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Lithium Recovery from Brines, Hard Rock Deposits, and Clay

Rogel Fernando Retes Mantilla[1], Adrian Cardona Sanchez[2], Ricardo Rodriguez Figueroa[3], Roberto Ademar Rodriguez Diaz[4*]
[1,2,3,4]Professor, National Technological Institute of Mexico, TES de Coacalco, Mexico, Coacalco de Berriozabal, Mexico

***Abstract*: Lithium is a critical resource to produce batteries, which are fundamental for electric vehicles and energy storage systems. The demand for lithium has spurred interest in improving extraction technologies from three main sources: brines, hard rock deposits, and clays. Each source presents unique challenges and opportunities for the extractive metallurgy of lithium. This review provides an overview of the current technologies employed for lithium extraction from these sources, examining advancements in brine evaporation, spodumene and petalite processing, and emerging techniques for clay-based lithium recovery. The discussion also covers environmental impacts, efficiency, and potential improvements in sustainability. Prospects for improving lithium extraction processes are highlighted, with a focus on reducing costs and minimizing environmental damage.**

***Keywords*: Brines, Clays, Extractive metallurgy, Hard rock, Hydrometallurgy, Lithium extraction, Sustainability.**

1. Introduction

The growing demand for lithium, driven by the expanding markets of electric vehicles (EVs) and renewable energy storage systems, has made the efficient extraction of lithium from various sources a critical area of research. Lithium is primarily extracted from three sources: continental brines, hard rock (such as spodumene and petalite), and clays. Each of these sources requires specific techniques within the broader framework of extractive metallurgy, often involving complex hydrometallurgical and pyrometallurgical processes [1].

Lithium extraction from brines, mainly concentrated in the "Lithium Triangle" (Argentina, Bolivia, and Chile), is currently the most common source of global production. The process involves solar evaporation of large brine pools followed by selective recovery of lithium salts through precipitation. Although this method is cost-effective, it is slow and heavily dependent on climatic conditions, which makes it susceptible to environmental challenges, particularly in water-scarce regions [2].

In contrast, lithium extraction from hard rock involves traditional mining techniques and more complex metallurgical processing. The principal lithium-bearing minerals, spodumene and petalite, undergo crushing, roasting, and subsequent leaching. Although these processes are energy-intensive, hard rock deposits offer higher lithium concentrations, providing potential advantages in certain regions [3].

Lithium extraction from clays is an emerging area of interest, with deposits primarily found in the United States and Mexico. Clay-based extraction is still in developmental stages, requiring effective methods of leaching and selective lithium recovery. Despite challenges such as low lithium concentrations and complex mineral compositions, clays represent a promising alternative source, especially as technology advances [4].

This review aims to consolidate the recent advancements in lithium extraction technologies from these three sources, exploring the processes involved, the efficiency of current methods, and the environmental impact. Additionally, it seeks to identify gaps in current research and propose avenues for future development, particularly regarding the sustainability and scalability of these extraction methods [5].

2. Hard Rock Deposits: A Detailed Analysis

A. *Minerals of Interest and their Mineralogy*

The main minerals of interest in hard rock deposits, from which the useful lithium compound is extracted, are presented below [6], [7].

- *Spodumene*: This mineral is an inosilicate of lithium and aluminum. There are two main varieties: the alpha variety, which is the stable form at low temperatures, and the beta variety, which is the stable form at high temperatures. The beta variety is the most common in lithium deposits and is the one primarily used for lithium extraction.
- *Petalite*: This mineral is a tectosilicate of lithium and aluminum. It is less common than spodumene but can be a significant source of lithium in some deposits.

Figure 1 displays the process block diagram, detailing the sequence of operations and processes involved in the lithium extraction phase from hard rock deposits.

B. *Extraction Process*

The following section presents and describes in detail each of the processes that make up the extraction technology route, such as mining, concentration, and conversion. Their respective subprocesses are also mentioned and described [8]-[10].

*Corresponding author: ademar@tesco.edu.mx

1) *Mining*

Deposit Selection: Deposits with an economically viable lithium concentration and a lower environmental impact are selected.

Extraction Methods: The choice between open-pit and underground mining depends on the deposit's depth, the geology of the deposit, and other economic and environmental factors.

