

Review

Lithium Production and Recovery Methods: Overview of Lithium Losses

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Abstract: The objective of this study is to describe primary lithium production and to summarize the methods for combined mechanical and hydrometallurgical recycling of lithium-ion batteries (LIBs). This study also aims to draw attention to the problem of lithium losses, which occur in individual recycling steps. The first step of hydrometallurgical treatment is leaching, which is an effective method capable of transferring over 99% of the present metals to the leach solutions. Extraction of metals after leaching can be conducted using various methods, with precipitation being the most commonly used. The precipitation of other metals can result in the co-precipitation of lithium, causing total lithium losses up to 30%. To prevent such losses, solvent extraction methods are used to selectively remove elements, such as Co, Ni, Al, and Mn. Solvent extraction (SX) is highly effective, reducing the losses to 3% per extraction stage and reducing overall lithium losses to 15%. After the refining, lithium is precipitated as lithium carbonate. High lithium carbonate solubility (1.5 g/L) and high liquid to solid leaching ratios require costly and avoidable operations to be implemented in order to enhance lithium concentration. Therefore, it is suggested that more studies should focus on multistage leaching with lower L/S ratios.

Keywords: lithium-ion battery; recycling; lithium; hydrometallurgy; leaching; lithium losses; critical raw materials; solvent extraction



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1. Introduction

In recent years, there has been a noticeable increase in lithium production due to the growing interest in this valuable resource, which aligns with the escalating demand for electric vehicles and cordless consumer electronics [1]. This highly reactive and flammable alkali metal is used for the production of lithium-ion batteries (LIBs), in ceramics and glass, lubricants, polymer production, and air conditioning [2]. The production of lithium batteries is expected to increase in the coming years due to the decarbonization of key markets [3]. World lithium reserves in 2023 are estimated at 26,000 kt according to the US Geological Survey [4]. The world's largest reserves are found in Chile (9200 kt) in the form of brine and Australia (4700 kt) in the form of hard rocks [5]. In Europe, lithium is found in Portugal (60 kt) and the north of the Czech Republic (1.5 kt) [6]. The largest lithium deposit in Europe is the Adriatic in Serbia (125 kt). The annual lithium production in 2020 was 82.2 kt. The largest producers are Australia (40 kt), Chile (18 kt), and China (14 kt) [7–9].

Batteries, ceramics, glass, and lubricants have been the main use for lithium. The demand for lithium carbonate is expected to increase from 265 kt in 2015 to 498 kt in 2025. Lithium is currently produced from primary raw materials, which are brines and minerals

(e.g., spodumene, petalite) [9,10]. The most efficient and cost-effective way to produce lithium is from brines [11]. Brines contain lithium from the leaching of volcanic rocks and widely differ in lithium content. They come from highly concentrated lithium deposits in high mountain salars in Chile, Argentina, Bolivia, and China [9,12]. The extraction from brine, however, carries great environmental risks due to the large consumption of water and the pollution of underground sources of drinking water [11,13]. Therefore, it is advisable to replace part of lithium primary sources with secondary ones, which can be spent LIBs, in order to support the concept of circular economy [14].

Like any electrochemical cell, lithium-ion batteries are composed of a negative electrode (anode), a positive electrode (cathode), a separator, and an electrolyte. Different types of lithium-ion batteries differ in the materials currently used as the anode material, cathode material, lithium salt, solvent, and separator material, which have different properties [15,16]. Primary lithium cells (batteries) use metallic lithium as the cathode. Lithium secondary cells (rechargeable batteries) do not contain metallic lithium. Most lithium-ion systems use a material such as Li_xMA_2 on the positive electrode and graphite on the negative electrode [17]. Some materials used at the cathode include LiCoO_2 , LiNiO_2 , LiMn_2O_4 , and LiFePO_4 . Lithium-ion batteries contain a toxic and flammable electrolyte, an organic liquid with solutes, such as LiClO_4 , LiBF_4 , and LiPF_6 . Lithium cells consist of heavy metals, organic chemicals, and plastics in proportions of 5–20% cobalt, 5–10% nickel, 5–7% lithium, 15% organic chemicals, and 7% plastics, with the composition varying slightly from manufacturer to manufacturer. For this reason, a considerable effort is needed for the complex processing of all types of lithium cells [18–21].

Generally, lithium batteries and accumulators can be processed via pyrometallurgy, hydrometallurgy, and bio-metallurgy. However, almost all lithium battery recycling processes are hybrid processes. They consist of a mechanical and pyrometallurgical treatment before the final metal recovery by hydrometallurgical processes. Substances such as the electrolyte, binder, and plastic packaging can only be removed by heat treatment or mechanical treatment [22,23]. In many industrial plants, the full material potential is not used for LIB processing, as lithium is transferred into the slag during pyrometallurgical processing, and metals such as Ni, Co, Mn, Cu, and their alloys are recovered [24–26].

Lithium production can be divided into two parts: lithium production from raw materials and production from waste or secondary materials. In the case of primary lithium processing methods, lithium is made from brines and minerals, such as spodumene, petalite, or lithium clays [24,27]. The main source of lithium from waste is lithium batteries. There are other waste streams with lithium content, such as glass and ceramics, lubricants, or aluminum alloys, but there are no commercially available processes for the recovery of lithium from those materials [26,28,29].

The aim of this article is to provide an overview of lithium production from primary and secondary sources, describe the recycling of lithium-ion batteries on an industrial scale, and focus on scientific publications concerning mechanical and hydrometallurgical recycling methods. Regarding hydrometallurgical processing, the main focus is placed on leaching and extraction of lithium from the solutions, including precipitation, solvent extraction, ion exchange, electrodialysis, and others.

One current issue with published articles is the fact that each step of lithium leaching and extraction leads to lithium losses, which is an intentionally undiscussed fact. Additionally, improperly designed leaching processes (e.g., high solid to liquid ratios) can result in high lithium leaching efficiencies but with low lithium concentration, which is not suitable for further lithium extraction. The aim of this article is to also compare and discuss individual methods for obtaining lithium from LIBs from the point of view of the effectiveness of individual steps and their applicability in real conditions.

2. Raw Materials Lithium Production

2.1. Lithium Production from Brines

Brine contains a mixture of salts, such as chlorides and sulfates of sodium, potassium, calcium, magnesium, boron, and lithium, which are recovered by evaporation in ponds. Lithium is obtained mostly as lithium carbonate (Li_2CO_3) from an evaporation process (Equation (1)), which consists of evaporating salty water for 12–18 months in ponds using solar energy. The most interfering element is magnesium, which is removed by two-step precipitation using sodium carbonate (Na_2CO_3) and lime (CaO) [29]. Brines are classified into three categories as geothermal brines, oilfield brines, and continental brines, with the latter being the largest source of world production (59%). The lithium content in most brines is estimated to be from 200 to 700 ppm, and a few brines contain 600 to 1500 ppm Li. Due to the differing chemistry in different salt brines around the world, the specifics of a process may differ in each lithium plant [30,31].

