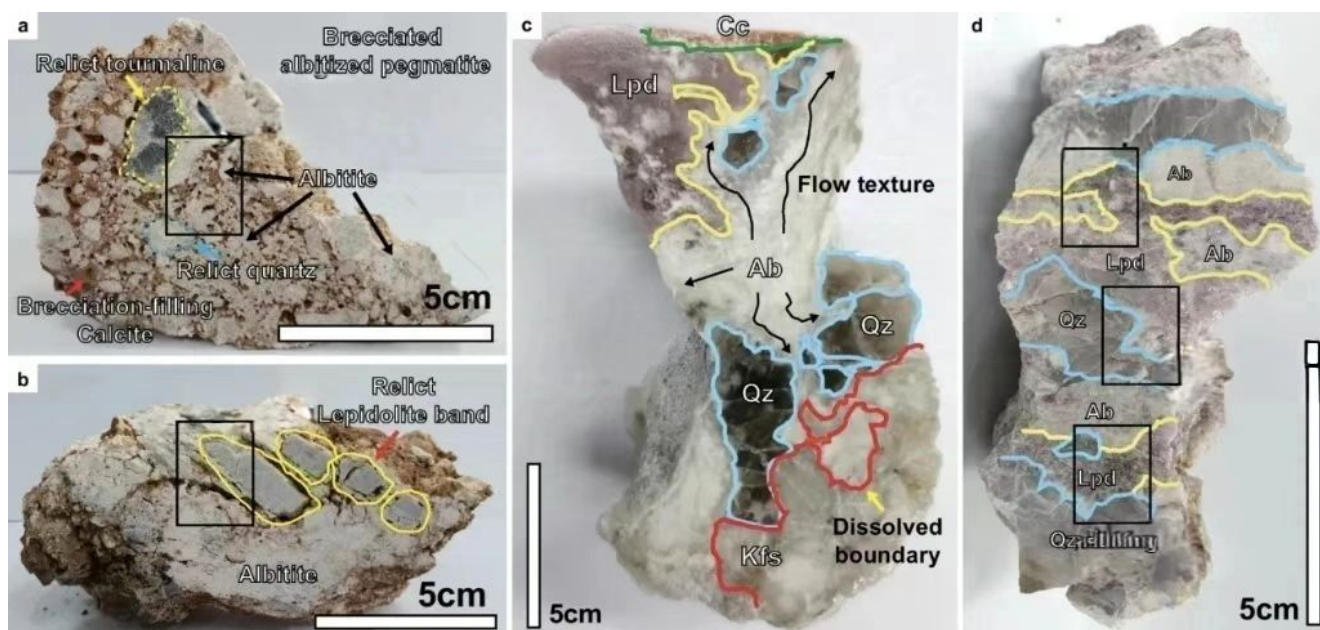


Figure 3. Representative lithologies of outcrop samples from the main orebody (MO) (a–c) and eastern orebody (EO) (d). (a) Brecciation of the albittized part of MO. Dark-gray fragment is tourmaline–quartz aggregate. (b) Brecciation of blocky lepidolite layer. (c) Locations with less albite and brecciation show clear textures of primitive pegmatite. Lepidolite, quartz, and K-feldspar layers are identified, infiltrated by late-stage albite. (d) Rhythmic layering of lepidolite–quartz–albite units in EO. Textural similarity with primitive pegmatite from MO shows their connection. Abbreviations; Lpd: lepidolite; Qz: quartz; Kfs: K-feldspar; Ab: albite [29].

Lepidolite typically occurs in lithium–cesium–tantalum (LCT) pegmatites, alongside a variety of gangue minerals, including the following: (1) Quartz and feldspar—common silicate gangue minerals that dominate the host rock. Their similar physical properties to lepidolite (e.g., density and hardness) complicate beneficiation processes. (2) Spodumene and petalite—lithium-bearing minerals that are often co-mined with lepidolite. While their presence enhances the overall lithium grade of the ore, it necessitates differentiation in downstream processing. (3) Iron-bearing minerals (e.g., hematite and magnetite)—these impurities can reduce concentrate quality and require removal through magnetic separation or other techniques. A few advanced analytical and mass spectrometry techniques to the characterization of micaceous lithium-bearing ores have applied, as seen in Figure 4 [30].

Lepidolite ores are characterized by their complex aluminosilicate layered structure, high fluorine content, and association with alkali metals (K, Rb, Cs) and gangue minerals (e.g., quartz, feldspar), which collectively dictate their treatment strategies. The layered crystal lattice, stabilized by interlayer potassium ions, necessitates aggressive acid leaching (e.g., H_2SO_4/HF) or high-temperature alkali roasting to disrupt the Si–O–Al framework and release lithium. Simultaneously, the presence of fluorine demands specialized corrosion-resistant equipment, while the co-occurrence of Rb and Cs requires tailored recovery processes (e.g., composite salt roasting) to maximize multi-element extraction. Furthermore, the fine-grained texture and variable surface charge of lepidolite (zeta potential ≈ -30 mV at pH 6–8) mandate selective flotation systems, such as mixed cationic/anionic collectors (e.g., DDA/SDBS), to enhance hydrophobicity and minimize gangue entrainment. These intrinsic properties underscore the need for integrated, mineral-specific approaches to achieve efficient and sustainable lithium recovery.

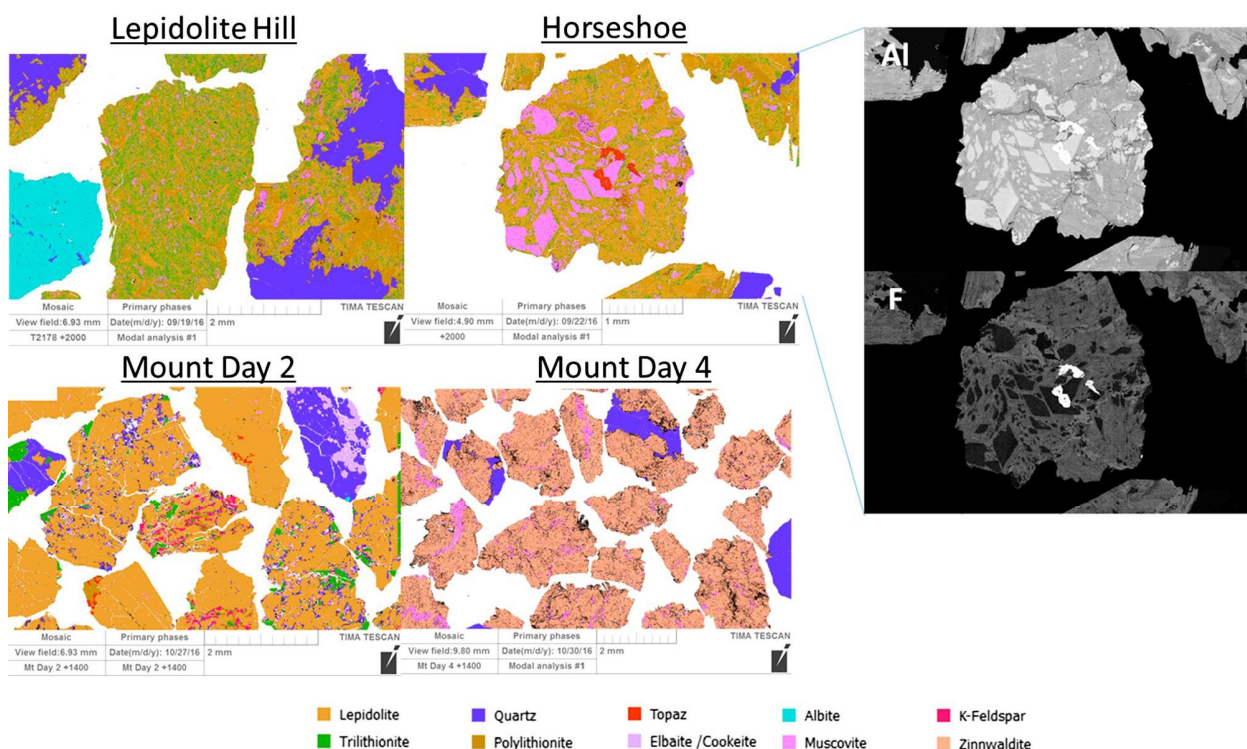


Figure 4. Applications of advanced analytical and mass spectrometry techniques in the characterization of micaceous lithium-bearing ores [30].

3. Beneficiation Techniques for Lepidolite

The production of high-performance lithium-containing chemical raw materials firstly requires the enrichment of lepidolite concentrate through beneficiation, and then the concentrate is used to extract lithium carbonate. The beneficiation methods for lepidolite ore include flotation, optical sorting, magnetic separation, and so on. Flotation is the most commonly used and effective method for separating lepidolite, which utilizes the different physical and chemical properties of the mineral surface to separate the minerals. Magnetic separation is commonly used to remove ferromagnetic veins and impurities from lepidolite ore. The optical sorting method utilizes the different physical and chemical properties of the mineral surface to sort the minerals.

3.1. Froth Flotation

Froth flotation is one of the most commonly employed techniques for concentrating lepidolite. The froth flotation method attaches lepidolite to the froth by means of the difference in the surface wettability of the minerals, and mineral enrichment is achieved by carrying it out with a scraper.

The grade and recovery of lepidolite concentrates strongly relies on the flotation agent and process. In general, the flotation agents are categorized into collectors, modifiers, and frothers.

Collectors are adsorbed on lepidolite surfaces (primarily at Al/Si–O sites) to induce hydrophobicity. Modifiers are adopted for adjusting pulp chemistry (pH, ionic strength) to optimize collector selectivity. Frothers are effective in stabilizing bubbles at the air–water interface to facilitate mineral transport.

3.1.1. Fundamental Mechanism of Lepidolite Flotation

The froth flotation process for lepidolite typically involves four key stages: ore conditioning, reagent addition, bubble–particle attachment, and froth separation. During

conditioning, the ground ore slurry is homogenized, and pH modifiers (e.g., sulfuric acid or NaOH) adjust the pulp to an optimal range (pH 3–8, depending on the collector system). Collectors (e.g., cationic amines like DDA or Gemini surfactants like HBDB) are then introduced to selectively adsorb onto the negatively charged lepidolite surface via electrostatic interactions or hydrogen bonding, enhancing its hydrophobicity. Activators (e.g., Ca^{2+} or Mg^{2+}) may be added to promote collector adsorption by neutralizing surface charges (zeta potential shifts). Subsequently, frothers (e.g., MIBC) stabilize air bubbles injected into the flotation cell, enabling hydrophobic lepidolite particles to attach to bubbles and rise into the froth layer. Finally, the enriched froth is mechanically scraped, while hydrophilic gangue minerals (e.g., quartz, feldspar) remain in the pulp.

The main lepidolite flotation collectors are cationic amine collectors and mixed collectors. As shown in Figure 5, after the dissociation of lepidolite, the lattice surface releases a significant amount of K^+ , which dissolves into the aqueous medium, leaving the mineral surface negatively charged. Additionally, the active sites on the lepidolite surface—primarily oxygen (O) and silicon (Si)—bind hydroxyl groups, contributing further to its negative charge across a wide pH range [17].

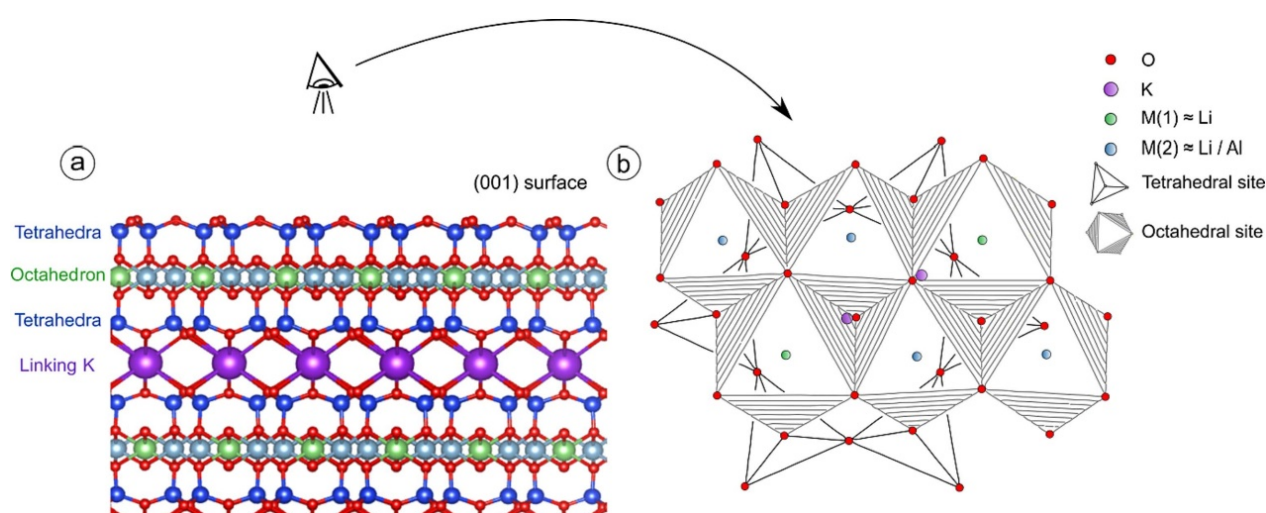


Figure 5. M2—Lepidolite atomic structure. (a) The t-o-t form and layered structure of lepidolite. (b) Deformation of octahedral sites according to Al-Li isomorphous replacement. Atom colors: red—O, blue—Al, green—Li, and purple—K [17].

Cationic amine collectors, such as dodecylamine and hexadecylamine, can adsorb onto the negatively charged lepidolite surface through electrostatic interactions. However, these collectors have problems such as high foam viscosity, poor fluidity, sensitivity to pulp, and the need for acidic conditions for flotation, which limit their application in lepidolite flotation. Recently, the use of a combination of anionic and cationic collectors, utilizing the synergistic effect of the two types of collectors, can float lepidolite under neutral or natural mild pH conditions, improving the flotation environment and efficiency, which is a research hotspot for lepidolite flotation collectors.

It is well known in the literature that lepidolite can be floated using amine cationic collectors. However, other parameters are mandatory in order to obtain a good flotation performance of lepidolite. Bulatovic [31] reported that good flotation behavior of lepidolite is also related to the pulp density and grinding fineness. Therefore, in order to improve metallurgical results, lepidolite flotation should be carried out at low pulp densities (<25 wt.%). In addition, a reduction in grinding size can improve the recovery.