Rock Fragmentation: Once extracted, the rock is fragmented into smaller pieces to facilitate subsequent processes.

2) *Concentration:*

Crushing and Grinding: The ore is reduced to a suitable particle size to liberate the lithium minerals.

Flotation: This is the most common method for concentrating on lithium ore. Frothing agents and collectors are used to separate the lithium particles from the gangue (undesirable minerals).

Leaching: In some cases, acid or alkaline leaching can be used to dissolve the lithium from the ore.

3) *Conversion*

Roasting: The concentrate is heated at high temperatures to convert the lithium into a more soluble form.

Leaching: An acid or base is used to dissolve the roasted lithium.

Precipitation: Chemical reagents are added to precipitate the lithium as lithium carbonate or lithium hydroxide.

C. Factors Influencing Extraction

Mineralogy: The mineralogical composition of the deposit affects the efficiency of concentration and conversion processes.

Particle Size: An appropriate particle size is essential for good liberation of lithium minerals.

Chemical Reagents: The selection of appropriate chemical reagents is crucial for the efficiency and cost of the process.

Operating Conditions: Temperature, pH, and reagent concentration are important factors that affect the kinetics and selectivity of the reactions.

D. Additional Advantages and Disadvantages

The main advantages and disadvantages of the lithium extraction process from hard rock deposits are presented below, considering aspects such as flexibility, technological development, environmental impact, energy consumption, and costs [11], [12].

1) *Advantages*

Flexibility: Lithium extraction processes from hard rocks are relatively flexible and can be adapted to different types of minerals and deposits.

Technological Development: There is great interest in developing new technologies to improve efficiency and reduce the cost of lithium extraction.

2) *Disadvantages*

Environmental Impact: Open-pit mining can cause significant disturbance to the landscape and generate mining waste.

Energy Consumption: Concentration and conversion processes require a large amount of energy.

Costs: The investment and operating costs of a lithium mine can be very high.

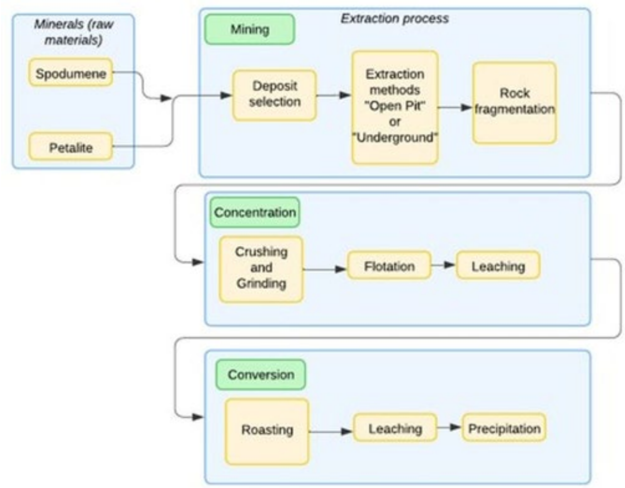

Fig. 1. Schematic diagram of the lithium extractive metallurgy process from hard rock

3. Lithium Extraction from Brines and its Refinement

Lithium, a lightweight alkali metal, has experienced a surge in demand due to its fundamental role in lithium-ion batteries, which are crucial for the energy transition towards renewable sources and the electrification of transportation. One of the primary sources of lithium is brines, aqueous solutions rich in this metal, found abundantly in certain regions of the world, especially in the so-called "Lithium Triangle" (Argentina, Bolivia, and Chile). This article will explore the processes of lithium extraction from brines and its subsequent refinement to obtain commercial products. Additionally, it will present the challenges and technological advances in this field, as well as relevant references from recent research [13].

Lithium Extraction from Brines: The extraction of lithium from Brines involves a series of stages that vary depending on the lithium concentration, the impurities present, and the local climatic conditions [14], [15]. Figure 2 presents the process block diagram, which includes the sequence of operations and/or processes developed during the technological pathway for lithium extraction from brine.

A. Solar Evaporation

Traditionally, the most widely used method has been solar evaporation. It consists of pumping the brine into large ponds where the sun gradually evaporates the water, increasing the lithium concentration. As the brine concentrates, different minerals precipitate, leaving a solution rich in lithium. While simple, this method has disadvantages such as its dependence on climatic conditions, the long time required (it can take years), and the high environmental impact due to the extensive use of land and the potential contamination of water resources [16].