For solar brines from Salar de Atacama and Salar de Uyuni, which contain high levels of Mg, solar evaporation will precipitate Mg as carnallite, bischofite, and lithium carnallite. The high content of Mg (1% and above) represents an increased value if Mg products can be recovered. An et al. developed a process for treating brines from Salar de Uyuni (Bolivia), which involves the use of lime to precipitate Mg as hydroxide, as shown in Figure 1. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and borate are also co-precipitated with $\text{Mg}(\text{OH})_2$. The mixed slurry must be further processed to recover Mg. Alternatively, the $\text{Mg}(\text{OH})_2 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The second precipitation stage uses sodium oxalate to remove Ca as calcium oxalate. The calcium oxalate precipitate is calcined to CaO and reused in the first precipitation stage. The next stage is purifying by precipitation in order to remove contaminants, such as Fe, Al, and base metals, before lithium is concentrated via evaporation and recovered as 99.5% Li_2CO_3 at 80–90 °C by carbonation using Na_2CO_3 [31–33].

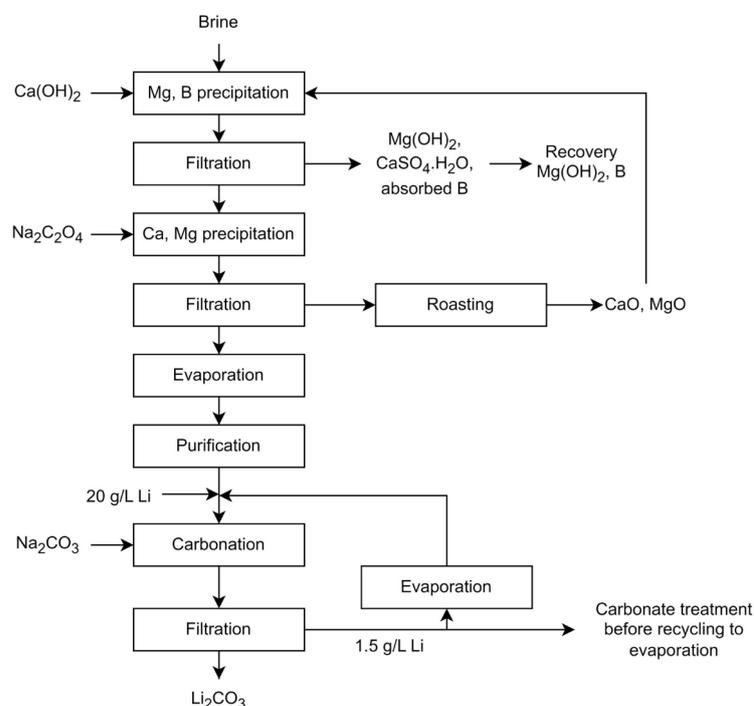


Figure 1. Flow sheet of lithium recovery from Salar de Uyuni brine, reproduced from [32] with permission from Elsevier, 2023.

Jiachun Xiong et al. developed a process of extraction of Li from raw brines (shown in Figure 2) by the chemical redox method with LiFePO_4 . This method can directly extract Li

from brines. LiFePO_4 battery material was used to directly extract lithium from the brine by the chemical redox method. This method exhibited a high adsorption capacity (9.13 mg/g), good selectivity, and stable cycling performance. The recovery rate of Li reached 91.11%, and the rejection rate of impurities exceeded 99%. Notably, the desorption process was carried out in 5 g/L $\text{Na}_2\text{S}_2\text{O}_8$ solution, so that part of Na^+ in the desorption solution was introduced. Furthermore, the obtained desorption solution with higher lithium content and a low concentration of impurity would reduce the difficulty and cost of preparing Li_2CO_3 products [34].

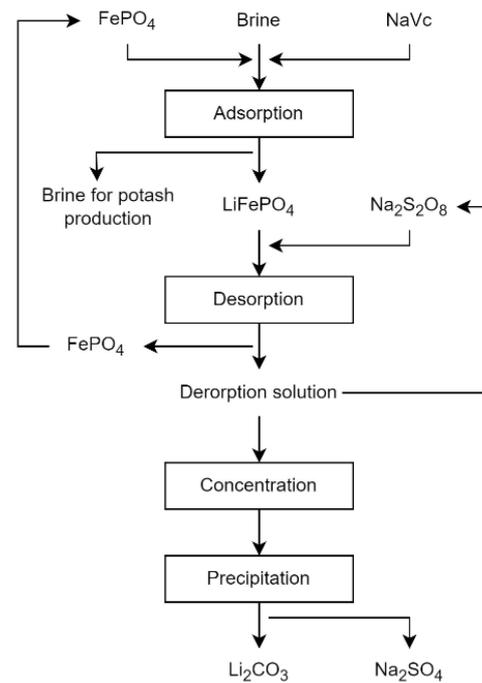
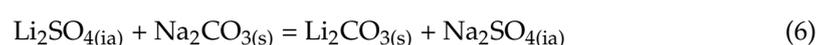
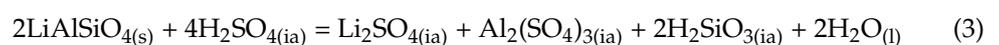
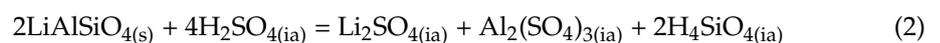


Figure 2. Lithium extraction method by FePO_4 , reproduced from [34] with permission from Elsevier, 2023.

2.2. Lithium Production from Minerals

Among lithium-bearing ores, spodumene is the most common mineral, which has been commercially mined and processed to produce lithium compounds around the world. Lithium is produced from spodumene (as shown in Figure 3) by recrystallization roasting in a rotary kiln at $1100\text{ }^\circ\text{C}$ ($\alpha > \beta$). Subsequently, the β -spodumene is cooled to $65\text{ }^\circ\text{C}$, milled ($<149\text{ }\mu\text{m}$), and roasted with conc. H_2SO_4 at $250\text{ }^\circ\text{C}$ to obtain soluble Li_2SO_4 and $\text{Al}_2(\text{SO}_4)_3$ and an insoluble residue (Equations (2)–(5)). The roasted mixture is dissolved in water, and excess H_2SO_4 is neutralized with CaCO_3 , which causes precipitation of CaSO_4 , iron, and aluminum impurities. The magnesium content is precipitated with CaO , and added calcium is precipitated with Na_2CO_3 . After filtration, the pH of the solution is adjusted with sulfuric acid and concentrated by evaporation. Li_2CO_3 is precipitated at $90\text{--}100\text{ }^\circ\text{C}$ with Na_2CO_3 solution, centrifuged, washed, and dried [29–31,35,36].



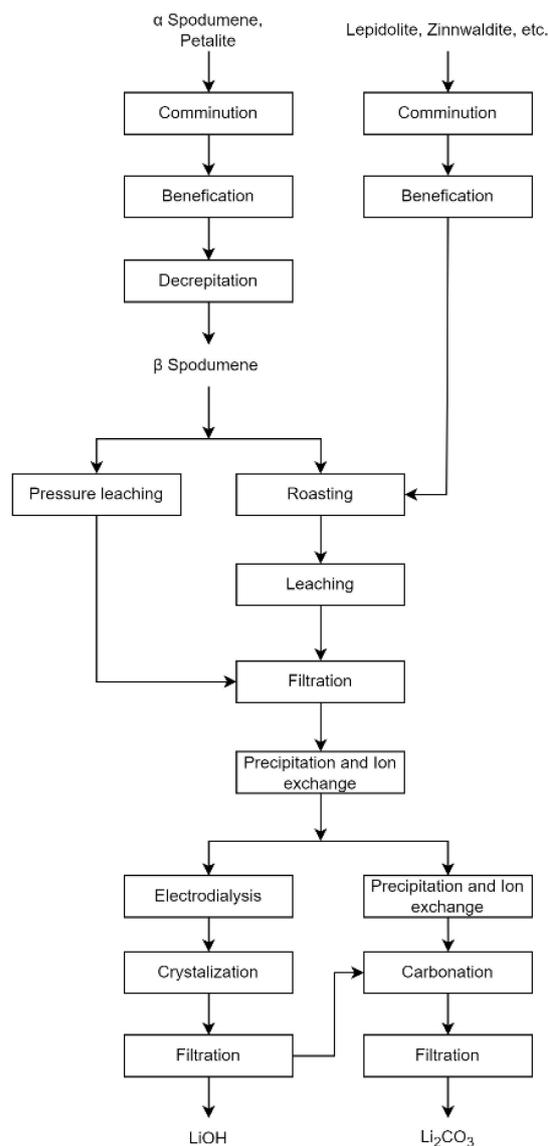


Figure 3. Flow sheet of spodumene processing, reproduced from [31] with permission from Elsevier, 2023.