3.1.2. Flotation Collectors

■ Primary Amines

Dodecylamine (DDA), a widely used amine collector, exhibits a strong collection performance for lepidolite and can effectively float it under both alkaline (pH 10–11) and acidic (pH $\sim$ 3.5) conditions [32,33]. The disparity in flotation behavior under acidic versus alkaline conditions stems from the pH-dependent surface charge of lepidolite and gangue minerals. Under acidic conditions (pH $<$ 4), lepidolite surfaces are predominantly negatively charged due to the dissociation of hydroxyl groups ($-\text{OH} \rightarrow -\text{O}^- + \text{H}^+$), facilitating strong electrostatic adsorption of cationic DDA. Conversely, in alkaline environments (pH $>$ 10), the mineral surface charge becomes less negative, reducing electrostatic interactions but promoting hydrogen bonding between DDA and lepidolite's aluminosilicate framework. This dual adsorption mechanism enables selective separation: in acidic pulp, DDA preferentially adsorbs on lepidolite over quartz and feldspar ($\Delta\zeta > 15$ mV), whereas alkaline conditions favor coarser particle recovery but risk the entrainment of muscovite due to similar surface properties. For example, Qin Wu et al. used sulfuric acid as a modifier and DDA as a collector to concentrate lepidolite from a deposit in Jiangxi, achieving a Li_2O grade of 3.77% with recovery rates of 76–86% [34].

Despite its effectiveness, DDA struggles with the separation of lepidolite from muscovite due to their similar adsorption energies, using quantum mechanics/molecular mechanics calculations [35,36], as shown in Figures 6 and 7. However, under acidic conditions, the adsorption energies of DDA on lepidolite, quartz, and feldspar differ significantly, enabling the selective flotation of lepidolite.

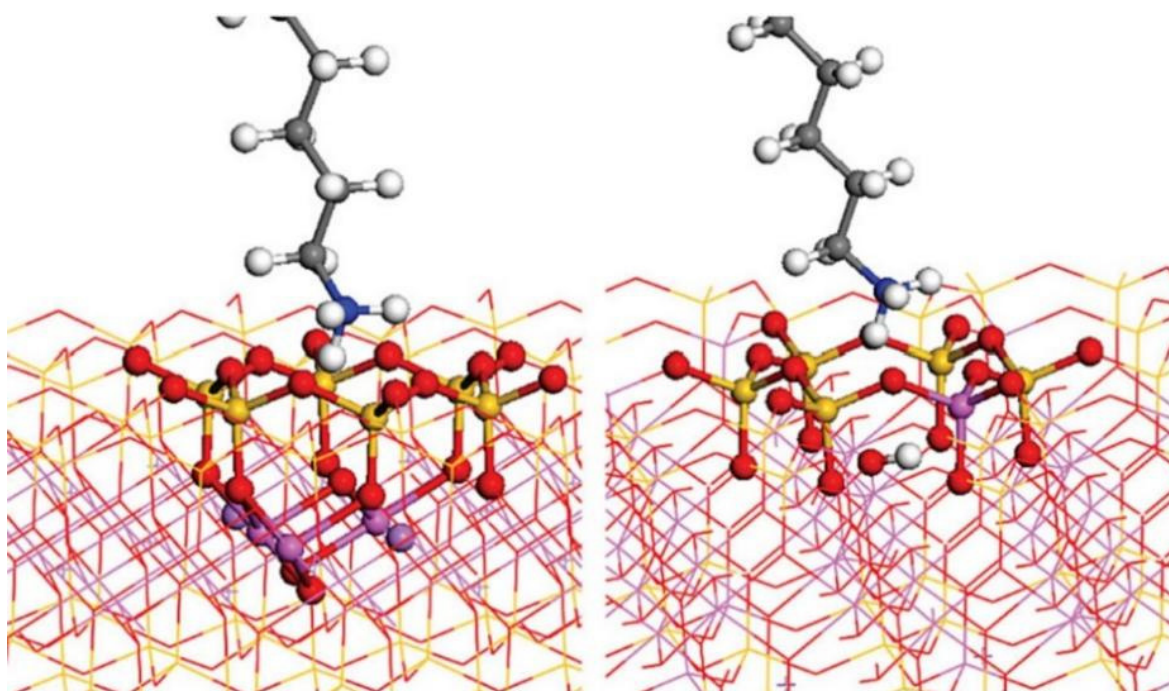


Figure 6. The adsorption of DDA on lepidolite (left) and muscovite (right). QM atoms are displayed by the ball–rod model with MM atoms displayed as lines. The red, yellow, purple, white, and black beads represent oxygen, silicon, aluminum, hydrogen, and potassium atoms, respectively [35].

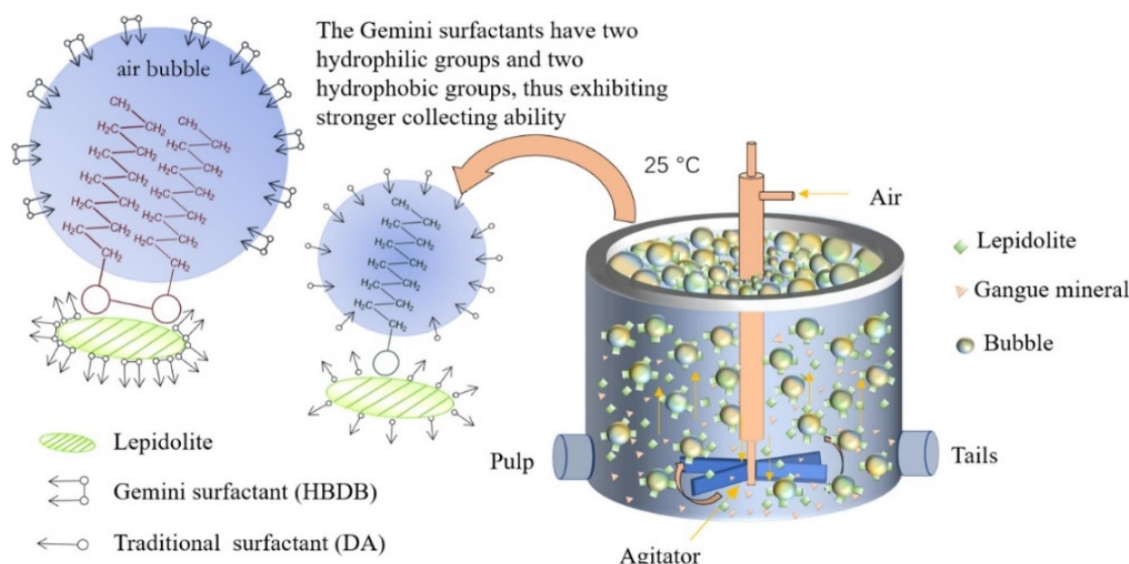


Figure 7. Comparative analysis of lepidolite flotation performance using novel Gemini surfactant HBDB versus conventional monomeric collector DA [36].

Other primary amines, such as tallow amine, coconut amine, and octadecylamine, have also been explored [37–39]. For instance, Liu et al. [40] recovered refined lepidolite from Ta and Nb waste minerals by using coconut amine, achieving a Li_2O grade of 2.45% and a recovery of 56.08%. Zou et al. [41] employed the amine collector DXLD-152 to process a low-grade iron lepidolite ore, resulting in a Li_2O grade of 3.1% with a recovery of 75.48%.

While inexpensive and widely available, they present challenges such as low enrichment ratios, high foam viscosity, sensitivity to pulp conditions, and equipment corrosion under acidic flotation environments [42,43].

■ Secondary Amines and Quaternary Ammonium Salts

Secondary amines and quaternary ammonium salts are less commonly reported but offer potential advantages. For example, Jiao et al. [13] used dodecylamine polyoxyethylene ether as a collector, obtaining a Li_2O grade of 3.17% and a recovery of 66.38% for lepidolite flotation under neutral pH conditions. This collector showed good adaptability to the pulp and produced non-sticky, easily breakable foam. Choi et al. [30] employed octadecyltrimethyl ammonium chloride to float lepidolite at pH ~2, achieving selective adsorption on lepidolite due to its negative charge and weak interaction with gangue. Yang et al. [44] applied a novel hybrid anionic/cationic collector of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) to the flotation of lithium mica from quartz. The results show that the adsorption strength of SDS on lithium mica is greater than that on quartz, and the co-adsorption of SDS and CTAB on the surface of lithium mica will further extend the differences in their flotation behaviors. These may be the essence of achieving selective separation of the two minerals. Huang et al. [15] investigated the performance of a novel amine-based Gemini surfactant, hexanediyl- α , ω -bis (Dimethyldodecylammonium bromide) (HBDB), for lepidolite flotation from tantalum–niobium mine tailings under low-temperature conditions, comparing it with the traditional monomeric collector 1-dodecylamine (DA). An integrated magnetic separation–flotation approach was developed for lepidolite enrichment from tailings, utilizing HBDB (80 g/t) or DA (160 g/t) as collectors under natural pulp pH conditions (~6.8). Comparative analysis revealed that HBDB outperformed DA in Li_2O recovery, exhibiting enhancements of 10.96% at ambient temperature (298 K) and 31.85% under low-temperature conditions (275 K), while maintaining concentrate Li_2O grades consistently near 4%.

The enhanced efficacy of BDB is ascribed to its Gemini surfactant configuration, which reduces the Krafft point to below 275 K, ensuring optimal solubility and surface activity in chilled environments. Hydrophobicity evaluations through contact angle measurements demonstrated a significant disparity: BDB-treated lepidolite attained 89.5° at 298 K, whereas DA yielded only 64.7° , confirming stronger adsorption capacity and superior hydrophobic modification by BDB. Furthermore, the hybrid process successfully reduced impurities including iron, tantalum, and niobium, thereby elevating Li_2O content in the flotation feed material [45,46]. While less commonly reported than primary or secondary amines, tertiary amines have shown potential in lepidolite flotation due to their unique adsorption mechanisms.

■ Ether Amines

Ether amines, such as Flotigam, show excellent performance in low-temperature environments and acidic conditions. For instance, Sousa et al. [47] used Flotigam to process Gonalo lepidolite ore, achieving a Li_2O grade of 4.7% at pH 3.5. Filippov et al. [48] investigated an integrated approach combining dry processing and flotation to recover lepidolite from low-grade hard-rock pegmatite ore. The study used a Gonalo lepidolite ore sample from Portugal that had an initial Li_2O grade of 2.02%. After screening, crushing, and wet milling, the ore underwent optical sorting, electrostatic separation, and froth flotation. Optimal electrostatic separation settings (30 kV voltage, 50 rpm roll speed) resulted in a concentrate with a 3.77% Li_2O grade and 20.3% recovery from coarse fractions (0.84–2 mm). Using a 65 g/t PX4815 collector, froth flotation of fine fractions ($-210 + 63 \mu\text{m}$) produced rougher concentrates with Li_2O grades of up to 4.5% and recoveries ranging from 87% to 95% at pH 3–5. This study demonstrates the feasibility of combining dry and wet processing technologies for low-grade lithium ores. The combination of electrostatic separation and flotation effectively improves concentrate grade and recovery. However, the complete liberation of lepidolite particles remains a key limitation, requiring the optimization of grinding and collector conditions. Additionally, the economic feasibility and scalability of the dry processing method warrant further assessment, especially for industrial applications.

■ Anionic collector

Deng et al. [35] investigated the selective adsorption mechanism of sodium lauroyl glutamate (SLG), a green collector, for the flotation separation of lepidolite and albite. Lepidolite and albite samples were sourced from Brazil and Liaoning, China, respectively, with particle sizes of $-74 + 38 \mu\text{m}$. Optimized flotation conditions were pH = 5, Ca^{2+} concentration $2 \times 10^{-4} \text{ mol/L}$, and SLG concentration $5 \times 10^{-4} \text{ mol/L}$. Under these conditions, lepidolite recovery reached 87.95%, with a Li_2O grade of 5.28%, while albite recovery was only 10.6%, achieving effective separation. By implementing characterization methods, including contact angle, FTIR, zeta potential, adsorption measurements, and XPS, elucidated the selective adsorption mechanism of SLG. The results revealed that Ca^{2+} acted as an activator, preferentially binding to O sites on lepidolite surfaces, providing abundant active sites for SLG chemisorption. SLG formed complexes with Ca^{2+} through its carboxyl ($-\text{COO}^-$) and amide ($-\text{CON}^-$) groups, significantly enhancing lepidolite hydrophobicity (contact angle increased from 13.36° to 87.91°). In contrast, SLG adsorption on albite was weak, causing only a slight increase in wettability (contact angle increased from 17.53° to 36.20°). Adsorption measurements and XPS analysis confirmed strong chemisorption of SLG on lepidolite surfaces, while adsorption on albite was minimal.

■ Mixed Collectors

In contemporary lepidolite flotation practices, the strategic implementation of mixed-collector systems, specifically the synergistic combination of cationic and anionic collectors,

has gained prominence as an innovative strategy to overcome the inherent constraints of single-collector methodologies. These hybrid formulations capitalize on molecular-level complementarity between collector components, achieving threefold benefits: enhanced mineral recovery efficiency (typically 8–12% improvement), significant collector dosage reduction (20–30% lower consumption), and operational flexibility through effective neutral pH flotation (6.5–7.2 range), thereby substantially minimizing acid-induced corrosion in processing equipment [49,50].

The technical superiority of dual-collector systems stems from their ability to synergistically combine surface activation mechanisms while compensating for individual component deficiencies. The anionic constituents (typically fatty acids or sulfonates) effectively lower foam viscosity and improve pulp phase adaptability through steric stabilization effects, while their cationic counterparts (commonly amine derivatives) demonstrate superior selectivity towards lepidolite surfaces via specific adsorption on aluminosilicate layers. Notably, industrial trials at 500 tons per day scale have demonstrated 4.2% Li_2O grade improvements with 86–89% recovery rates when employing optimized dodecylamine (DDA)/sodium oleate (NaOl) combinations compared to conventional single-collector operations.

Current research priorities focus on developing next-generation mixed collectors through three key approaches: (1) engineering cost-effective biobased collectors from modified vegetable oil derivatives, (2) designing smart collector molecules with pH-responsive functional groups, (3) optimizing formulations of collectors through molecular dynamics simulations. These advancements aim to achieve sustainable processing parameters while maintaining >90% lithium recovery efficiency, particularly crucial for exploiting complex pegmatite deposits with declining ore grades (average 0.8–1.2% Li_2O) [51].