B. Direct Lithium Extraction (DLE)

As a more efficient and sustainable alternative, Direct

Lithium Extraction (DLE) has emerged. This technology employs various methods to remove lithium from the brine without the need for prior evaporation [17]. Some of the most common methods are:

- *Adsorption*: Uses adsorbent materials with a high affinity for lithium to capture it from the solution.
- *Ion Exchange*: Employs resins that exchange lithium ions for other ions present in the brine.
- *Solvent Extraction*: Uses organic solvents to extract lithium from the aqueous phase. DLE offers advantages such as shorter processing times, lower water consumption, and a reduced environmental footprint. However, its large-scale implementation still faces technical and economic challenges.

C. Lithium Refinement

Once the lithium concentrate is obtained, it is refined to produce high-purity lithium compounds, such as lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH), which are the most used precursors in battery manufacturing. The refinement process generally involves the following stages:

- *Precipitation*: Chemical reagents are added to precipitate the lithium as a carbonate or hydroxide.
- *Filtration*: The solid precipitate is separated from the residual solution.
- *Washing*: Impurities adhering to the precipitate are removed.
- *Drying*: Water is removed from the obtained solid.
- *Calcination*: In some cases, a heating process is carried out to obtain the final product with the required specifications.

Challenges and Perspectives: Lithium production faces challenges related to resource availability, environmental impacts, extraction and refining costs, and geopolitical competition. Despite these challenges, the growing demand for lithium batteries will drive research and development of new technologies to improve the efficiency and sustainability of the processes [18].

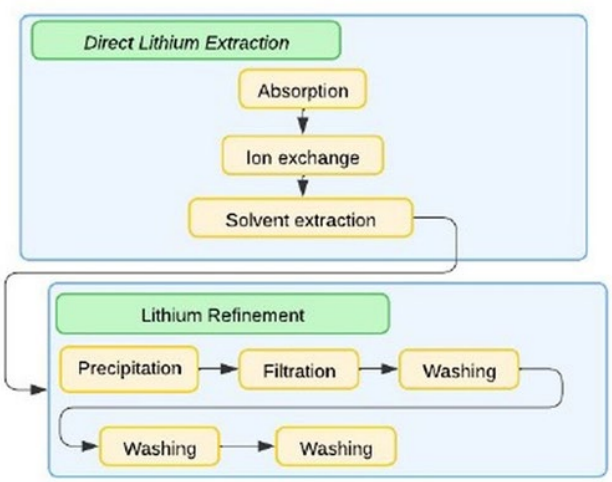

Fig. 2. Schematic diagram of the lithium extractive metallurgy process from brine

4. Lithium Extraction Clay

Lithium extraction from clay has gained significance due to the increasing demand for this metal in the battery industry for electric vehicles and energy storage. Unlike other traditional sources of lithium, such as brine or spodumene, clays contain lithium in lower concentrations, requiring specific extraction and refinement processes. This article addresses the key stages of the lithium extraction process from clays, highlighting the importance of each stage in extractive metallurgy [19], [20].

A. Stages in Extractive Metallurgy

The most used stages in the extractive metallurgy of lithium from clay are presented below, including the processes of ore beneficiation, leaching, purification, lithium carbonate precipitation, and final refining [21]-[24]. Figure 3 displays the process block diagram, describing the sequence of operations and/or processes conducted during the technological pathway for lithium extraction from clay.

1) Mineral Beneficiation

The first step in extracting lithium from clay is the concentration of the mineral. Since clays contain low amounts of lithium, the beneficiation process involves techniques such as crushing, grinding, and in some cases, gravity separation or flotation to increase lithium concentration.

2) Leaching

In this stage, lithium is extracted from the clays through acid or alkaline leaching. Depending on the type of clay and lithium concentration, acids such as sulfuric acid or hydrochloric acid are used. Acid leaching is more efficient in lithium-rich clays, releasing lithium ions from the mineral matrix.

3) Purification

The leach liquor, containing dissolved lithium, undergoes a series of purification stages. These processes include the selective precipitation of impurities such as iron and magnesium. Additionally, ion exchange or solvent extraction techniques can be used to separate lithium from other metals present.