3. Secondary Lithium Production

3.1. Lithium Waste Processing—Large Scale

Lithium batteries can be processed using pyrometallurgy (PM), hydrometallurgy (HM), and bio-metallurgy. However, almost all lithium battery and accumulator recycling processes are hybrid processes, which consist of mechanical and pyrometallurgical treatment before the final metal recovery through hydrometallurgical processes. Electrolytes, binders, and plastic packaging can only be removed through heat or mechanical treatments [37]. In many industrial plants, the full material potential is not utilized for LIB processing, since lithium passes into slag during pyrometallurgical processing, and only metals such as Ni, Co, Mn, Cu, and their alloys are recovered [38]. To recycle all metals in the LIB, a mixture of hydrometallurgical and pyrometallurgical processes must be used to obtain a specific metal. Several commercial methods have been used to process LIB, but many are tailored to specific cell types, which means that a given technology may not be able to process all types of LIB [39].

The Accurec GmbH process is a hybrid process, which utilizes mechanical pretreatment, pyrometallurgy, and hydrometallurgical processes. In this process, LIBs are first

mechanically treated to remove plastics. Then, the material is subjected to pyrolysis at 250 °C to remove the electrolyte and organic solvents. The next step involves dimensional adjustment (−200 μm), screening, magnetic, and gravitational separation to recover the metals. The electrode material is mixed with a binder and subjected to pyrometallurgical processing in a shaft furnace. The pyrometallurgical treatment produces a Co–Mn alloy and slag, which is subsequently leached and precipitated to obtain Li₂CO₃ [27,38,40,41].

In the OnTo process, discharged LIBs are cleaned and disassembled before processing. The material is inserted into a high-pressure reactor and immersed in a mixture of liquid CO₂, ammonia, ether, and other additives. The increase in both the temperature and pressure causes cell failure, which removes electrolytes and renders the cells inert. Subsequently, the LIBs are dimensioned, and they undergo separation on water rafts, gravity, and magnetic separation [27,38].

The Retrieval process employs cryogenic physical–mechanical pretreatment, followed by hydrometallurgical treatment. The initial step involves cooling the LIBs with liquid nitrogen to −196 °C. The LIBs are then crushed in a hammer mill with the addition of lithium brines. The dimensioned material is then separated on a wet shaking table, yielding a plastic fraction, a Cu–Co concentrate, and a slurry, which is filtered. The filter cake contains Cu, Co, Ni, Mn, and Fe in the form of a marketable concentrate. Subsequently, Li₂CO₃ is obtained from the filtered solution by precipitation with Na₂CO₃ [27,37,42–44].

The Umicore ValÉas process combines pyrometallurgical and hydrometallurgical processing of LIBs. LIBs are fed directly to furnaces without pretreatment, where plastics and graphite serve as fuel and reducing agent in the melting process. The result of pyrometallurgical processing is an alloy of Ni, Co, Cu, and Fe, which is subsequently treated by leaching in sulfuric acid. The individual metals are separated by solvent extraction. The resulting processing products are NiSO₄, CoCl₂, and Ni(OH)₂. One disadvantage of the process is a failure to utilize the full material potential of the used LIBs, as the lithium passes into the slag, which is not further processed [27,37,45,46].

The Akkuser process employs physical–mechanical pretreatment for LIB processing, which includes dimensional adjustment on a knife mill for fractions −25 + 12.5 mm. Emerging gases are subsequently filtered through a series of cyclones to recover dust. The next step is the dimensional adjustment per fraction −6 mm. Subsequently, the material is magnetically separated, creating a marketable product for subsequent metallurgical processing [27,47–49].

The first step in the LithoRec process consists of discharging the LIBs in order to reduce the risk of cell explosion. Subsequently, the LIBs are manually dismantled (in the case of large blocks, e.g., from electric vehicles) and crushed. A fraction under 20 mm is heat-treated at a temperature from 100 to 140 °C in an inert atmosphere of N₂ in order to achieve the evaporation of organic solvents and electrolytes. The crushed LIBs are separated on a zigzag separator, thereby separating the electrode material (Al, Fe, Cu) and plastics. The electrode material is sieved to a fraction −500 μm, which is then leached. The resulting solution is filtered to separate the graphite; then, the solution is precipitated to obtain Co, Ni, and Mn oxides or obtained by electrochemical methods. The refined solution is then precipitated or crystallized to obtain Li₂CO₃ or LiOH [50–54].

The Sumitomo Metal Mining Co., Ltd. process for recycling of LIBs starts with calcination at 1000 °C to remove electrolytes and other organic substances. The remaining material is processed through pyrometallurgy to recover a Cu, Co, Ni, and Fe alloy, while Li is being collected in the slag residue. Both the alloy and the slag are leached separately. From the alloy leach solution, copper is selectively recovered, which is probably achieved by cementation, and the remaining solution containing Co, Ni, and other metals is further refined to remove impurities. The leach solution from slag leaching is also refined. The intermediates from both leaching steps are mixed, and a new battery material is prepared [50,55–57].

The main challenge in LIB recycling is the constant advancement and development of electrode materials, which can result in varying chemical compositions of LIBs even among identical vehicle models from the same manufacturer [58]. For this reason, py-

rometallurgical processing of the used LIB has the widest input possibilities, in contrast to the hydrometallurgical methods, which must be designed specifically for a given type of cathode and anode material. The overview of large-scale technologies shown in Table 1 confirms the capacity difference between pyrometallurgical and hydrometallurgical technologies. Changing the chemical composition of LIBs can negatively affect the process of transferring metals into a solution or their recovery by extraction methods, as well as the purity of the final product. One of the reasons for the predominance of pyrometallurgical processes is the inappropriate labeling and disposal of batteries. Appropriate labeling could easily identify the composition of the battery, which is not indicated on the packaging, and consequently, its proper recycling with the least possible losses through sorting, and the selection of a suitable hydrometallurgical recycling procedure for a particular type of anode and cathode material [59–61].

Table 1. Overview of large-scale lithium-ion battery recycling.