Tang et al. [52] explored how the combined use of dodecylamine (DDA) and sodium dodecyl diphenyl ether disulfonate (SLDED) as collectors could effectively separate lepidolite from feldspar during flotation. By optimizing collector concentrations (DDA: 4×10^{-4} mol/L, SLDED: 7×10^{-4} mol/L), the study achieved a high lepidolite recovery of 89.52% and a Li_2O grade of 5.55%, while feldspar recovery was restricted to just 13.36%. The tailings had a minimal Li_2O grade of 0.41%. Mechanistic insights revealed that SLDED reduced DDA adsorption on feldspar through competitive interactions, while promoting selective adsorption on lepidolite, enhancing its hydrophobicity and minimizing that of feldspar. Molecular dynamics simulations corroborated these findings, showing reduced water molecule concentration on lepidolite and increased hydration on feldspar surfaces, enabling efficient separation, as shown in Figure 8. This work underscores the promise of combining collectors to improve selectivity and lithium grade but highlights the need for further study in more complex pulp systems for industrial-scale application.

Bai et al. [33] analyzed the synergistic effects of mixed cationic/anionic collectors (DDA/NaOl and DDA/sodium dodecyl benzene sulfonate (SDBS)) in lepidolite flotation, focusing on foam properties and interfacial behavior. Using lepidolite from Yichun, Jiangxi Province (−0.074 to +0.038 mm), and a total collector concentration of 5.0×10^{-4} mol/L at a 1:1 molar ratio, the DDA/SDBS system outperformed DDA/NaOl. Under optimal conditions, DDA/SDBS achieved a remarkable Li_2O grade of 4.99% with a 98% recovery rate. Its enhanced performance was attributed to the strong polarity of the sulfonic and benzene groups, which increased surface activity and reduced surface tension. Molecular dynamics simulations further showed that this mixed system minimized electrostatic repulsion between cations and formed a denser hydrophobic layer, improving adsorption efficiency. Additionally, DDA/SDBS produced less stable froth, which reduced gangue entrainment and improved concentrate quality.

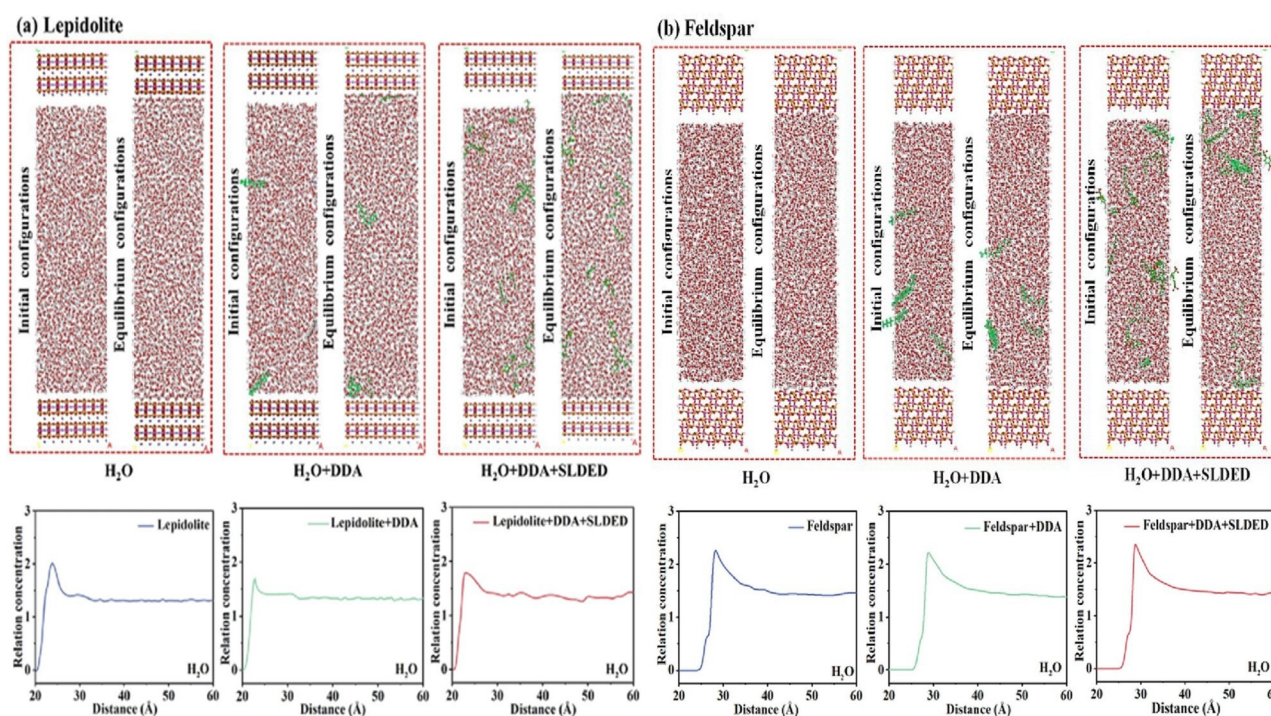


Figure 8. Different interaction models and relative concentration profiles of H₂O in relation to the vertical distance from (001) surfaces of (a) lepidolite and (b) feldspar [52].

Zhang et al. [53] systematically evaluated the anti-slime efficacy of the novel collector DDA/HQ330 against conventional DDA/NaOl systems in lepidolite beneficiation. The investigation employed Brazilian-sourced lepidolite (74–38 μm) and Chinese feldspar slimes (<10 μm) under neutral pH conditions with optimized parameters (1:3 mass ratio, 150 mg/L total concentration). Experimental data revealed DDA/HQ330's exceptional slime resistance, maintaining >80% lepidolite recovery at 5 g/L slime loading and a 35–40% improvement over DDA/NaOl counterparts under equivalent conditions.

Mechanistic analysis through zeta potential measurements and adsorption studies demonstrated DDA/HQ330's selective interaction patterns: (1) limited electrostatic modification on feldspar surfaces ($\Delta\zeta < 2$ mV), (2) formation of dense hydrophobic layers (≈ 100 nm thickness) preferentially on lepidolite, (3) reduced solution surface tension (41.2 mN/m vs. 48.5 mN/m in DDA/NaOl) promoting stable microbubble generation. These synergistic effects were attributed to HQ330's unique molecular architecture combining hydrogen-bonding moieties with branched hydrocarbon chains, enabling both selective mineral attachment and foam stabilization.

Wei et al. [49] investigated the selective co-adsorption mechanism of the combined collector system sulfhydryl-oleate ligand (SOL)/DDA for the separation of lepidolite from quartz. They utilized samples sourced from Yunnan, China, with a particle size range of -74 to $+38$ μm , and applied a mass ratio of SOL to DDA of 4:1, maintaining a total collector concentration at 60 mg/L. The study observed enhanced separation efficiency at a neutral pH level of approximately 7.0. The use of the mixed collector significantly increased the Li₂O grade in the ore from an initial 2.65% to 4.99%, achieving a high recovery rate of 96.35%. Contact angle measurements indicated that the hydrophobicity of lepidolite surpassed 100° post-treatment, contrasting with quartz, which remained hydrophilic with angles below 30° . Zeta potential assessments and adsorption studies confirmed that the SOL/DDA mixture promoted the adsorption of DDA on lepidolite while inhibiting it on quartz. Atomic force microscopy (AFM) observations highlighted the differential adsorption patterns, with a more concentrated layer on lepidolite and a sparser distribution on quartz.

Huang et al. [54] conducted a study on the adsorption behavior of an amidoxime-based collector, DPA, in lepidolite flotation, with the aid of Density Functional Theory (DFT) calculations. They employed lepidolite samples from Jiangsu Province, with a particle size of $-75 + 38 \mu\text{m}$. The use of DPA at a concentration of $3 \times 10^{-4} \text{ mol/L}$ demonstrated superior performance over the traditional DA collector, increasing the recovery rate from 77.5% to 90% while reducing the dosage by half. The hydrophobicity of lepidolite was significantly enhanced with DPA, as evidenced by a contact angle of 86.2° compared to 68.1° with DA. FTIR analysis suggested that DPA adsorbed through electrostatic interactions rather than chemical complex formation, and zeta potential measurements indicated an increase in positive charge on the lepidolite surface. DFT calculations revealed that DPA's enhanced adsorption was due to its lower HOMO–LUMO energy gap and higher electron density at its active sites.

In a separate investigation, Huang et al. also explored the use of a novel Gemini surfactant, HBDB, in lepidolite flotation and compared it with the traditional DA collector. They used lepidolite ore from Yichun, Jiangxi, with an initial Li_2O grade of 1.18%. The optimal flotation conditions showed that HBDB required a dosage of 175 g/t, compared to 350 g/t for DA, at an optimal pH of 3. Under these conditions, HBDB achieved a Li_2O grade of 4.12% and a recovery rate of 71.15%, which was a 16.18% improvement over DA, while also reducing consumption by 50%. Contact angle measurements indicated that HBDB significantly improved the hydrophobicity of lepidolite, with a contact angle of 85.2° compared to 62.6° for DA. Zeta potential results showed that HBDB had a stronger electrostatic adsorption on the lepidolite surface, leading to a higher positive surface charge and better flotation performance. The Gemini structure of HBDB, with its dual hydrophobic and hydrophilic groups, provided it with enhanced surface activity and selectivity, effectively increasing mineral hydrophobization while suppressing gangue flotation.

Zhang et al. [51] conducted a study to understand the synergistic effects of nanobubbles (NBs) with a blend of cationic and anionic flotation agents, DDA and NaOl, on the flotation performance of fine-grained lepidolite. The Brazilian-origin lepidolite was pulverized to achieve a median particle size of $D_{50} = 12 \mu\text{m}$. The flotation agents, DDA and NaOl, were mixed in a 4:1 mass ratio with a combined concentration of 50 mg/L. To adjust the pH, NaOH and H_2SO_4 were utilized, and the process involved the use of ultrapure water with a resistivity of $18.25 \text{ M}\Omega\cdot\text{cm}$. The research employed a suite of methods including flotation tests, nanoparticle size analysis, contact angle measurements, settling tests, and high-speed camera observations to elucidate the role of NBs in enhancing the hydrophobicity, flocculation, and settling of lepidolite. The combined use of DDA and NaOl decreased the surface tension of the solution, which in turn increased the concentration and stability of NBs; however, it was noted that surface NBs were more vulnerable to mechanical disruption. The study highlighted that bulk NBs were crucial for improving the flotation of lepidolite. At the optimal pH of 8, the recovery of fine lepidolite improved from 31.55% with a single collector to 45.86% with the combination of mixed collectors and NBs. In Figure 9, NBs were found to promote hydrophobic flocculation through a “bubble-bridge” mechanism, which also improved settling efficiency. The findings offer significant contributions to the understanding of fine lepidolite recovery processes, although the instability of NBs and the need for further optimization of collector dosages are identified as areas requiring further research.

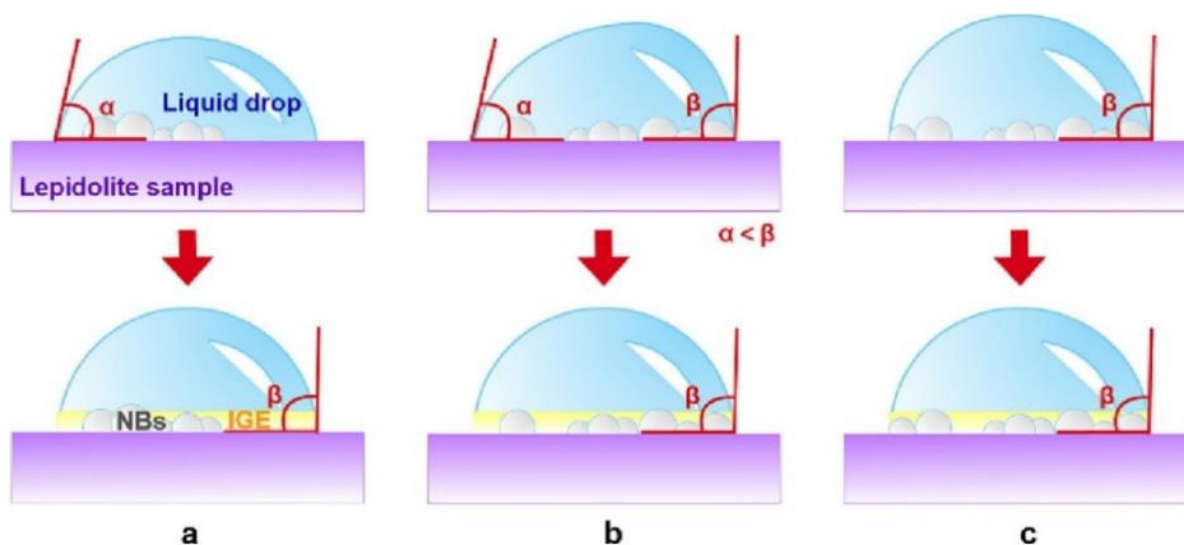


Figure 9. Schematic diagram of lepidolite–NBs–IGE contact angle. (a) Schematic illustration of contact angle on pure lepidolite surface without nanobubbles (NBs) and interfacial gas enrichment (IGE). (b) Contact angle on lepidolite surface with adsorbed NBs under the action of mixed cationic/anionic collector (DDA/NaOL). (c) Synergistic effect of NBs and IGE on enhancing lepidolite surface hydrophobicity through co-interaction [51].

The benefits of employing mixed collectors are manifold, particularly in enhancing the selectivity of lepidolite flotation. These benefits include the following:

- (1) Enhanced Selectivity: The combined action of mixed collectors boosts the hydrophobicity of lepidolite while minimizing the adhesion of unwanted gangue minerals.
- (2) Broad pH Tolerance: The effectiveness of mixed collectors across a range of neutral-to-mild pH levels lessens the reliance on extreme acidic or alkaline conditions.
- (3) Efficiency and Sustainability: By improving adsorption efficiency, the need for high collector dosages is reduced, which also alleviates equipment corrosion and mitigates the environmental impacts associated with single collectors.

The following are examples of the differences in the flotation behavior of lepidolite and quartz, and lepidolite and feldspar, in different collector systems to analyze the advantages of the combination of collectors, as shown in Figure 10 [35,44,49,53,55].

Significant differences are noted in the effects of surfactants like SDS and CTAB on zeta potential. SDS, with its negative charge, substantially reduces zeta potential and shifts the isoelectric point to lower pH values, while CTAB, being cationic, raises the isoelectric point due to adsorption. The combination of these surfactants showcases synergistic effects on surface charge, highlighting their potential in customized mineral separation processes.