4) Precipitation of Lithium Carbonate

Once purified, lithium is precipitated as lithium carbonate (Li_2CO_3), the most produced form. This process generally involves adding sodium carbonate (Na_2CO_3) to the purified liquor, causing the formation of solid Li_2CO_3, which is then filtered and dried.

5) Final Refinement

The obtained lithium carbonate may require additional refinement to remove residual impurities. In some cases, it is converted to lithium hydroxide (LiOH), another valuable product, using chemical conversion techniques.

B. New Trends and Challenges

Lithium extraction from clays presents technical challenges, including high processing costs due to low lithium concentrations and the need for intensive chemical treatments. However, recent research seeks to develop more efficient and sustainable methods, such as the use of bioleaching or the development of direct lithium extraction technologies [25], [26].

Key Terms and Concepts Preserved in the Translation:

- *Beneficiation*: This term is used to describe the processes of preparing an ore for further processing, such as crushing, grinding, and concentration.
- *Leaching*: This is a process of extracting a soluble substance from a solid by dissolving it in a liquid.
- *Precipitation*: This is the process of forming a solid from a solution.
- *Ion exchange*: This is a process in which ions are exchanged between a solid and a liquid.
- *Solvent extraction*: This is a process of separating components of a mixture using a solvent.

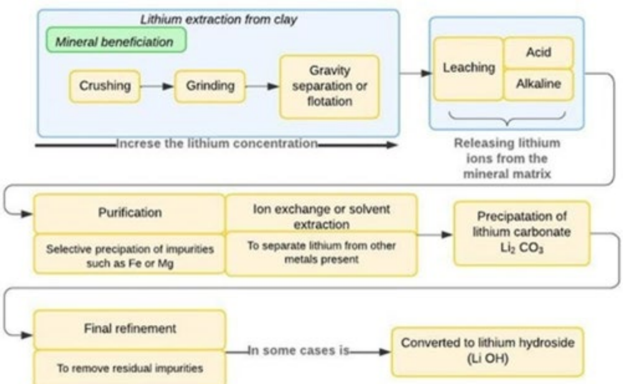

Fig. 3. Schematic diagram of the lithium extractive metallurgy process from clay

5. Conclusion

The recovery of lithium from brines, hard rock deposits, and clays presents specific advantages and limitations in the field of mining and extractive metallurgy. This analysis highlights the following key conclusions:

A. Brines

Lithium extraction from brines, primarily through solar evaporation, is the predominant method due to its relatively low cost. However, its efficiency is highly dependent on climatic conditions and poses significant environmental challenges in areas with water scarcity, such as the "Lithium Triangle" in South America. Although evaporation allows for the economic recovery of lithium, there is an urgent need for alternative, more sustainable techniques that minimize the impact on water resources in these regions.

B. Hard Rock Deposits

Lithium extraction from minerals such as spodumene and petalite utilizes traditional mining techniques along with pyrometallurgical and hydrometallurgical processes. Despite higher energy consumption and operating costs, these deposits offer significantly higher lithium concentrations than brine, making them attractive in regions with access to adequate energy infrastructure. Advances in roasting and leaching methods could improve efficiency and reduce the environmental impact of this type of mining.

C. Clays

Lithium extraction from clays is an emerging field with considerable potential, although it faces technical challenges due to low lithium concentrations and the mineralogical complexity of the deposits. Currently, leaching methods and selective lithium recovery in clays are under development, and future technological advances will be essential to make their commercial exploitation viable. Given their ubiquity in regions of the United States and Mexico, clays could become a viable and complementary source to brines and hard rocks.

D. Sustainability Outlook

Improvements in lithium extraction processes should focus on reducing costs and minimizing environmental impacts. In particular, the adoption of hydrometallurgical techniques and cleaner processing technologies, which allow for the reuse of byproducts and the efficient use of water, are emerging as crucial research areas to achieve a more sustainable industry. Innovations in each type of source could complement global lithium demands without compromising key environmental resources.

In conclusion, advancements in lithium recovery from these diverse resources can contribute to meeting the growing global demand, particularly in energy storage and electric vehicle sectors, if sustainability and efficiency practices are prioritized in each of these extraction methods.

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