Company	Input	Process	Output	Capacity (t/y)
Accurec GmbH	LIBs/Ni-Cd/MH-Ni	Pyrolysis/Mech. treatment/Pyrometallurgy	Co–Ni–Mn–Fe alloy and Li_2CO_3	6000
OnTo	LIBs	Mechanical treatment	Cathode and anode active material	-
Retriev	Non-rechargeable Li batteries and LIBs	Mechanical/Hydrometallurgical	Metal concentrate, Li_2CO_3 , graphite	4500
Umicore ValÉas	LIBs/Ni-Cd/MH-Ni	Pyrometallurgy/Hydrometallurgy	Co–Ni–Mn–Fe–Cu alloy, Li–Al slag	7000
Akkuser	LIBs	Mechanical	Cathode and anode active material	4000
LithoRec	LIBs	Mechanical, Hydrometallurgical	Active material, Co, Li, Ni compounds	100
Sumitomo	LIBs	Hydrometallurgy	Co, Li, Ni, compounds	150

3.2. Lithium Waste Processing—Laboratory Scale

The processing of spent LIBs can be divided into physical–mechanical and chemical methods. Physical processes mainly involve mechanical treatments, such as crushing, grinding, sieving, or heat treatment. Mechano-chemical and chemical processes mainly include acidic and basic leaching, bioleaching, solvent extraction, precipitation, and electrochemical methods for metal recovery. However, it is not possible to fully appreciate the material potential through a single process. Therefore, a combination of several recycling processes is often necessary to effectively recycle or recover the main components from used LIBs.

3.2.1. Pretreatment of Lithium-Ion Batteries

The physical–mechanical treatment of used LIBs poses a risk to the health of workers. While LIBs do not contain metallic lithium (which is highly reactive), they do contain flammable components, which can pose a fire risk. The main flammable components in LIBs are the organic electrolyte and the flammable solvents used in the electrolyte, which are typically highly volatile and can ignite under certain conditions. In addition, the separator, which is a thin polymeric film separating the positive and negative electrodes, can also be flammable. If the separator is damaged or compromised, this can lead to a short circuit and potentially result in a fire or explosion.

Various procedures have been proposed to minimize this risk during LIB crushing. Some solutions involve freezing the LIB with liquid nitrogen before crushing or treating the LIB in an inert atmosphere, either in a vacuum or in the presence of inert gases, such as Ar_2 , N_2 , or CO_2 . Another possibility is to crush small quantities of cells to minimize the impact on the processing plant when some of them explode, leading to deterioration. However, all these approaches are cumbersome, expensive, and consume valuable resources [62–64].

In addition, these procedures do not consider the hazardous potential during storage and transport.

Nowadays, it is common practice not to organize the collection and storage of used mixed batteries, resulting in the risk of short circuits due to unwanted contact between the batteries or due to possible errors and damage to the battery packaging. Stored LIBs have been identified as a cause of fires in recycling plants, warehouses, and during transport. Such fires are attributed, for example, to accidental short circuits due to the absence of suitable containers in the presence of water [65,66]. One possible solution to this problem is to completely discharge the batteries before handling, as this would release all stored chemical energy, which would cause the battery to become unresponsive. Discharge could also have a positive effect on crushing safety, potentially even reducing the costs associated with additional safety measures [61,67].

One option to discharge the batteries is to use an external resistor, which would require manual work on an industrial scale. To ensure the economic viability of the discharge step, the method used should be able to discharge LIBs from different manufacturers in bulk. One of the proposed methods for discharging LIBs in large volumes is to immerse them in a saline solution, as the combined effect of short circuit and saline electrolysis is expected to discharge the batteries [67,68].

Ojanen et al. investigated the electrochemical discharge of LIBs. The authors compared various electrolytes, including NaCl, Na₂SO₄, ZnSO₄, FeSO₄, their concentrations, the effect of mixing, and the addition of metal powders on the length and efficiency of the discharge process. In ex situ experiments, NaCl was found to be the most efficient electrolyte for LIBs discharge, and increasing its concentration to 20% shortened the discharge times to 4.4 h. However, the formation of chlorine gas can be a safety issue. Therefore, the authors also investigated the use of sulfate salts. The disadvantage of using sulfate salts was the formation of a precipitate on the Pt wires, which prevented the discharge reactions. However, when stirring was introduced into the Na₂SO₄ solution, the discharge rate accelerated, and the battery was completely discharged within 3.1 h [69]. Xiao et al. developed a method for processing used LIBs by discharging in 5% NaCl solution for 24 h, crushing, and desaturating the active material. Subsequently, the active materials are roasted in an inert atmosphere of nitrogen and leached in water for 45 min, whereby a transfer of lithium in a solution is achieved, and subsequently, the lithium is crystallized from the extract in the form of carbonate. The solid filter cake from the leaching step containing manganese and graphite is heat-treated in an oxidizing atmosphere to obtain Mn₃O₄ with a purity of 95.11% [70]. Shin et al. developed a process for processing of spent LIBs, which involves two-stage sizing, followed by crosslinking to separate the plastics, Fe, Al, and Cu. The fine Fe fraction was separated magnetically. The next step involved grinding and sieving, which separates fine pieces of aluminum foil [18]. By crushing, grinding, and sieving, it is possible to obtain metals such as Co, Ni, and Mn concentrate in smaller fractions, while the content of Cu, Al, and Fe increases with increasing grain size [71].

The majority of research papers are focused on the recovery of active materials from spent LIBs; however, the separation of other components, such as separators and current collectors, does not receive enough attention. Mennik et al. [72] and Çuhadar et al. [73] focused on separation of these materials by froth flotation and magnetic separation. The first step was shredding of discharged EOL LIBs followed by screening to recover active materials. The size of the coarse fraction (−8 mm + 0.3 mm) was reduced by a cutting mill and screened again to increase the active material yield. The mixture of casings, separators, and current collectors (−2 + 0.3) was subjected to froth flotation of plastics with 1.4% of metal loss. Subsequently, the flotation of copper was performed with addition of Na₂S, potassium amyl xanthate, and methyl isobutyl carbinol. A copper concentrate containing 53.1% Cu could be obtained with 74.8% Cu recovery at the −2 mm + 0.3 mm fraction. The copper flotation sink product was subsequently processed using a dry magnetic separator

to separate ferromagnetic metals from aluminum. This process yielded a magnetic product of 67.21% Fe and 24.12% Ni.

Zhan et al. studied froth flotation of active materials from EOL lithium-ion batteries using kerosene as the collector. More than 90% of the anode materials were observed to float in the froth layers during the flotation process. On the other hand, approximately 10–30% of the cathode materials were found to be floating in the froth layers, caused by the presence of binders and residual electrolytes. The tailings' low purity of cathode materials can potentially be enhanced through fine grinding. This process exposes freshly liberated hydrophobic surfaces, leading to an increased floatability of anode materials. The current findings validate the froth flotation technique as a viable and versatile method for producing high-purity cathode materials from lithium-ion batteries [74].

Saneie et al. investigated the possibilities of separating Cu and Al after mechanical separation of active masses from LIBs using froth flotation. They employed Na_2S , PAX, and MIBC for flotation. Through the experimental design, the optimal dosages of reagents were determined as Na_2S 225 ppm, PAX 100 ppm, and MIBC 100 ppm. A 20 min activation time, 10 min collector conditioning time, and impeller tip speed of 7.69 m/s resulted in 100% separation efficiency for Cu [75].

Saeki et al. developed a mechano-chemical process of LIB processing, which is based on grinding LIB with the addition of PVC. In this process, PVC serves as a source of Cl, which, upon mechano-chemical activation in the planetary ball mill, produces water-soluble chlorides of Co and Li. The authors found that 90% of the chlorine from PVC reacts with Co and Li during grinding for 30 h. The resulting material was leached in water to achieve extractions of 90% Co and almost 100% Li [76].