Divalent cations, such as Ca, are also critical, as they significantly diminish zeta potential more effectively than monovalent ions by neutralizing surface charges, thus promoting particle aggregation and suggesting that ionic strength and type can regulate suspension stability.

Feldspar and albite exhibit distinct interactions with collectors and ions. Feldspar shows a weaker adsorption of DDA and SLDED, complicating its separation from lepidolite, whereas albite maintains a more negative zeta potential even after treatment with Ca²⁺ and SLG, indicating its unique surface chemistry.

These insights underscore the intricate relationship between surface charge, reagent adsorption, and ionic strength, offering a valuable framework for the precise design of reagent schemes in mineral processing.

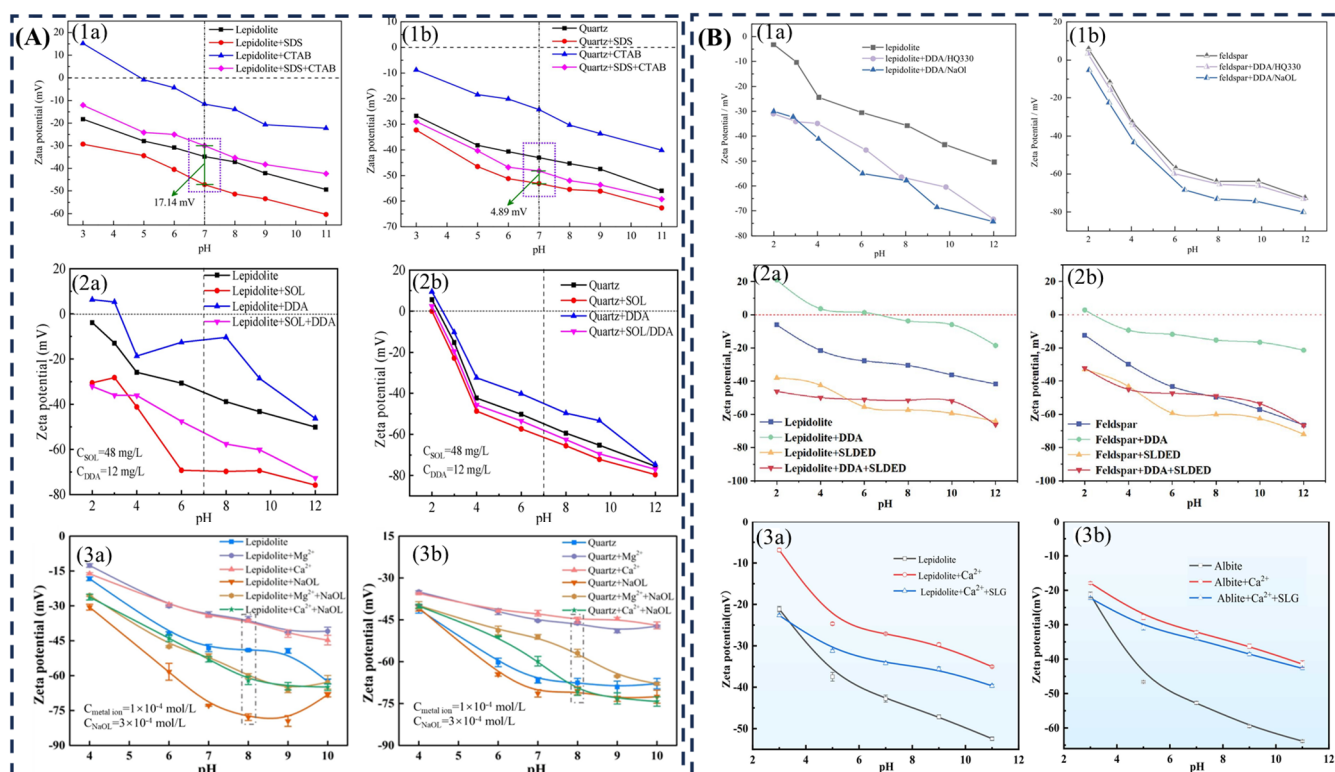


Figure 10. (A) Zeta potentials of (1a) lepidolite and (1b) quartz under different collector systems as a function of pH [44]. Contact angles of lepidolite and quartz as a function of pH in the presence of (2a) single SOL and single DDA; (2b) mixed-collector SOL/DDA [49]. Zeta potentials of lepidolite (3a) and quartz (3b) under various conditions as a function of pH [55]. (B) Zeta potentials of lepidolite (1a) and feldspar (1b) as a function of pH [53]. Zeta potentials of (2a) lepidolite and (2b) feldspar at different pH values after treatment with different collectors [52]. Zeta potentials of lepidolite (3a) and albite (3b) as a function of pH [35].

Figure 10 also presents a comprehensive investigation into the flotation behavior of lepidolite, feldspar, and albite in response to varying concentrations and combinations of collectors. The data collectively demonstrate the impact of experimental conditions, such as pH and dosage, on the recovery and grade of lithium-bearing minerals.

Figure 11a shows an inverse relationship between grade and recovery. As the collector dosage increases, recovery improves, but grade slightly decreases, suggesting that excessive collector addition may lead to the entrainment of gangue minerals [37].

Figure 11d highlights the importance of collector selectivity in flotation efficiency. Lepidolite exhibits superior recovery compared to feldspar across a wide concentration range of DDA and SLDED, indicating a stronger affinity between these collectors and the lepidolite surface. Conversely, feldspar recovery sharply decreases under the same conditions, underscoring the selective nature of these collectors [44].

Figure 11b shows that the combination of DDA with anionic collectors (e.g., NaOl and SDBS) results in an improved grade and recovery compared to single-collector systems. This synergistic effect indicates the potential of hybrid collector systems to optimize both grade and recovery [33].

Figure 11c emphasized the role of mixed-collector systems. For instance, the combination of SDS and CTAB significantly enhances the recovery of lepidolite while maintaining a low recovery of quartz, highlighting the potential of dual-collector strategies for selective flotation [44].

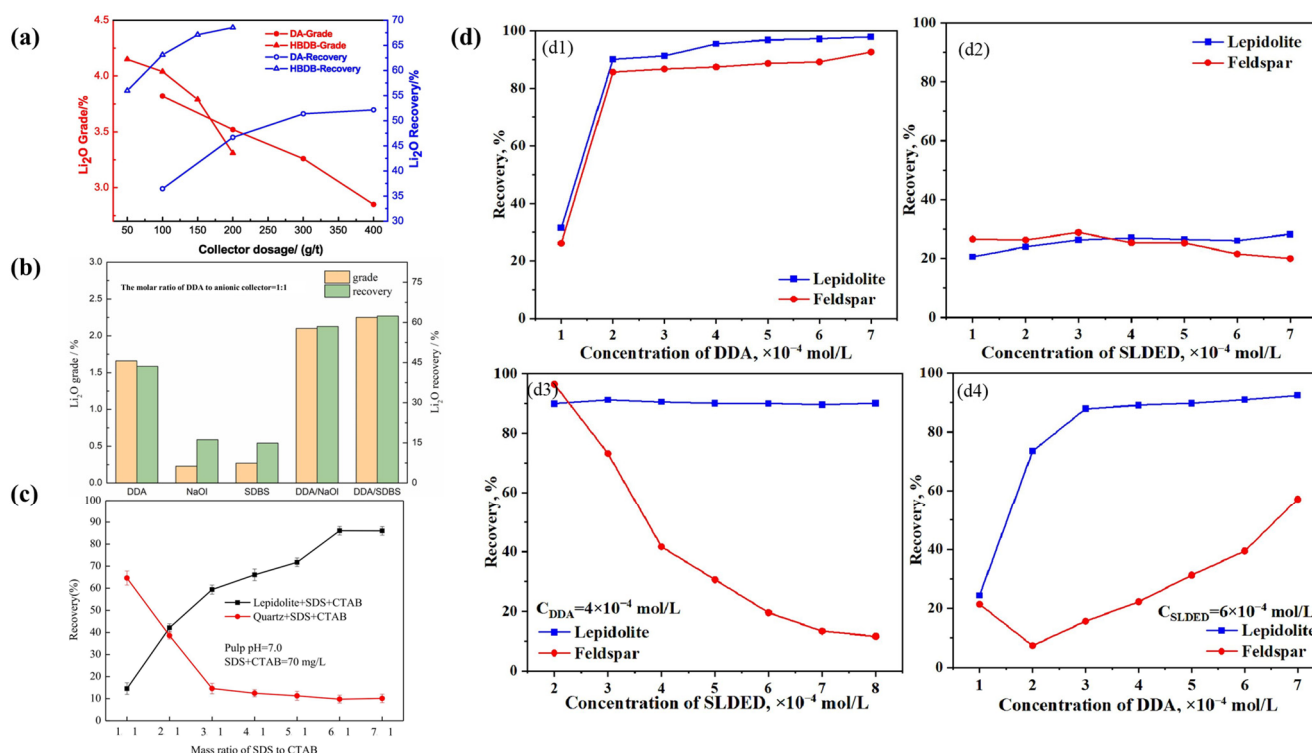


Figure 11. (a) The content of Li_2O in lepidolite concentrate by HBDB or DA at pH 3 [37]; (b) Effects of mixed cationic/anionic collectors on lepidolite flotation at pH = 7 [33]. (c) Effect of SDS and CTAB dosage on the flotation recovery of minerals [52]. (d) Effect of collector concentrations on the flotation recovery of lepidolite and feldspar [44].

The intricate relationship between collector chemistry, dosage, and mineral properties in lepidolite flotation has garnered significant research interest. Utilizing Fourier transform infrared (FTIR) spectroscopy has shed light on the interactions at the mineral–collectors interface, which is pivotal for comprehending the adsorption mechanisms that directly influence flotation efficiency.

Figure 12a presents the spectra of feldspar, both untreated and treated with DDA and SLDED. Key absorption peaks in the 2850–3000 range, corresponding to C–H stretching vibrations, are significantly enhanced after the introduction of SLDED and DDA, indicating the adsorption of these collectors on the feldspar surface. Additionally, shifts in the O–H stretching region suggest hydrogen bonding between the collectors and surface hydroxyl groups.

In Figure 12b, lepidolite and quartz exhibit similar trends under SDS, CTAB, and SDS + CTAB treatments. Notably, the combination of SDS and CTAB results in the appearance of new peaks and a shift in the Si–O stretching region (0–1100), indicating a synergistic adsorption mechanism. These shifts highlight changes in surface properties that enhance selectivity during flotation [44].

Figure 12c reveals the interaction between SLG and different minerals. For lepidolite and albite, the addition of SLG results in notable changes in the 1000–1200 range, suggesting a strong interaction between SLG and the Si–O framework of these minerals. Furthermore, the spectra of albite with Ca2 and SLG display additional shifts, indicating a modified surface chemistry that may improve flotation selectivity [52].

Overall, the FTIR analysis demonstrates that adsorption alters surface chemical environments in a specific manner, directly impacting flotation performance. These findings are critical for optimizing selection and dosages to achieve efficient mineral separation.

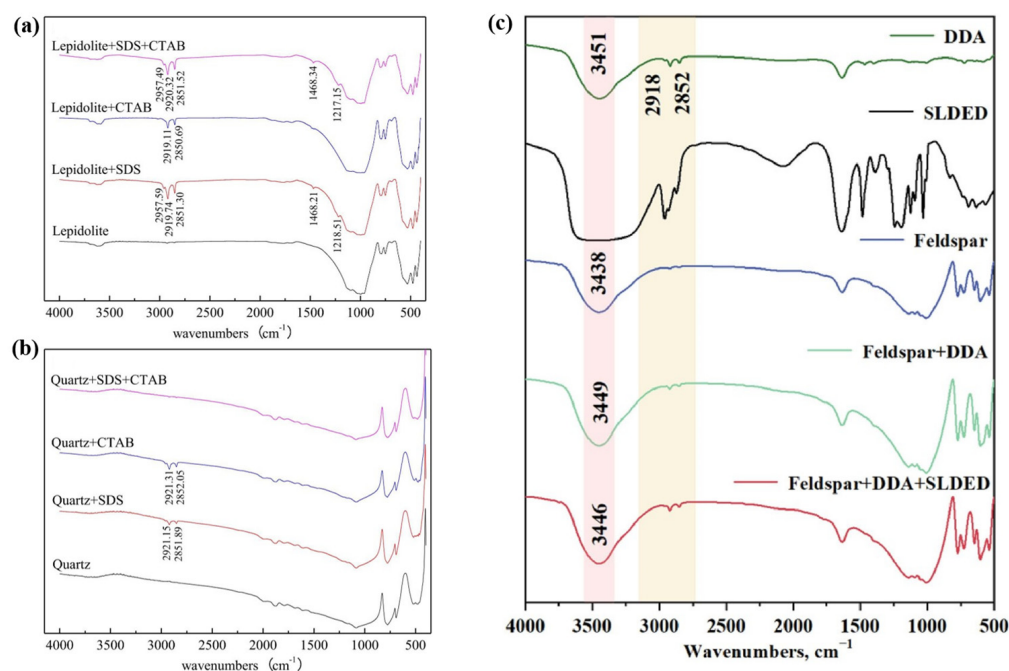


Figure 12. FTIR spectra of (a) lepidolite and (b) quartz before and after reaction with different collectors [44]. (c) FTIR spectra of collectors and feldspar in the different collector system [52].

The selection of optimal collector systems for lepidolite ores is highly dependent on their mineralogical composition, particularly the presence of gangue minerals such as albite, muscovite, or quartz. For high-albite ores, where albite (Na-feldspar) is the dominant impurity, mixed cationic/anionic collector systems demonstrate superior selectivity. For instance, Tang et al. [52] achieved an 89.52% lepidolite recovery with a Li_2O grade of 5.55% using a dodecylamine (DDA)/sodium dodecyl diphenyl ether disulfonate (SLDED) combination (4×10^{-4} mol/L DDA, 7×10^{-4} mol/L SLDED). The anionic SLDED competitively inhibited DDA adsorption on albite, while enhancing its selective adsorption on lepidolite via hydrophobic modification. Molecular dynamics simulations further confirmed reduced hydration layers on lepidolite surfaces, facilitating efficient separation (Figure 8). In contrast, albite's weaker interaction with cationic collectors necessitates tailored formulations to suppress its entrainment.

For muscovite-associated ores, which share similar aluminosilicate layers with lepidolite, conventional cationic amines like DDA struggle due to overlapping adsorption energies. Here, Gemini surfactants (e.g., HBDB) or hybrid anionic/cationic systems offer distinct advantages. Huang et al. [54] reported that HBDB, with its dual hydrophobic/hydrophilic groups, achieved a 16.18% higher recovery than DDA (71.15% vs. 55%) in muscovite-rich ores, while halving collector dosage (175 g/t vs. 350 g/t). The Gemini structure selectively increased lepidolite hydrophobicity (contact angle: 85.2° vs. 62.6° for DDA) while suppressing muscovite flotation through steric hindrance. Similarly, Wei et al. demonstrated that a sulfhydryl-oleate ligand (SOL)/DDA mixture enhanced lepidolite-quartz separation, achieving 96.35% recovery at pH 7, with quartz recovery below 30%. The SOL component disrupted hydrogen bonding on muscovite, reducing its affinity for cationic collectors.

The performance disparities among flotation collectors can be attributed to distinct molecular mechanisms. Gemini surfactants, such as HBDB, exhibit superior low-temperature stability compared to conventional primary amines (e.g., DDA) due to their dual hydrophilic/hydrophobic architecture, which reduces the Krafft point and maintains high surface activity even under chilled conditions (Figure 9). In contrast, the linear structure of primary amines promotes crystallization at low temperatures, severely limiting

their practical utility. Charge compatibility further differentiates collector behaviors: anionic reagents like SLG rely on Ca^{2+} bridging to adsorb onto negatively charged mineral surfaces, a process validated by zeta potential shifts (Figure 10), whereas cationic collectors directly bind via electrostatic interactions. Beyond individual mechanisms, mixed-collector systems (e.g., DDA/SDBS) leverage synergistic effects to optimize flotation efficiency. By reducing surface tension and electrostatic repulsion, these hybrid formulations form dense hydrophobic layers on lepidolite surfaces, as demonstrated by molecular dynamics simulations (Figure 8). This integrated approach not only enhances mineral selectivity but also addresses the challenges inherent to single-component collectors, underscoring the importance of molecular design in advancing flotation technologies. A comparison of typical flotation collectors is shown in Table 1.

Table 1. Comparison of typical flotation collector performance.

Collector Type	Applicable pH	Li_2O Grade (%)	Recovery (%)	Advantages	Limitations	Refs
Primary amines (DDA)	3.5–11	3.77–5.55	76–98	Broad applicability, high selectivity	High foam viscosity, equipment corrosion (under acidic conditions)	[34]
Gemini surfactants (HBDB)	3–6.8	4.12–4.5	71–90	High efficiency at low temperatures, reduced dosage	High synthesis cost	[33]
Mixed collectors (DDA/NaOl)	6.5–8	4.2–4.99	86–95	Synergistic effects, wide pH adaptability	Complex formulation optimization	[44]
Anionic collectors (SLG)	5	5.28	87.95	Eco-friendly, high selectivity	Requires Ca^{2+} activation, limited applicability	[54]

3.1.3. Modifiers and Frothers

Modifiers play a critical role in improving flotation performance by enhancing mineral selectivity and optimizing reagent adsorption. Generally, there are three types of modifiers: (1) pH adjusters: A comparative test using sulfuric acid (pH 4) and sodium hydroxide (pH 10) demonstrated that neutral to slightly acidic conditions (pH 6–7) achieved the best recovery and grade balance for lepidolite ores. (2) Activators: In a test ore with high feldspar content, the addition of MgCl_2 as an activator increased lepidolite recovery by 8% due to enhanced collector adsorption. (3) Depressants: Sodium silicate effectively suppressed quartz and feldspar during laboratory flotation, increasing the lithium concentrate grade from 3.5% to 4.0% Li_2O [55–57].

Frothers such as methyl isobutyl carbinol (MIBC) are commonly used to stabilize the froth [58–61]. A production-scale trial revealed that reducing frother dosage by 20% improved froth fluidity, reducing gangue entrainment and increasing the concentrate grade by 0.3%. The activation role of magnesium ions (Mg^{2+}) in lepidolite flotation has been investigated by Xu et al. [55]. This investigation established a flotation separation system employing high-grade lepidolite from Yunnan and quartz from Guangdong, both with particle sizes of 38–74 μm . Sodium oleate (NaOl) served as the collector, while magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and anhydrous calcium chloride (CaCl_2) acted as activators, pH adjustments were achieved using NaOH and HCl, and ultrapure water (resistivity $>16 \text{ M}\Omega \cdot \text{cm}$) ensured experimental integrity. As shown in Figure 13, the results demonstrated that Mg^{2+} exhibited remarkable selective activation toward lepidolite at pH 8, achieving a flotation recovery exceeding 85%, whereas quartz recovery remained below 15%. Mechanistic studies revealed that (1) FTIR spectra confirmed characteristic adsorption bands of NaOl on Mg^{2+} -activated lepidolite surfaces; (2) zeta potential analysis indicated Mg^{2+} significantly increased surface positive charge density, promoting electrostatic inter-

actions with anionic collectors; (3) XPS characterization elucidated Mg^{2+} coordination with oxygen, fluorine, and aluminum sites on lepidolite, accompanied by Mg –OOCR colloidal complex formation, which substantially enhanced surface hydrophobicity. In contrast, Ca^{2+} displayed an inferior activation performance, underscoring Mg^{2+} 's unique advantages in selective lepidolite enrichment.

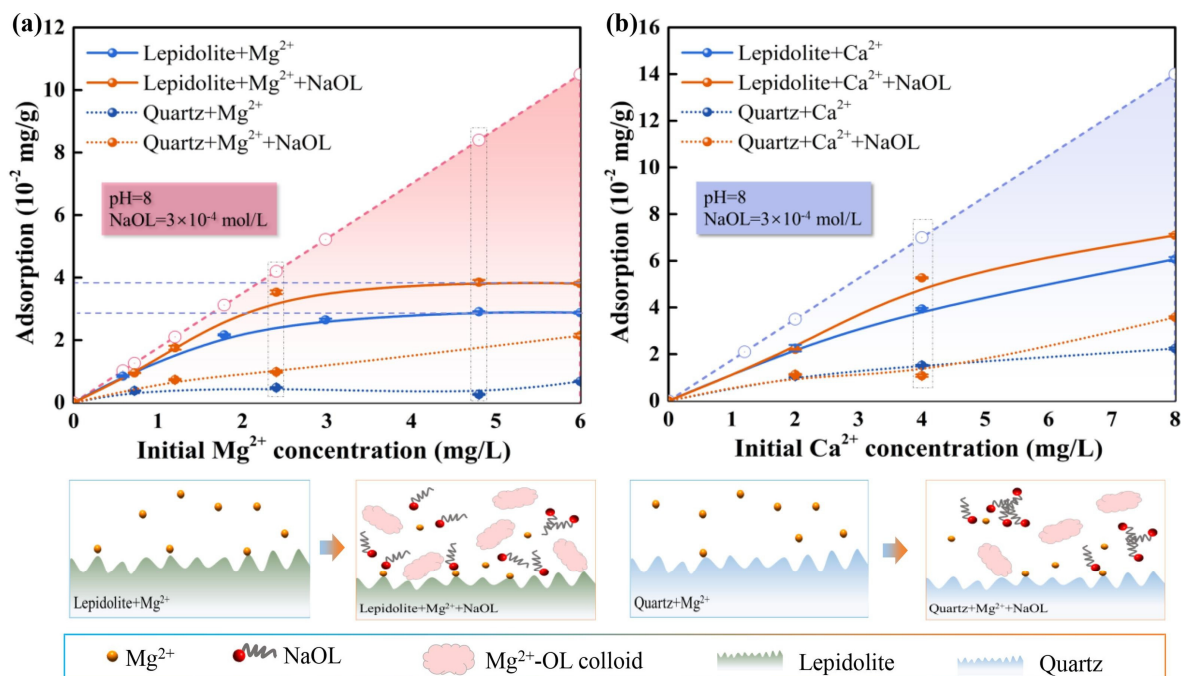


Figure 13. Adsorption amount of Mg^{2+} (a) and Ca^{2+} (b) on the surface of lepidolite and quartz in the presence and absence of NaOl [55].

3.1.4. Challenges and Future Prospects

Despite notable advancements in lepidolite flotation, persistent challenges underscore the need for continued innovation to bridge laboratory successes with industrial scalability. A critical limitation lies in the recovery of fine-grained particles ($d_{80} < 30 \mu\text{m}$), where laboratory tests reveal a 15% reduction in recovery efficiency compared to coarser fractions, attributed to inadequate bubble–particle attachment dynamics. This issue demands the integration of nanobubble flotation technologies, which enhance hydrodynamic interactions and bubble–particle collision probabilities. Concurrently, the reliance on conventional cationic amine collectors, such as dodecylamine (DDA), introduces operational challenges under acidic conditions, including accelerated equipment corrosion that necessitates costly corrosion-resistant materials like titanium alloy reactors, elevating maintenance frequency by 30% in industrial trials [43]. While Gemini surfactants (e.g., HBDB) offer a promising alternative by reducing reagent consumption by 50% [17], their synthesis costs remain economically prohibitive, highlighting the urgency to develop cost-effective, biodegradable collectors with pH-responsive functionalities to minimize environmental impacts.

Industrial-scale integration further complicates these challenges, as evidenced by a 500 ton per day (tpd) facility employing hybrid electrostatic pre-concentration and flotation, which achieved a 12% improvement in Li_2O recovery [48]. However, the suboptimal recovery of ultrafine particles ($<30 \mu\text{m}$) persists, necessitating advancements in grinding strategies and reagent regimes tailored to fine-particle systems. To address these multi-faceted hurdles, a holistic approach combining nanobubble-enhanced flotation systems, green collector development, and machine-learning-driven process optimization is essential. For instance, AI models could dynamically adjust collector dosages and pH levels in

response to real-time mineralogical variations, while nanobubbles improve the hydrophobicity and attachment kinetics of ultrafine particles. Such innovations promise to enhance both the economic viability and sustainability of lepidolite flotation, positioning it as a cornerstone for meeting the growing global demand for lithium resources.

3.2. Optical Sorting

Optical sorting utilizes color and reflectivity differences between lepidolite and gangue minerals. Advanced sensors and machine-learning algorithms are increasingly being integrated into sorting systems to enhance accuracy and throughput [18,61].

As particles pass through the detection zone, they are illuminated by light sources (e.g., visible light, near-infrared/NIR, or X-ray). Advanced sensors capture real-time data:

- Color sensors distinguish minerals by surface color (e.g., separating diamonds from kimberlite).
- NIR sensors identify chemical composition via spectral absorption (e.g., quartz vs. feldspar).
- X-ray transmission (XRT) or laser-induced breakdown spectroscopy (LIBS) detect internal density or elemental composition.

However, its effectiveness depends on particle size uniformity and detectable property contrasts. Dust, moisture, or overlapping particles may reduce accuracy. Despite this, its eco-friendliness and adaptability make it a growing solution in lepidolite processing.

4. Metallurgy

Based on the medium and processing techniques, lithium extraction methods from lepidolite can be classified into acid, alkali, salt, pressure-cooking, and other emerging methods [62–64]. The relationship between Gibbs free energy (ΔG) and temperature for key reactions involving Li_2O under these methods was analyzed using HSC Chemistry 9.5 software [65], as shown in Figure 14. According to thermodynamic principles, a reaction is spontaneous when $\Delta G < 0$, and its spontaneity increases as ΔG becomes more negative.

From analysis of the figure, the following recommendations emerge. (1) Low-temperature processes ($<473\text{ K}$): Acid, fluorochemical, and alkali dissolution methods are suitable for lower-temperature lithium extraction. (2) High-temperature processes: Sulfation and chlorination roasting require elevated temperatures for optimal efficiency. (3) Ultra-high-temperature processes ($>1131\text{ K}$): Limestone roasting demands extremely high temperatures to achieve spontaneity. (4) Pressure-cooking processes: Both lime milk and soda methods are constrained by the operational limits of autoclaves, requiring temperatures below 473 K .

By integrating thermodynamic insights with industrial applications, the selection of optimal processes for lithium extraction from lepidolite can be guided to balance efficiency and practicality.

Hydrometallurgical processes provide a versatile approach for extracting lithium from lepidolite ores. These methods typically involve leaching lithium into solution using acid or alkali, followed by selective separation and purification. The process's success hinges on understanding the solubility behavior, reaction kinetics, and impurity control mechanisms.

Pyrometallurgical methods involve the high-temperature processing of lithium-bearing minerals such as lepidolite to extract lithium. These methods rely on thermal activation to disrupt the mineral structure, making lithium more amenable to subsequent chemical processing or direct recovery. Given the complexities of lepidolite ore, often accompanied by feldspar, quartz, and iron-bearing minerals, pyrometallurgical processes must be tailored to address the unique challenges posed by gangue minerals and impurities.