Zhang et al. noted that most of the current research employs manually separated electrode materials. Manual separation can affect the purity of active materials and subsequent research; therefore, it is necessary to develop an effective crushing method. The authors compared wet and dry crushing methods. The separation of electrode materials, such as LiCoO_2 and graphite, from aluminum foil and copper foil, allowing them to concentrate in the fine fraction with fewer impurities and a looser structure using the dry crushing method, is considered beneficial for the efficient crushing of spent LIBs and their recycling [77].

In addition to discharging and mechanical methods for obtaining concentrates, roasting methods can also be included in the pretreatment of lithium-ion battery intermediates. The principle of roasting is the conversion of components from cathode materials into easily leachable phases. After roasting, the most common subsequent step is leaching in water, which dissolves the newly formed phases. Among these processes applicable to the cathode material of lithium batteries, we can mention sulfation, carbonation, chlorination, fluorination, and similar methods. For these processes, reagents such as Na_2SO_3 , K_2SO_4 , or H_2SO_4 [78] are used for sulfation; CaO or Na_2CO_3 for carbonation; KCl , NaCl , CaCl_2 , FOSU , Cl_2 for chlorination; and NaF or HF for fluorination [79,80].

The authors Zhang et al. investigated the interesting utilization of waste copperas for the roasting of active material in LMO batteries. Through the roasting process, LMO decomposed into basic oxides, such as Li_2O , MnO_2 , and Mn_2O_3 , with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ serving to convert the oxides into easily soluble lithium and manganese sulfates, partially reducing Mn^{4+} ions. The roasting resulted in the formation of Fe_2O_3 oxides from the waste copperas. Subsequently, the authors examined the leaching efficiency of Li, Mn, and Fe, varying the stoichiometric ratio of copperas to LMO from 1 to 5, the roasting temperature from 400 to 800 °C, and the roasting time from 30 to 180 min. The optimal conditions for effective leaching of Li and Mn during the neutral leaching step were 700 °C, 150 min, and a Copperas/LMO ratio of 4. Under these conditions, the conversion efficiency of lithium and manganese reached 100% and 82%, respectively, while Fe remained unextracted. Manganese was subsequently precipitated by the addition of NaOH until reaching a pH of 11, and lithium was precipitated as lithium carbonate through the addition of Na_2CO_3 [81].

Figure 4 shows a schematic representation of pretreatment methods with the aim of recovering the cathode material and other marketable products.

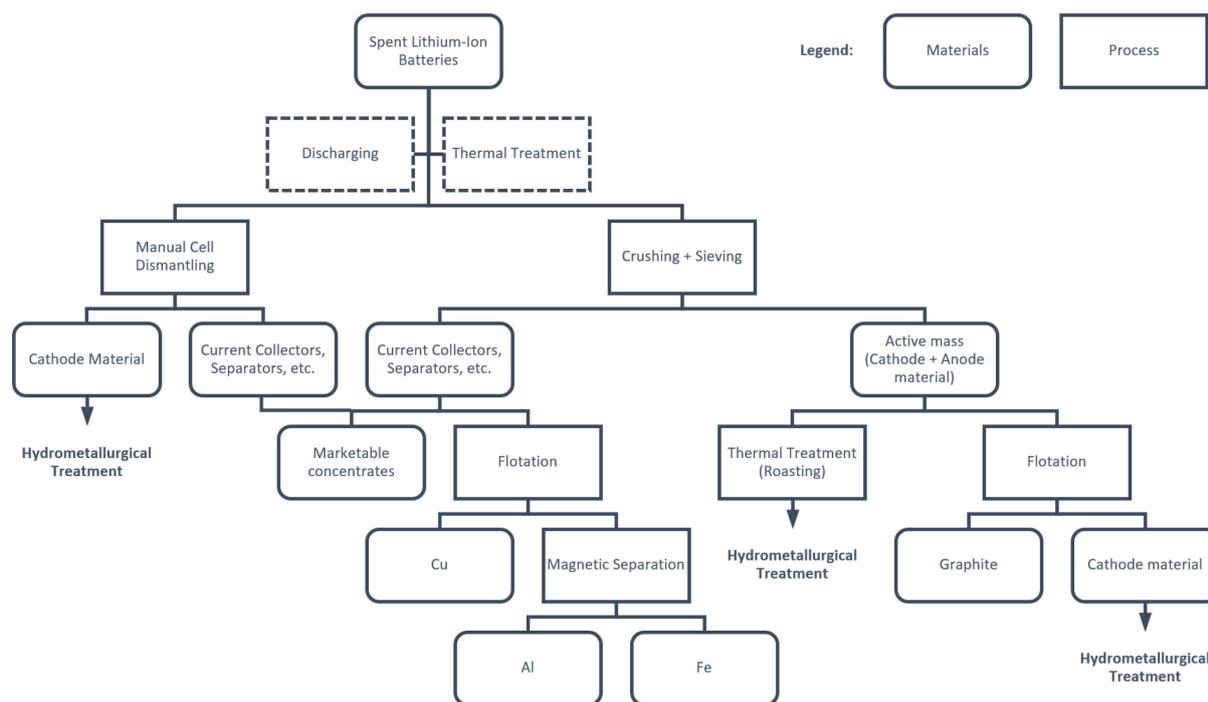


Figure 4. Overview of spent LIBs lab-scale pretreatment methods.

3.2.2. Leaching of the Lithium-Ion Batteries

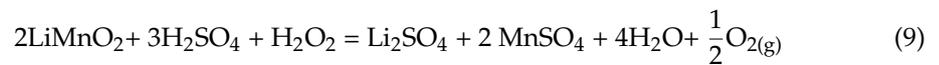
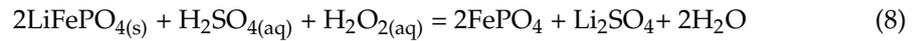
The first step of hydrometallurgical treatment is leaching, the kinetics of which depend on the type of concentration of leaching agents, the mixing speed, temperature, leaching time, and liquid to solid ratios. Table 2 shows an overview of leaching conditions and their yields.

Table 2. Review of leaching condition efficiency.

Leaching Agent	Leaching Conditions	Efficiency (%)	Ref.
H ₂ SO ₄ + H ₂ O ₂	75 °C, L/S = 20 (mL/g), 15% H ₂ O ₂	95% Co, >99% Li	[18]
H ₂ SO ₄	25 °C and 75 °C, L/S = 10 (mL/g) and 5 (mL/g)	>90% Co, >90% Li	[82]
H ₂ SO ₄ + H ₂ O ₂	60 °C, L/S = 10 (mL/g), 2 M H ₂ SO ₄ , 6% H ₂ O ₂	98% Co, 97% Li	[73]
H ₂ SO ₄ + H ₂ O ₂	75 °C, L/S = 10 (mL/g), 2 M H ₂ SO ₄ , 5% H ₂ O ₂	93% Co, 94% Li	[83]
HNO ₃ + H ₂ O ₂	75 °C, L/S = 100 (mL/g), 1.7% H ₂ O ₂	95% Co, 95% Li	[84]
HCl	80 °C, 4 M HCl	>99% Co, >99% Li	[85]
HCl, NH ₂ OH.HCl	80 °C, L/S = 100 (mL/g)	>90% Co, >90% Li	[86]
Citric acid + H ₂ O ₂	90 °C, L/S = 50 (mL/g)	>90% Co, >99% Li	[87]
H ₂ SO ₄ + H ₂ O ₂	75 °C, L/S = 20, 2 M H ₂ SO ₄ , 10% H ₂ O ₂	Co 95%, Li >99%	[88]
NaOH, H ₂ SO ₄ + H ₂ O ₂	40 °C, 4% H ₂ SO ₄ , 1% H ₂ O ₂	Co 97%, Li >99%	[89]
HCl	4 M HCl, 80 °C	Co 99%, Li 97%	[90]
C ₆ H ₈ O ₇ , H ₂ O ₂	2 M C ₆ H ₈ O ₇ , 80 °C, 90 min, L/S = 30. 2 H ₂ O ₂	Ni 97%, Co 95%, Mn 94%, Li 99%	[91]
H ₂ SO ₄ , + H ₂ SO ₂ , Na ₂ S, C ₂ H ₂ O ₄	2 M H ₂ SO ₄ , 6% H ₂ O ₂ , 1 h, 60 °C, 300 rpm	Co 98%	[92]
H ₂ C ₂ O ₄ , H ₂ SO ₄	0.25M H ₂ C ₂ O ₄ , L/S = 10, 0.5% H ₂ O ₂ , 80 °C, 90 min	Co, Ni, Mn > 99%	[93]

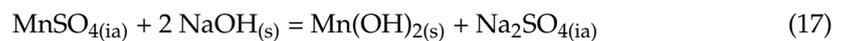
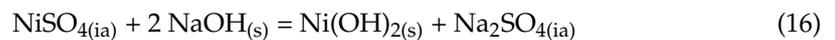
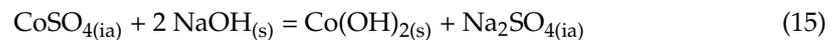
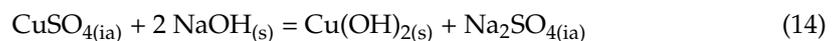
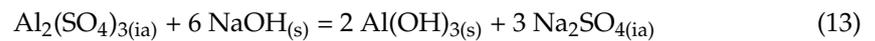
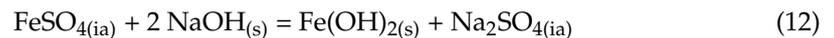
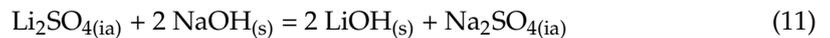
The most suitable and commonly used leaching reagent for many LIBs cathode materials is H₂SO₄ with the addition of H₂O₂ (Equations (7)–(10)). The main advantages of sulfuric acid are its low price and lower investment costs of equipment. Additionally, sulfuric acid can be considered a safer agent than hydrochloric acid, thereby reducing the cost of safety and handling.





3.2.3. Recovery of the Metals from Lithium-Ion Battery Solutions Precipitation

Precipitation is a process where the metal ions react to form a product with low solubility. Precipitation of metals is the most common method for obtaining metals in compound form. The most common salt used as precursor for the production of new LIBs is Li_2CO_3 , which can be extracted from leach solution with addition of Na_2CO_3 (Equation (6)). Ions of other metals, such as Co, Ni, Cu, Fe, Al, and Mn, form different precipitates of OH^- , $\text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , S^{2-} , and PO_4^{3-} [54,94–96]. The examples of precipitations from sulfate leach solutions are hydroxide precipitations represented by Equations (12)–(18). Each precipitation starts and ends with different pH values, which partially enables the selective recovery of the elements from the leach solution.



Zhu et al. investigated the leaching and subsequent precipitation of Li_2CO_3 from the LiCoO_2 extract in sulfuric acid with the addition of H_2O_2 . NaOH was used to adjust the pH of the extract to 5. A 1.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution was used to precipitate the cobalt, with stirring at 300 rpm for 1 h at 50 °C. The resulting CoC_2O_4 precipitate was filtered off and dried. A 1.1 M Na_2CO_3 solution was used to precipitate Li_2CO_3 under the same conditions. The resulting Li_2CO_3 precipitate contained 0.52% impurities. The efficiency of Li precipitation was mainly influenced by temperature, pH, Na_2CO_3 concentration, and $\text{Na}_2\text{CO}_3:\text{Li}^+$ ratio. The precipitation efficiency increased with increasing temperature. The highest efficiency of 81% Li was obtained at 50 °C, while at 20 °C, the authors obtained 78% Li. Subsequently, lithium precipitation efficiencies at pH 4, 6, 8, and 11 were compared, with yields of 55%, 73%, 77%, and 82%. The precipitation efficiency at $\text{Na}_2\text{CO}_3:\text{Li}^+$ 1:1 was 72.76%. A larger amount of Na_2CO_3 1.1:1 resulted in an increase in the process yield to 80.61%; increasing the ratio to 1.4:1 no longer had a positive effect on the precipitation of lithium from solution. The authors consider the optimal conditions as temperature 50 °C, 300 rpm for 1 h, pH = 10, and $\text{Na}_2\text{CO}_3:\text{Li}^+$ ratio = 1.1:1 [97].

X. Yang et al. proposed a multistage selective precipitation method to obtain valuable metals Ni, Co, Li, and Mn from used lithium batteries. The first step involved the selective precipitation of Mn^{2+} using ammonium persulfate $((\text{NH}_4)_2\text{S}_2\text{O}_8)$ under optimal conditions of pH = 5.5, temperature 80 °C, 90 min, and a molar ratio of reagent to Mn^{2+} of 3, resulting in 99.5% Mn^{2+} precipitation. Subsequently, a dimethylglyoxime reagent was used for the selective precipitation of Ni^{2+} under the optimal conditions of pH 6, temperature 30 °C,

20 min, and a molar ratio of reagent to Ni^{2+} of 2, resulting in 99.6% Ni^{2+} precipitation. The next step involved adjusting the pH to 10 with NaOH, and at a temperature of 30 °C for 15 min, where 99.2% Co^{2+} was obtained by precipitation. Finally, lithium was precipitated as Li_2CO_3 at 90 °C and pH 10 using sodium carbonate, resulting in 90% selective precipitation of Li from the solution [98].

X. Chen et al. proposed a process for recovering metals from solution by precipitation after the leaching of LIBs. Nickel and cobalt were selectively precipitated with dimethylglyoxime reagent ($\text{C}_4\text{H}_8\text{N}_2\text{O}_2$), followed by addition of the ammonium oxalate ($(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$). Manganese was recovered with Na-D2EHPA, and the manganese-containing D2EHPA was stripped with sulfuric acid. Lithium was precipitated with 0.5 mol/L sodium phosphate (Na_3PO_4). Under optimal conditions, 98% of nickel, 97% of cobalt, 98% of manganese, and 89% of lithium were recovered [91].

J. Li et al. proposed a process for obtaining Li and Co cathode materials from used lithium batteries. The material was leached in sulfuric acid. The optimal conditions were 3 M H_2SO_4 and 1.5 M H_2O_2 at a temperature of 70 °C for 1 h. The solution of 1M $\text{Na}_2\text{C}_2\text{O}_4$ was used for the precipitation of cobalt at a temperature of 50 °C, and it was obtained in the form of CoC_2O_4 , with a content of 99.5%. The next step consisted of the precipitation of lithium, which was obtained in the form of Li_2CO_3 with a content of 94.5% by adding Na_2CO_3 . Finally, the obtained CoC_2O_4 and Li_2CO_3 are used to produce LiCoO_2 for batteries [99].