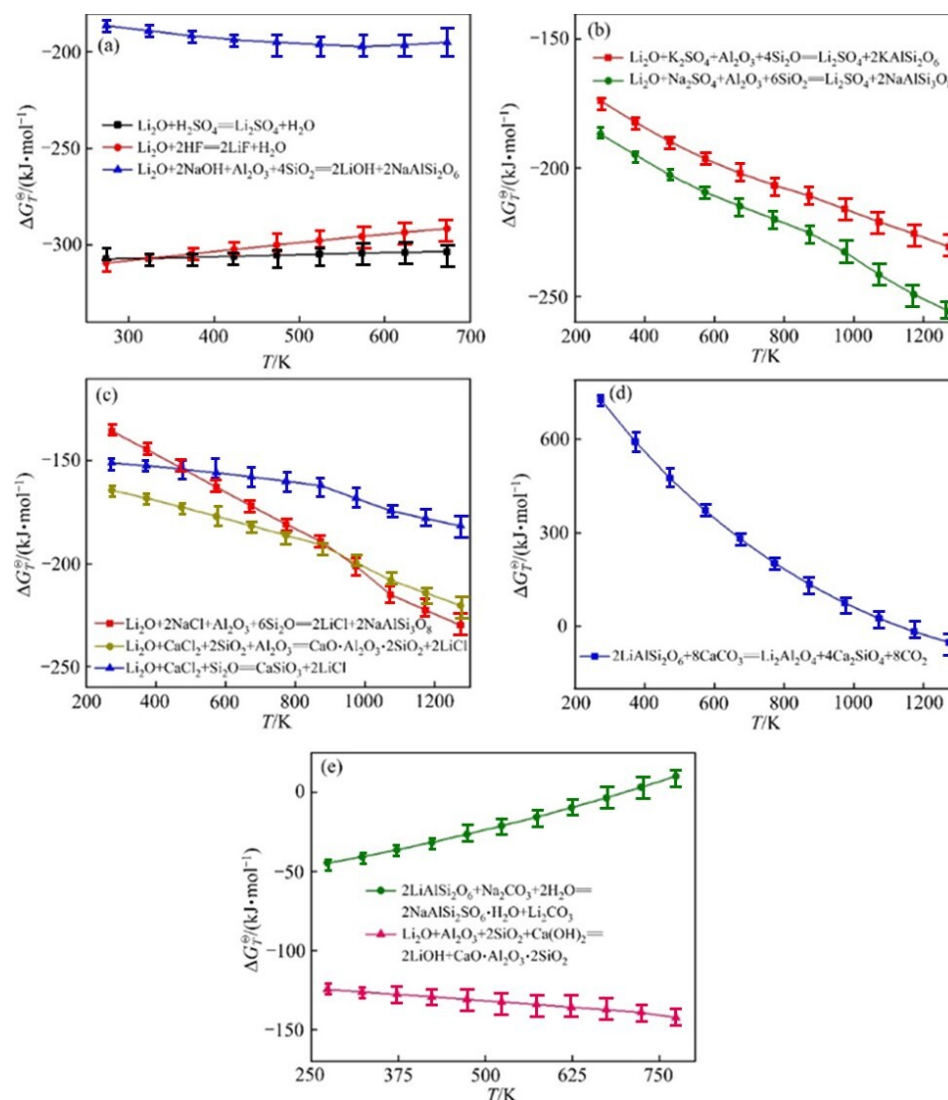


Figure 14. Relationship between change of Gibbs free energy of major chemical reactions of lepidolite under different lithium extraction processes with time: (a) Acid leaching process: Dynamic evolution of ΔG with reaction progress. (b) Roasting-leaching pathway: Time-dependent Gibbs energy dissipation pattern. (c) Hydrothermal treatment: Thermodynamic stability transitions over leaching duration. (d) Chloride volatilization: Free energy minimization kinetics. (e) Electrochemical extraction: Transient Gibbs energy fluctuations during ion migration [65].

However, the integration of hydrometallurgical and pyrometallurgical methods of lithium extraction from lepidolite has emerged as a prominent strategy due to the synergistic advantages offered by combining these approaches. Pyrometallurgical processes, such as roasting, serve to thermally activate the ore, disrupting the robust silicate structure of lepidolite and converting lithium into water-soluble or acid-soluble phases. This step enhances the efficiency of subsequent hydrometallurgical processes, which then selectively extract and purify lithium.

By addressing the challenges of gangue minerals like feldspar and quartz, the combined approach optimizes lithium recovery rates, reduces reagent consumption, and minimizes energy costs. For example, sulfation roasting followed by water or acid leaching has proven highly effective for complex ores, as it allows for the efficient removal of impurities while maximizing lithium extraction. Similarly, carbonization or chlorination roasting can produce lithium salts that are more easily processed in subsequent wet chemical steps.

4.1. Direct Leaching Methods

4.1.1. Acid Leaching

Acid leaching dissolves lithium using mineral acids such as sulfuric acid, hydrochloric acid, or mixed acids like HF combined with H_2SO_4 . Sulfuric acid leaching is the most widely adopted method due to its effectiveness in converting lithium into water-soluble lithium sulfate. Hydrochloric acid leaching produces lithium chloride, which is easier to purify but poses challenges due to its high corrosivity. Mixed acid systems enhance the dissolution of the silicate matrix, significantly improving lithium recovery to over 95%, but the toxic and corrosive nature of HF requires advanced precautions. Some of the different acid leaching process techniques are displayed in Table 2.

Lei et al. [66] investigated the leaching performance and mechanisms of lithium (Li), rubidium (Rb), and cesium (Cs) from lepidolite containing Rb and Cs using sulfate, chloride, and composite salt roasting systems. The study revealed that the sulfate system ($\text{Na}_2\text{SO}_4 + \text{CaSO}_4$) achieved a higher lithium recovery efficiency, with a leaching rate of 92.53%, while the recovery rates for Rb and Cs were relatively low, at 29.02% and 40.51%. The high lithium recovery is attributed to Na^+ in the sulfate system facilitating ion exchange with Li^+ in the mineral, forming water-soluble lithium sulfate (Li_2SO_4), while maintaining low impurity dissolution. In contrast, the chloride system ($\text{NaCl} + \text{CaCl}_2$) was more effective for extracting Rb and Cs, with recovery rates reaching 96.13% and 94.86%, respectively, though the lithium recovery was lower at 87.54%. The effectiveness of the chloride system arises from the formation of highly soluble RbCl and CsCl.

Additionally, the reaction between Ca^{2+} and Rb or Cs is thermodynamically more favorable (lower Gibbs free energy) than with Na^+ . The molten state of chloride salts further enhances the penetration of Cl^- into the mineral lattice, disrupting feldspar structures and facilitating the release of Rb and Cs.

Based on these findings, the proposed composite salt system ($\text{NaCl} + \text{CaSO}_4$) combines the advantages of sulfate and chloride systems, achieving efficient multi-element extraction. Under optimized conditions—880 °C roasting temperature, 45 min roasting time, and a mass ratio of 1:0.7 (ore to additive)—the leaching rates of Li, Rb, and Cs reached 94.52%, 92.03%, and 93.56%, respectively. The composite system leverages Na^+ in the sulfate component to promote the formation of Li_2SO_4 , while Cl^- in the chloride component facilitates the production of highly soluble RbCl and CsCl. This combination enhances both ion exchange and lattice disruption, providing an effective pathway for the comprehensive recovery of lithium, rubidium, and cesium.

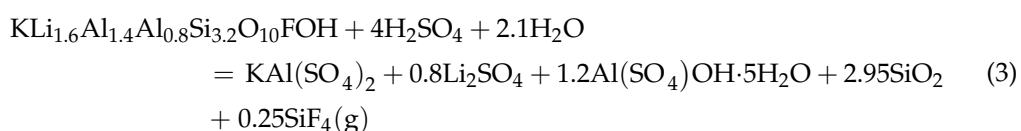
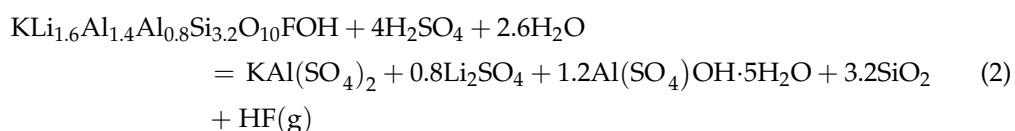
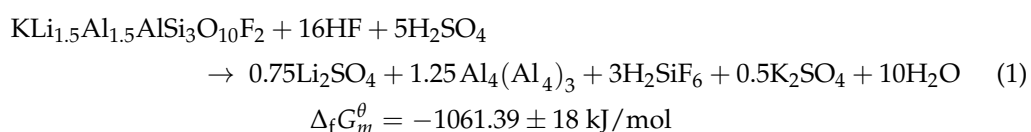
Zhang et al. [67] developed an energy-efficient sulfuric acid baking and water leaching method for the simultaneous extraction of lithium (Li), rubidium (Rb), and cesium (Cs) from lepidolite concentrate. Compared to conventional high-temperature roasting or mechanical activation methods, this process reduces energy consumption while achieving high recovery rates under moderate conditions. The study systematically optimized baking and leaching parameters and analyzed the reaction mechanisms. The optimized process employed 85 wt.% H_2SO_4 , a baking temperature of 200 °C, a baking time of 4 h, an acid-to-ore mass ratio of 1.7:1, a leaching temperature of 85 °C, and a particle size of 88% below 74 μm . Under these conditions, the recovery rates for Li, Rb, and Cs reached 97.1%, 96.0%, and 95.1%, respectively. Baking phase: Sulfuric acid reacts with lepidolite to form water-soluble sulfates (e.g., Li_2SO_4 , $\text{KAl}(\text{SO}_4)_2$, and $\text{Al}(\text{SO}_4)(\text{OH})\cdot 5\text{H}_2\text{O}$) and volatile fluorides (HF and SiF_4). Leaching phase: The high solubility of Li_2SO_4 ensures efficient lithium recovery, while higher leaching temperatures (>85 °C) are necessary to dissolve $\text{RbAl}(\text{SO}_4)_2$ and $\text{CsAl}(\text{SO}_4)_2$ due to their lower solubility. This method provides a green and economically viable approach for the efficient and simultaneous recovery of Li, Rb, and Cs from lepidolite, offering significant potential for industrial applications [68–72].

Table 2 summarizes the key advantages, limitations, and industrial viability of major acid systems for lepidolite leaching, emphasizing reagent cost, corrosion control, and residue management.

Table 2. Comparative analysis of acid systems for lepidolite leaching.

Acid System	Efficiency (Li Recovery)	Reagent Cost	Corrosion Control	Residue Handling	Industrial Viability
H ₂ SO ₄	90–97% [54,66]	Moderate	Requires corrosion-resistant reactors (e.g., Hastelloy, glass-lined steel)	Slag valorization (e.g., cement substitution); SO _x scrubbing (NaOH wet scrubbers)	High (mature technology)
HCl	85–95% [68,72]	High	Limited material compatibility (titanium or tantalum required)	High chloride waste; requires neutralization (Ca(OH) ₂)	Moderate (niche applications)
HF/H ₂ SO ₄	95–98% [69,70]	Very High	PTFE-lined reactors mandatory; HF handling increases operational complexity	Fluoride sludge (CaF ₂ precipitation); hazardous waste disposal	Low (environmental risks)
H ₂ SiF ₆	95–98% [70]	High	Moderate corrosion (stainless steel acceptable with short exposure)	Fluorosilicate residues; requires alkaline neutralization	Emerging (needs scaling)

Fluorine additives like hydrofluoric acid and calcium fluoride have been proposed to enhance the lithium extraction from lepidolite at a much lower temperature without high-temperature roasting [73–75]. The fluorine additives participate in the dissolution by forming HF molecules with sulfuric acid, which are the actual reaction components of the fluorine additives [76]. Guo used an acid mixture of hydrofluoric acid and sulfuric acid (HF/H₂SO₄) as a lixiviant to theoretically investigate the reaction mechanism of the improved sulfuric acid method [70]. The structure of lepidolite was destroyed by HF and then further reacted with H₂SO₄ to convert Li and Al into soluble sulfates. The total reaction equation is shown in Equations (1)–(3) as stepwise reactions. About 98.6% of Li, along with 91.7% of Al, 90.3% of Rb and 97.8% of Cs, has been leached at 85 °C.



The acid leaching of lepidolite, while critical for lithium extraction, imposes significant environmental burdens that necessitate comprehensive mitigation strategies. A primary concern lies in its carbon footprint, driven by energy-intensive processes such as ore roasting (200–300 °C) and fossil fuel-dependent acid production. Studies indicate that producing 1 ton of lithium carbonate equivalent (LCE) via this method emits 5–7 tons of CO₂, though transitioning to renewable energy sources like solar–thermal systems could

reduce emissions by 30–40%. Concurrently, the water footprint of acid leaching remains substantial, with 10–15 m³ of water consumed per ton of ore and effluent pH often below 2. Advanced water recycling technologies, such as membrane distillation integrated with neutralization, offer solutions by achieving over 90% water recovery while minimizing freshwater dependency.

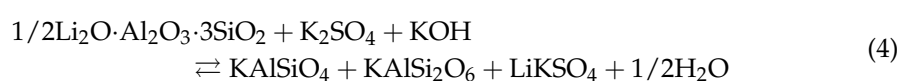
Environmental risks extend to toxic leachates containing heavy metals like aluminum (50–200 mg/L Al³⁺) and iron (10–50 mg/L Fe²⁺), which threaten aquatic ecosystems. Rigorous risk assessment tools, including toxicity characterization leaching procedures (TCLP) and hazard quotient (HQ) models, are essential for quantifying contamination potential and guiding remediation efforts. Solid waste management further compounds challenges, as silica-rich slags (20–30% of processed ore) traditionally landfilled pose groundwater contamination risks through residual acid and metal leaching. Sustainable alternatives are emerging, such as co-processing slags in construction materials (10–15% cement substitution), which not only reduce clinker demand but also immobilize heavy metals via geopolymerization, yielding compressive strengths of 35–40 MPa—values compliant with industrial standards. Additionally, hydrometallurgical reprocessing using chelating agents like EDTA enables the recovery of over 85% aluminum and iron from slags, transforming waste into secondary resources.

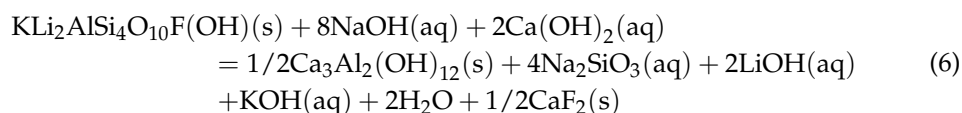
Acidic effluent treatment remains a critical focus, where conventional neutralization–precipitation methods generate hazardous sludge (5–10% of effluent volume). Innovations like selective ion exchange with functionalized resins (e.g., sulfonated polystyrene) address this by preferentially adsorbing Li⁺ and H⁺, enabling acid regeneration and reducing sulfuric acid consumption by 20–30%. Electrochemical techniques, such as electrodialysis or capacitive deionization (CDI), further enhance efficiency by concentrating lithium from dilute streams (<100 mg/L) to over 1000 mg/L, optimizing downstream recovery.

Gaseous emissions, particularly sulfur oxides (SO_x) and hydrogen fluoride (HF), demand multi-stage control systems. Dry adsorption techniques, such as lime (CaO) injection, neutralize HF into stable calcium fluoride (CaF₂), while activated carbon filters capture SO₂. Wet scrubbing with alkaline solutions (e.g., NaOH) converts SO_x into marketable sodium sulfate (Na₂SO₄), with real-time monitoring via Fourier-transform infrared (FTIR) spectroscopy ensuring compliance with stringent emission thresholds (<50 mg/Nm³ SO₂, <5 mg/Nm³ HF). Together, these strategies underscore the potential to align lithium production with circular economy principles, balancing operational efficiency with environmental stewardship.