Solvent Extraction

Solvent extraction (SX) or liquid–liquid extraction has a wide range of applications in inorganic and organic chemistry, industry, analytical chemistry, pharmacy, biochemistry, and waste treatment. In addition, SX is a good tool for studying the basic understanding of equilibrium and the kinetics of complex-forming processes. SX extraction methods have now become a routine in separation technologies. For metals in the first transition series, this will generally follow the Irving–Williams series—that is, for divalent metals, $\text{V} < \text{Cr} < \text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$. Thus, unless other factors are involved, copper will be extracted at lower pH values than the other elements. In addition, it is found that $\text{M}^{4+} > \text{M}^{3+} > \text{M}^{2+} > \text{M}^+$; therefore, thorium(IV) will be extracted before iron(III) in turn before copper(II) before sodium [100,101].

Dorella and Mansur designed a process aimed at recovering cobalt, aluminum, and lithium from used LIB. The process consists of manual disassembly to separate iron and steel, plastics, and electrode material containing Co and Li. This is followed by manual anode/cathode separation aimed at lead separation. The next step involves leaching in H_2SO_4 with H_2O_2 . The resulting leachate is then precipitated with NH_4OH to prevent the addition of another metal to the system. The resulting precipitate in the form of $\text{Al}(\text{OH})_3$ is then filtered off. The next step involves solvent extraction with Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid] to separate cobalt from lithium. Experimental results showed that approximately 55% Al, 80% Co, and 95% Li were leached. Using solvent extraction, the authors obtained 85% Co [88].

Kang et al. dealt with the selective recovery of Co from LIB by solvent extraction using saponified CYANEX 272. After physical–mechanical pretreatment, the authors performed acid leaching of fine fraction (1.19 mm) for 1 h at 60 °C with 2 M H_2SO_4 and 6 vol.% H_2O_2 , which led to the high leaching efficiency of cobalt (98%) and lithium (97%). Subsequently, the pH of the solution was adjusted to 6.5, resulting in the precipitation of >99% Fe, Cu, and Al as hydroxides together with 7% Co. The recommended system for the selective extraction of cobalt from nickel and lithium is 50% saponified with 0.4 M Cyanex 272 at an optimal equilibrium pH of 5.5–6.0 for 30 min and a temperature of 25 °C, thus achieving a 95–98% extraction of Co and ~ 1% Ni extraction. Lithium losses after the precipitation process and SX reached 32.27% (Li concentration in the leachate 3000 mg/L and after precipitation, and SX 2023 mg/L) [102].

Takáčová et al. investigated the use of SX to recover cobalt from LIB active mass leachate. The effects of pH, A:O ratio (for SX), O:A ratio (for stripping) in the range of 0.5, 1, and 2 were investigated. The mixture of 0.1 M CYANEX 272 with kerosene was chosen as the extraction agent with an extraction time of 15 min, stripping time of 10 min, and temperature of 20 °C. First, a model Co solution with a concentration of 3.7 mg/L was created by leaching a mixture of Co_2O_3 and Co_3O_4 in 2 M H_2SO_4 . The effect of pH and A:O ratio on Co extraction was investigated in the model solution, while the pH of the solution was adjusted with NaOH (250 g/L). A yield of almost 100% Co was achieved at pH 8 and an A:O ratio of 0.5. Stripping was performed using 2 M H_2SO_4 . The ideal conditions are O:A 2 ratio at pH 6. With SX real LIB leaching at pH 8, almost 100% Mn, 60% Ni, and less than 10% Li were converted to the organic phase. For this reason, pH 7 was chosen under optimal conditions, when 90% Co, 100% Mn, and 5% Li were converted to the organic phase, thus selectively separating Co from Ni. The highest Co stripping efficiency (80%) was achieved in the pH range 6–7, while 80% Mn and 100% Li were also transferred to the solution [103].

Pattamart Waengwan and Tippabust Eksangsri were dedicated to obtaining lithium through SX. The authors investigated the effect of pH in the range of 1.5–3 by adding HCl and NaOH. The test solution was prepared by mixing Li_2CO_3 and CoCO_3 solutions with a concentration of 10 mg/L. The authors used six types of solvent extractors, namely 98% n-butanol, 92.5% trioctylamine (TOA), 98% 4-methyl-2-pentanol (MIBC), 97% bis (2-ethylhexyl) phosphate (DEHPA), 98% trioctylphosphine oxide (TOPO), and 99% kerosene. The experiments were performed at an A:O ratio of 1:1 at 32 °C for 2 h. The authors concluded that DEHPA was the most effective extractant. Using DEHPA, the authors separated 75% Li at pH 1.5, with the highest yield being reached at 6 h of the experiment. Less than 40% of Co was removed from the solution using DEHPA [104].

P.E. Tsakiridis et al. dealt with solvent extraction of Al in a sulfate extract with the composition $\text{Ni}^{2+} = 4$ g/L, $\text{Co}^{2+} = 0.6$ g/L, $\text{Fe}^{2+} = 22$ g/L, $\text{Al}^{3+} = 6$ g/L, $\text{Cr}^{3+} = 1$ g/L, $\text{Mg}^{2+} = 5$ g/L. The authors used 20% Cyanex 272 along with 5% TBP diluted in Exxsol D-80. The results of the study indicate that 99.5 wt.% of Al can be recovered from the solution via Cyanex 272 at pH 3, temperature of 40 °C, stirring at 1200 rpm, and A:O ratio of 1:1. Subsequently, using 2 M H_2SO_4 at the ratio O:A = 2:1, it is possible to strip Al from the extractant at 40 °C with 99.6% efficiency [105].

Choubey et al. focused on obtaining Li, Co, and Mn from LIBs sulphate leachate. After LIBs pretreatment, the authors leached the active mass in 2 M H_2SO_4 with the addition of 10% H_2O_2 at a temperature of 75 °C. The resulting extract contained 1.7 g/L Cu, 1.4 g/L Ni, 6.9 g/L Mn, 11.9 g/L Co, and 1.2 g/L Li. The authors separated 99.5% Cu using 10% LIX84-IC with kerosene at pH 3 with stirring. The losses of Mn, Co, Ni, and Li were <1%. The next step involved SX Ni with 10% LIX84-IC at pH 4.6, achieving an extraction efficiency of 99.1%. However, Co, Mn, and Li losses accounted for 3.1%, 2.4%, and 1.7%. Cobalt was selectively precipitated using 10% ammonium sulfate at 30 °C for 30 min at pH 3. The losses of Mn and Li in Co precipitation were 0.89% and 0.6%, respectively. Subsequently, 98.9% Mn was obtained from the leachate containing 6.4 g/L Mn and 1.01 g/L Li using 10% D2EHPA at the ratio O:A = 1:1 and stirring for 10 min; 2.9% Li was co-extracted. After multistage SX and precipitation, the lithium losses were 18.33% [106].

Nguyen and Lee investigated the possibilities of recovering Li from primary and secondary raw materials using commercially available solvent extractors. Li was selectively extracted from brine or alkaline solutions with simple acidic extractants and a mixture of acidic and neutral extractants. However, the efficiency of lithium extraction with these extractants was low. The mixture of neutral extractants, TBP/TOPO, and chelating extractants in the presence of FeCl had a synergistic effect on the efficiency of extraction and separation of Li^+ from chloride solutions containing Na, Ca, K, and Mg. A small amount of co-extracted divalent metal cations in the TBP/TOPO system was scrubbed, and then, LiCl was obtained by stripping. In acidic extracts of secondary raw materials, divalent/trivalent metal cations are selectively extracted before Li ions by acidic extractants,

which complicates the Li^+ recovery process. Therefore, these divalent/trivalent cations Na, Ca, K, and Mg should be removed from the solution before Li is obtained. Among the acidic extractants and their mixtures, the Cyanex 272 system showed a high extraction capacity for divalent and trivalent cations. After removing Na, Ca, K, and Mg from the raffinate, Li can be precipitated as Li_2CO_3 by adding sodium carbonate [107].