4.1.2. Alkali Leaching

Alkali leaching extracts lithium from lepidolite by reacting it with a concentrated alkaline solution (e.g., NaOH/KOH) under elevated temperatures. Hydroxide ions (OH[−]) disrupt the mineral's layered structure, dissolving lithium as soluble Li⁺ ions while converting silica into soluble silicates. Aluminum and other impurities often precipitate as hydroxides, enabling subsequent lithium recovery via filtration and purification. NaOH or KOH is usually adopted to selectively dissolve lithium while precipitating impurities such as silica and aluminum. The reaction equations are shown in Equations (4)–(6). By forming insoluble hydroxides, alkali leaching simplifies the subsequent purification steps [77–79]:





However, the method requires high temperatures and pressures (180–250 °C) to achieve satisfactory recovery, making it energy-intensive and demanding specialized equipment.

While acid leaching dominates lepidolite processing due to its high efficiency (90–98% Li recovery) and scalability, alkali leaching is niche but favored where ultra-high lithium purity or strict environmental compliance is critical. Alkali systems (NaOH/KOH) selectively dissolve lithium while precipitating silica/aluminum, simplifying purification and avoiding toxic byproducts like HF/SO_x. For example, the Livent Corporation employs alkali methods for silicate minerals under high temperatures (180–250 °C) to recover > 85% Li, yielding marketable silicates (e.g., Na₂SiO₃). However, alkali leaching's high energy demands, specialized equipment (titanium reactors), and lower recovery rates (70–85%) limit its industrial adoption. Thus, acid leaching remains mainstream, while alkali methods are reserved for contexts prioritizing purity or circular byproduct utilization.

4.1.3. Bio-Leaching

Bio-leaching utilizes microorganisms, particularly sulfur-oxidizing bacteria, to create an acidic environment that facilitates lithium extraction. This approach is highly sustainable, as it uses naturally occurring microbial processes to generate leaching agents. However, its slow reaction kinetics and sensitivity to environmental conditions limit its scalability for industrial applications [80].

Wang et al. [81] compared the bioleaching efficiencies of autotrophic bacterium AF and heterotrophic bacterium *Bacillus mucilaginosus* (B.M.) on lithium silicate ores with three different crystal structures: chain-structured spodumene, layered-structured lepidolite, and ring-structured elbaite. The results demonstrated that AF exhibited a higher leaching efficiency due to its ability to oxidize Fe²⁺ and S, which actively disrupted the mineral lattice, whereas BM primarily relied on passive mechanisms, such as organic acid secretion and adsorption. The leaching efficiencies varied significantly with crystal structure, following the order of layered (lepidolite) > chain (spodumene) > ring (elbaite). AF achieved the highest leaching rate for lepidolite at 9.06%, significantly outperforming BM. The study highlights the importance of crystal structure in determining mineral stability and bioleaching efficiency. While the research provides valuable insights into the decomposition mechanisms of different bacteria, the relatively low leaching rates and prolonged experimental duration suggest that further optimization is needed to meet industrial requirements.

Xu et al. [82] investigates the influence of chemical surfactants (such as sodium dodecyl sulfate, SDS, and Tween-20) and a biological surfactant (rhamnolipid) on bacterial adsorption and lithium leaching efficiency during the bioleaching of lepidolite. The mechanism is shown in Figure 15. The results showed that rhamnolipid significantly reduced the contact angle of the mineral surface from 75.22° to 6.8°, enhancing bacterial adhesion and increasing the contact area between bacteria and the mineral. FTIR analysis revealed that surfactants weakened the Si–O and Al–O chemical bonds in lepidolite, promoting the breakdown of its lattice structure. The leaching experiments demonstrated that the addition of rhamnolipid achieved a lithium release of 6.8 mg/L, an increase of over 30% compared to the group without surfactants. This study highlights the mechanism by which surfactants reduce interfacial tension and improve bacterial adsorption to facilitate lithium extraction, providing new insights into developing efficient and green bioleaching technologies. However, the study lacks detailed evaluation of the economic feasibility of rhamnolipid and its performance in complex ore systems, which require further exploration for industrial-scale applications.

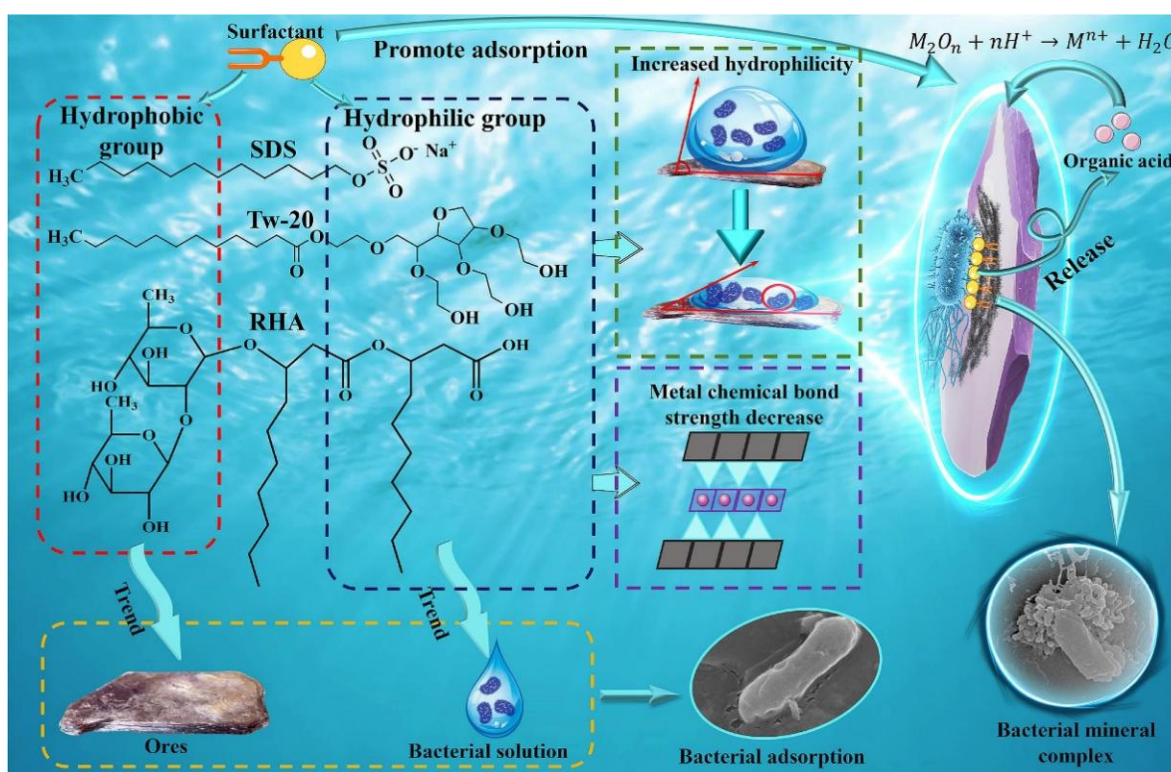


Figure 15. Mechanism of surfactant effect on bacterial adsorption during bioleaching process [82].

Duan et al. [45] investigated lithium bioleaching from three lithium-bearing minerals, jadarite, spodumene, and lepidolite, using the acidophilic bacterium *Acidithiobacillus ferrooxidans* (A.F.). The experiments revealed that the bacterial oxidation of Fe^{2+} and S contributed significantly to lithium release, particularly from jadarite, where lithium concentrations reached 120 mg/L, a 50% increase compared to abiotic controls. Spodumene and lepidolite showed lower leaching efficiencies, with maximum lithium recovery rates of 14% and 11%, respectively. Microscopic analyses indicated that biofilm formation and bacterial attachment were critical to enhancing leaching efficiency, as they facilitated the breakdown of mineral lattices. The study highlights the potential of *Acidithiobacillus ferrooxidans* (A.F.) for lithium extraction from unconventional sources, although the leaching rates remain lower than those required for industrial application. Future research should explore the integration of bioleaching with pre-treatment processes to enhance overall efficiency.

Zhao et al. [83] focused on the leaching performance of *Raoultella* sp. Z107 and *BM* on lithium silicate ores, including spodumene and lepidolite. The results indicated that *Raoultella* sp. Z107 produced high concentrations of organic acids, particularly lactic acid (up to 11 g/L), which significantly contributed to acid etching and lattice distortion. In contrast, *B. mucilaginosus* secreted large amounts of polysaccharides (14.84 mg/L), facilitating bacterial adhesion and mineral weathering. Lepidolite exhibited a higher leaching efficiency than spodumene due to its layered structure, which is more susceptible to bacterial metabolites. The combination of acid corrosion and complexation effects by organic acids was more effective than the singular impact of polysaccharides. This study advances the understanding of how bacterial metabolic diversity influences mineral decomposition and highlights the potential of tailoring bacterial systems for targeted applications. However, the study notes the need for improved strain adaptability and faster leaching kinetics for practical use.

Sedlakova-Kadukova et al. [78] compared the lithium recovery performance of three bioleaching systems: a bacterial consortium of *Acidithiobacillus ferrooxidans* and *Acidithiobacil-*

lus thiooxidans, the fungus *Aspergillus niger*, and the yeast *Rhodotorula mucilaginosa*. The results showed that the bacterial consortium achieved the highest lithium extraction, dissolving 11 mg/L of lithium over 336 days. Although fungal and yeast systems were faster, requiring only 40 days, their extraction efficiencies were lower, with *Aspergillus niger* (*A. niger*) achieving 0.2% and *Rhodotorula mucilaginosa* (*R. mucilaginosa*) achieving 1.1%. XRD analyses indicated significant differences in mineral alterations caused by bacterial versus fungal leaching mechanisms. Bioaccumulation was a dominant process for *A. niger* and *R. mucilaginosa*, with 92% and 77% of extracted lithium retained in biomass, respectively. This study highlights the potential of bacterial consortia for higher leaching efficiencies and suggests a two-step bioleaching process, utilizing fungal systems first followed by bacterial consortia, to improve kinetics and yields. However, the long duration and low efficiency of single-step processes remain challenges for industrial scalability.

The comparison of bioleaching and hydrometallurgy is shown in Table 3. From the perspectives of efficiency and reaction kinetics, bioleaching relies on microbial metabolic activities to decompose minerals, resulting in inherently slow reaction rates. For instance, the study by Xu et al. [82] demonstrated that the addition of a biosurfactant (rhamnolipid) increased lithium release to only 6.8 mg/L, with leaching cycles spanning days to months (e.g., 336 days for bacterial leaching in Sedlakova-Kadukova's work [78]). Mineral crystal structure significantly influences efficiency; layered lepidolite (e.g., 11% leaching efficiency in Duan et al.'s experiment) is more susceptible to decomposition compared to chain- or ring-structured minerals, though its performance remains far below industrial requirements. In contrast, hydrometallurgy employs strong acids (e.g., sulfuric acid) or bases to rapidly dissolve minerals, achieving short reaction times (typically hours to days) and high leaching efficiencies (>80%). For example, conventional acid leaching demonstrates markedly superior lithium extraction efficiency for lepidolite compared to bioleaching, albeit requiring high-temperature and high-pressure conditions.

Table 3. Different applications of acid leaching process techniques.

Method/Route	Condition	Efficiency	Environmental Concerns
Hydrochloric acid (HCl) [68]	6.21 mol/L HCl at 381 K for 8 h, followed by calcination at 623 K	95.7% of Li recovered	High HCl usage; manageable Al/F emissions
Stepwise heat treatment HF + H ₂ SO ₄ adopting PTFE reactor	120 °C for 3 h and 200 °C for 6 h	98.6% of Li leached and 0.68% F in liquid phase	remove fluorine and unreacted sulfuric acid more effectively
HF + H ₂ SO ₄ adopting stirred tank reactor [69]	85 °C, 3 h, analytical pure HF and H ₂ SO ₄	98% of Li leached	Toxic HF; fluorine control required
H ₂ SO ₄ +H ₂ SiF ₆ adopting continuous tubular reactor [70]	80 °C, 15 min, 15 wt.% H ₂ SiF ₆ , 70 wt.% H ₂ SO ₄ , Ore:H ₂ SO ₄ :H ₂ SiF ₆ = 1:0.8:1.6	97.9% of Li leached	Fluorine residues; less hazardous than HF
H ₂ SO ₄ baking and water leaching [54]	200 °C, 4 h, 85 wt.% H ₂ SO ₄ , concentration: acid = 1.7:1, 85 °C leaching	97.1% of Li, 96.0% of Rb and 95.1% of Cs leached	
H ₂ SO ₄ baking, air roasting, water leaching, Li carbonation precipitation (CO ₂) reaction, Rb, Cs solvent extraction [71]	300 °C, 5 h, 98 wt.% H ₂ SO ₄ concentration: acid = 1.7:1, 800 °C, 2 h, 80 °C leaching	90.5% of Li, 91.2% of Rb, and 89.4% of Cs leached	High-efficiency sulfuric acid recovery reduces alkali consumption and waste discharge
Chlorination roasting and water leaching [72]	950 °C, 1 h, 25% CaCl ₂ , 20% Ca(OH) ₂ , 25 °C, 2 h, 2:1 mL/g, 300 rpm leaching	85.5% of Li, 80.9% of K, 94.5% of Rb, 90.2% of Cs extracted	Reduce the dosage of chlorinating agent and the volatilization of chlorination

Regarding environmental impact and sustainability, bioleaching minimizes the use of hazardous chemicals by leveraging microorganisms or biosurfactants (e.g., rhamnolipid), resulting in low-toxicity wastewater. Wang et al. highlighted that autotrophic bacteria such as *Acidithiobacillus ferrooxidans* generate acids indirectly through sulfur or iron oxidation, thereby reducing environmental burdens. Conversely, hydrometallurgy demands substantial quantities of strong acids/bases (e.g., H_2SO_4 , NaOH), generating high-salinity wastewater and heavy metal pollutants that necessitate complex post-treatment (e.g., neutralization, precipitation). Additionally, the synthesis and transportation of chemical reagents exacerbate carbon footprints.

In terms of cost and economic feasibility, bioleaching incurs low operational costs (due to microbial recyclability) but requires high initial investments (e.g., bioreactors, microbial cultivation). For instance, the organic acid concentrations (e.g., 11 g/L lactic acid) required by *Raoultella* sp. Z107 in Zhao et al.'s study may hinder large-scale application due to synthesis expenses. Hydrometallurgy, while mature and suitable for mass production, involves significant reagent consumption (e.g., acids account for 30–50% of costs), with total costs being vulnerable to price fluctuations.

Technologically, bioleaching exhibits sensitivity to ore properties. Layered lepidolite, being more vulnerable to microbial metabolites (e.g., organic acids), shows a relatively higher efficiency, whereas complex ores (e.g., quartz- or feldspar-bearing systems) pose challenges. Furthermore, microbial activity is strictly constrained by pH and temperature (e.g., *Acidithiobacillus ferrooxidans* requires $\text{pH} < 2$). Hydrometallurgy, however, adapts to diverse ore types by adjusting acid concentration, oxidants (e.g., H_2O_2), or temperature. For example, sulfuric acid roasting can process high-silica lepidolite, albeit at elevated energy costs.

For industrial scalability, bioleaching faces bottlenecks such as slow reaction rates, microbial instability, and challenges in reactor design (e.g., mass transfer limitations, temperature control). Hydrometallurgy, despite its technological maturity, confronts growing environmental pressures to mitigate chemical pollution and enhance sustainability. The comparison between bioleaching and hydrometallurgy is shown in Table 4.

Table 4. Comparison of bioleaching and hydrometallurgy.

Metric	Bioleaching	Hydrometallurgy
Efficiency	Low (<20% Li recovery rate), slow process	High (>80% Li recovery rate), rapid reaction
Environmental Impact	High (low carbon footprint, biodegradable reagents)	Low (chemical pollution risks, high energy consumption)
Cost	High initial investment, low operational cost	High reagent/energy costs, mature infrastructure
Technological Maturity	Laboratory stage, industrial challenges remain	Widely industrialized, mature processes
Ore Compatibility	Prefers layered structures, low impurity content	High adaptability, suitable for complex ores

To address the limitations of conventional bioleaching and hydrometallurgical methods, we propose the following synergistic optimization strategies:

- Hybrid Bio-Chemical Process**
- A sequential *bio-pre-leaching* step can be employed to soften mineral structures via silicate decomposition by *Acidithiobacillus ferrooxidans* (A.F.), followed by a short-duration acid leaching process to enhance efficiency. For instance, Zhao et al. demonstrated that organic acids (e.g., lactic acid) secreted by *Raoultella* sp. Z107 synergistically accelerate lithium dissolution by inducing lattice distortion and acid etching.
- Intelligent Surfactant Design**
Developing **bio-compatible chemical surfactants** (e.g., SLG-Gemini hybrid formu-

lations) could reduce interfacial tension while promoting microbial adhesion. This approach mimics the rhamnolipid mechanism reported by Xu et al., where biosurfactants significantly lowered mineral surface hydrophobicity (contact angle reduction from 75.22° to 6.8°), thereby optimizing bacterial–mineral interactions.

4. Genetically Engineered Microbial Strains

Enhancing the Fe/S oxidation capacity of native strains (e.g., *A.F.* via CRISPR-Cas9 editing) could expedite leaching kinetics. Duan et al. observed that Fe²⁺ oxidation by *AF* contributed to 50% of lithium release from jadarite, suggesting that engineered strains with amplified oxidative pathways could significantly improve process efficiency.

6. Green Hydrometallurgical Systems

Replacing traditional strong acids with **ionic liquids** (e.g., imidazolium-based solvents) or **low-toxicity lixiviants** (e.g., citric acid) could balance extraction efficiency with environmental sustainability. Wang et al. highlighted that heterotrophic bacteria like *Bacillus mucilaginosus* (*BM*) secrete polysaccharides and organic acids, providing a biochemical blueprint for designing eco-friendly leaching agents.

4.2. Thermal Activation Methods

4.2.1. Sulfation Roasting

Sulfation roasting involves heating lepidolite with sulfates, such as potassium sulfate or sulfuric acid, at 750–850 °C to produce lithium sulfate. This method effectively converts lithium into a soluble phase, facilitating easy leaching in subsequent steps. However, the process generates significant SO₂ emissions, necessitating advanced gas scrubbing systems.

Zhai et al. [84] proposed a novel lithium extraction method based on low-temperature synergistic roasting of α-spodumene and lepidolite, addressing the challenges of high energy consumption and environmental impact in conventional processes. Under optimal conditions, roasting at 900 °C for 60 min with 25% lepidolite addition achieved a lithium recovery rate of 97.60%, significantly reducing the phase transformation temperature of α-spodumene from 1050 °C to 900 °C. The study revealed that fluorine released from lepidolite disrupted the Si–O, Al–O, and Li–O bonds in α-spodumene, facilitating its phase transformation. Additionally, the process minimized impurity leaching, with Na, K, Al, and Si leaching rates at 50.96%, 10.96%, 5.75%, and 0.30%, respectively, enabling cleaner lithium extraction without additives. Sulfuric acid roasting at 230 °C for 20 min and subsequent water leaching at 45 °C with a liquid-to-solid ratio of 2:1 mL/g further optimized the process. This method not only reduces energy consumption but also enhances industrial feasibility by requiring minimal equipment modifications, while the role of other fluorine sources and further cost optimizations warrant future exploration.

4.2.2. Salt Roasting

Salt roasting employs chlorides like NaCl or CaCl₂ at 600–700 °C to form lithium chloride, which is easily leachable in water. This technique operates at lower temperatures than sulfation roasting, reducing energy consumption. Recent studies have explored closed-loop systems to recycle chloride residues (e.g., CaCl₂) into industrial processes such as cement production or wastewater treatment, reducing both waste generation and raw material consumption [51]. Additionally, the development of bio-derived chloride alternatives (e.g., choline chloride) has shown potential to mitigate corrosion while maintaining leaching efficiency under milder conditions, aligning with green chemistry principles. Nevertheless, managing corrosive salt residues remains a significant challenge, requiring specialized equipment.

Park et al. [77] simplified and improved this process by using only sodium sulfate (Na₂SO₄) at a molar ratio of 1:6. By reducing the lepidolite particle size to 45 μm and low-

ering the roasting temperature to 750 °C, the lithium extraction efficiency was significantly increased to 97.7%. These improvements stem from (1) enhanced contact between reagents due to reduced particle size, which increased reaction efficiency; (2) the excess sodium sulfate, promoting the thorough formation of LiNaSO_4 . Compared to Yan et al. [9,10,85], the study by Park et al. achieving a higher extraction efficiency, lower energy consumption, and greater industrial applicability.

Yan [9,10,86]'s study represents an improvement and optimization over the work by Park et al. on extracting lithium from lepidolite using sulfation roasting and water leaching. Yan et al. initially proposed a process involving sodium sulfate (Na_2SO_4), potassium sulfate (K_2SO_4), and calcium oxide (CaO) at a mass ratio of 1:0.5:0.1:0.1, roasted at 850 °C for 30 min. The process successfully achieved a lithium extraction efficiency of 91.61%, with LiNaSO_4 as the primary soluble product, alongside byproducts such as CaF_2 and $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$. While the inclusion of multiple additives improved the reaction outcomes, the high roasting temperature and complexity of byproduct formation increased energy consumption and process difficulty.

Su et al. [79] investigated the roasting process of lepidolite using different additives, including single potassium sulfate (K_2SO_4), single potassium hydroxide (KOH), and their mixtures, focusing on lithium extraction efficiency and the recovery of valuable metals such as potassium (K), rubidium (Rb), and cesium (Cs). Single K_2SO_4 roasting, under the conditions of 900 °C roasting temperature, 2 h duration, and a 1.5:1 additive-to-ore mass ratio, achieved a lithium extraction efficiency of 97.41% and a potassium recovery rate of 85.66%. The ion-exchange reaction of K_2SO_4 led to the formation of soluble LiKSO_4 , while byproducts such as KAlSiO_4 and KAlSi_2O_6 remained insoluble. Single KOH roasting validated its strong alkalinity in lattice destruction but resulted in a lithium extraction efficiency of 92.8% and a lower potassium recovery rate compared to K_2SO_4 -based methods. This is attributed to the formation of insoluble byproducts like KAlSiO_4 , which locked portions of lithium and potassium, while increasing silicon and aluminum in the leachate, complicating the separation process. The K_2SO_4 + KOH mixed additive achieved a lithium extraction efficiency of 92.78% and a potassium recovery rate of 81.72%. The mixed system significantly improved the solubility of rubidium and cesium, making it a promising method for multi-element recovery. Meanwhile, single K_2SO_4 remains the most efficient and practical method for lithium extraction due to its high efficiency, low impurities, and simplicity.

4.2.3. Carbonation Roasting

This method uses alkali carbonates (e.g., Na_2CO_3 or K_2CO_3) at 800–900 °C to directly produce lithium carbonate, a commercially valuable compound. Carbonation roasting is advantageous for its simplicity in downstream processing but is energy-intensive and less suitable for ores with significant amounts of coexisting rubidium or cesium.

4.3. Microwave-Assisted Roasting

Microwave roasting selectively targets lepidolite, thereby reducing reaction times and energy consumption. In a study by Zhang et al. [87], microwave external fields were utilized to enhance lithium extraction and optimize the roasting process. The microwave-enhanced roasting technique significantly shortened the heating duration from 43 min to 20 min, resulting in a notable decrease in energy consumption compared to traditional roasting methods. Experimental findings indicated that the optimal conditions were ferrous sulfate/potassium sulfate/calcium oxide/ore = 2:0.6:0.1:1, with a roasting temperature of 775 °C and a roasting time of 2 h, achieving a lithium leaching efficiency of 95.9%. Research into dielectric properties revealed that the addition of sulfate enhances the mi-

microwave absorption capabilities of lepidolite, enabling rapid heating within the microwave field [87]. Moreover, uniform microwave heating minimizes sample melting and adhesion, producing a looser clinker structure and thereby improving lithium leaching efficiency. The microwave-enhanced sulfate roasting technology is of substantial significance for the exploration of lithium extraction from lepidolite [88].

Jiang et al. [71] proposed a microwave-enhanced sulfate roasting method to extract lithium from lepidolite, utilizing ferrous sulfate and potassium sulfate as additives. This technique enhances lithium leaching efficiency while simultaneously lowering energy consumption and shortening processing time. When optimized conditions are applied, especially a ratio of ferrous sulfate/potassium sulfate/calcium oxide/ore of 2:0.6:0.1:1, a roasting temperature of 775 °C, and a roasting duration of 2 h, the lithium leaching efficiency achieves 95.9%, which is approximately 5% higher than that obtained through conventional roasting methods. Microwave heating notably reduces the heating time from 43 min to 20 min and decreases energy consumption by 26.9%. The even heating provided by microwaves prevents localized overheating and sample adhesion, thereby enhancing process stability. Mechanistic investigations show that the incorporation of sulfates boosts lepidolite's microwave absorption capabilities, facilitating rapid mineral phase transformations and yielding porous roasting residues. These porous residues enhance the dissolution of lithium sulfate during the leaching process. SEM and BET analyses confirm a marked increase in porosity and a reduced contact angle in samples subjected to microwave roasting, thereby improving reaction efficiency.

To effectively address the challenges associated with the complex composition of lepidolite and maximize lithium recovery, the integration of pyrometallurgical and hydrometallurgical approaches is crucial. This combined strategy capitalizes on the strengths of each method while mitigating their individual limitations [89].

Combining microwave-assisted roasting with acid leaching reduces energy consumption while maintaining high recovery rates. For instance, microwave roasting enhances Na_2CO_3 activation, lowering required roasting temperatures by 20–30% [90].

For environmental management, it can be explored from methods such as recycling leachates using membrane technologies or neutralization, minimizing waste discharge; converting silica residues into construction materials or chemical feedstocks; capturing and reusing SO_2 emissions from sulfation roasting for sulfuric acid production; scrubbing HF(g) emissions using limestone slurry (CaCO_3) to form stable CaF_2 precipitates, thereby mitigating fluoride release into the atmosphere or water systems.

The processing of lepidolite ores inevitably generates bulk tailings, primarily composed of aluminosilicate residues, quartz, and feldspar. These tailings pose environmental challenges due to their high fluoride content (up to 2–5 wt.%) and potential for acid drainage if improperly managed. Recent studies highlight the valorization of tailings as secondary resources for construction materials (e.g., ceramic tiles or geopolymers) or silica-rich feedstocks, reducing landfill dependency [91]. For instance, silica residues from acid leaching can be calcined (800–900 °C) to produce amorphous silica nanoparticles (98% purity), while feldspar-rich fractions may serve as fluxing agents in glass manufacturing. Implementing dry stacking with impermeable liners and real-time groundwater monitoring further mitigates environmental risks. Future efforts should prioritize closed-loop systems to recover residual lithium (<0.1% Li_2O) and alkali metals (K, Rb) from tailings via advanced hydrometallurgical or bioleaching techniques, aligning with circular economy principles [92].

5. Conclusions and Future Prospects

This review systematically analyzes lepidolite's mineralogical characteristics, beneficiation methods, and extraction techniques, and introduces some advanced technologies. The relevant conclusions and prospects are as follows:

1. For the beneficiation of lepidolite, mixed-collector flotation shows high selectivity and recovery under neutral pH, but fine-particle recovery is low, and collector costs are high. Molecular dynamics simulations need to be strengthened to reveal the interactions between collectors and mineral surfaces.
2. For the extraction of lepidolite, the integration of pyrometallurgical and hydrometallurgical methods has emerged as a promising strategy for enhancing lithium recovery rates, reducing reagent consumption, and minimizing energy costs. Efforts to recover co-occurring metals (Rb, Cs) and valorize tailings through industrial symbiosis (e.g., silica for solar panels) are critical for achieving zero-waste goals. The use of microwave-assisted roasting, bioleaching, and advanced flotation techniques has shown potential in improving the sustainability and efficiency of lithium extraction from lepidolite. However, challenges remain in fine-particle recovery, collector optimization, and the need for more sustainable and cost-effective reagents.

Lepidolite represents a promising alternative lithium resource, with significant potential for contributing to the global lithium supply. The key mechanisms and technologies in lepidolite beneficiation and extraction offer valuable insights for technological innovation and industrial advancement in the new energy materials sector [92–95].

Future research should focus on the following prospects:

1. **Innovation in Beneficiation Techniques:** Developing advanced flotation technologies that can selectively separate fine-grained lepidolite from gangue minerals with high efficiency. This includes the optimization of mixed collectors and the exploration of nanobubble technology to enhance fine-particle recovery.
2. **Sustainable Reagent Development:** The design and synthesis of biodegradable and cost-effective collectors that can replace traditional chemicals, reducing the environmental footprint of lepidolite processing.
3. **Thermodynamic Optimization:** Further investigation into the thermodynamics of lithium extraction processes to identify conditions that maximize lithium recovery while minimizing energy consumption and environmental impact.
4. **Adopting green chemistry principles**—such as replacing HF with biodegradable ligands or recycling process water via membrane technologies—fosters eco-efficient operations. Furthermore, collaboration with downstream industries (e.g., ceramics, batteries) to utilize tailings as raw materials exemplifies circular economy practices, ensuring resource efficiency across the lithium value chain.

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