Pranolo et al. dealt with the recovery of metals from LIB extracts and subsequent solvent extraction, employing the mixtures Acorga M5640, Ionquest 801, and Cyanex 272. In the first step of SX with a system of mixed extractants, the authors proposed to extract Fe, Al, and Cu with Acorga M5640. The extraction of these elements was performed at pH 3.75 and 22 °C. In the first 2 min of the experiment, 95% Fe, 77% Cu, and 33% Al were converted to the organic phase. By raising the temperature to 40 °C and adding 5% TBP, the authors achieved an increase in Al yield to 94% with an extraction time of 10 min and an A:O ratio of 2. The co-extracted ions can then be selectively eluted from the organic phase. In the second SX circuit with 15% Cyanex 272 and Shellsol D70, cobalt can be separated from lithium and nickel. The authors concluded that the ideal conditions for the separation of Co from Ni and Li are pH 5.5–6, a temperature of 22 °C, and an A:O ratio of 1:2, while the yield of single-stage SX is 90%. In the SX Co process, Li losses <20% occur, but Li can be washed out of the organic phase with Na_2CO_3 solution, followed by stripping Co. The Dowex M4195 ion exchanger can then be used to separate nickel from lithium. The advantage of the process is the possibility of obtaining pure cobalt, nickel, and lithium [108].

Ilyas et al. presented a novel recycling method for EOL Li-ion batteries. More than 84% Li was leached in water from the cathode material at 90 °C after 2 h at an L:S ratio of 40. A non-acidic solution containing lithium yielded 98% lithium by direct precipitation as Li_2CO_3 when the $\text{Li}^+:\text{CO}_3^{2-}$ ratio was 1:1.5. The Li-depleted cathode material was leached in 3M HCl at 90 °C for 3 h at an L:S ratio of 20. Selective precipitation of manganese was performed at 80 °C, pH = 2 by KMnO_4 with 1.25 overage. Ni and Co were separated by Cyphos IL 104 ionic liquid at pH = 5.4 and O:A = 1:1.5. The ionic liquid was fully stripped using 2M H_2SO_4 solution, resulting in the formation of high-purity $\text{CoSO}_4 \cdot x\text{H}_2\text{O}$ crystals by evaporation. In the next step, approximately 99% of nickel was recovered as nickel carbonate [$\text{NiCO}_3 \cdot 2\text{Ni}(\text{OH})_2$] from the Co-depleted raffinate. This precipitation process was carried out at a $\text{Ni}^{2+}:\text{CO}_3^{2-}$ ratio of 1:2.5, a pH value of 10.8, and a temperature of 50 °C [109]. In a different publication, the authors utilized recycled materials to develop a new ternary precursor through stepwise synthesis. They demonstrated similar electrochemical behavior with a capacity of 149 mAh/g [110].

Table 3 shows an overview of individual solvent extraction reagents for solvent extraction, the conditions under which they were used, and the efficiencies of separating individual metals.

Table 3. Review of solvent extraction used in LIBs recycling process.

Leaching Agent	Solvent	pH	Time (min)	Temp. (°C)	O:A	Yield	Ref.
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$	Cyanex 272	5	20	50	1:1	85% Co	[80]
H_2SO_4	Saponified CYANEX 272	5.5–6	30	25	2:1	95–98% Co	[102]
H_2SO_4	CYANEX 272 + Kerosene	7	10	25	2:1	90% Co, 100% Mn, 5% Li	[103]
HCl	D ₂ EHPA	1.5	120	32	1:1	75% Li	[104]
H_2SO_4	CYANEX 272 + Exxol D80	3	10	40	1:1	99.5% Al	[105]
H_2SO_4	10% LIX84-IC (PC-88A) + Kerosene	3	10	25	1:1	99.5% Cu	[106]
H_2SO_4	11% LIX84-IC (PC-88A) + Kerosene	4.6	10	25	1:1	99.1% Ni	[106]
H_2SO_4	10% D2EHPA	3	10	25	1:1	98.9% Mn	[106]
H_2SO_4	Acorga M5640 + 5% TBP	3.75	10	40	2:1	95% Fe, 77% Cu, 94% Al	[107]
H_2SO_4	15% Cyanex 272 + Shellsol D70	5.5–6	10	22	2:1	90% Co	[108]
H_2SO_4	HBTA + TOPO	13	2	25	1:1	90% Li	[111]
H_2SO_4	Saponified CYANEX 272 + kerosene	5.6	-	25	3:1	>99% Co	[112]
H_2SO_4	0.5 M D2EHPA	2.3	6	25	1:1	96% Mn	[113]
HCl	Cyanex 272	5	15	25	0.9:1	98% Co	[113]

Cyanex 272 was chosen as the most suitable reagent for SX, whose advantage is high selectivity. Depending on the pH of the solution, Cyanex 272 can selectively separate Al, Co, Ni, and Mn from Li. In the case of a high Al content in the aqueous solution, Cyanex 272 can be used to remove Al^{3+} at pH 3, thus obtaining another valuable raw material. Depending on the type of LIB, a large amount of Mn ions can also be present in the leachate, which can be selectively separated at pH 8 by Cyanex 272. Ni poses a significant challenge in SX, and various studies indicate that Cyanex 272 can only separate a maximum of 50% Ni. However, by implementing multistage SX, it would be possible to remove most of the Ni from the solution.

Ion Exchange and Membrane Processes

Multiple selective ion exchange resins can be used for ion exchange, which are suitable for lithium extraction from lithium salt solutions. This extraction method is suitable for obtaining ultra-pure lithium solutions necessary for the production of lithium batteries. The macroporous resin Lewatit TP 308 has been specifically developed for the treatment of low-concentration lithium salt solutions ($c_{\text{Li}} < 2 \text{ g/L}$) containing alkali metals, alkaline earth metals, and heavy metals at relatively high concentrations ranging from 100 milligrams to several grams per liter [113].

Other types of LEWATIT resins (K2629, TP207, and TP208) can also be considered suitable ion exchange resins, which have demonstrated high lithium retention capacity (>95%) from brines containing 0.6 mg/L of Li but no sodium. In the case of elution using 4 M HCl, the process efficiency achieved ranges from 74% to 90%. However, when both Li and Na are present in the solution, the retention performance is low, especially for the K2629 resin [114–116].

Another possibility of recovering Li from solutions involves “ion sieve” membrane processes. Ion sieves are adsorbents for specific metal ions with efficient ion separation. The adsorbents are derived from corresponding precursors, which contain target metal ions. The precursors typically represent molecular structures, which are stable even after the removal of target ions from the crystal lattice. The created voids in the crystal structure can only accept ions, whose ion radii are less than or equal to the target ions. A lithium-ion sieve (LIS) can only adsorb lithium ions to voids, as lithium has the smallest ionic radius of all metal ions. LIS can be divided into two types: lithium-manganese oxides (LMO type) and lithium-titanium oxides (LTO type). The LMO type LIS have a high lithium absorption capacity, good regenerative properties, and excellent lithium selectivity. In addition, the recovery of lithium from aqueous solutions has recently been significantly improved using electrochemical methods. However, in LMO type LIS, manganese is converted into an aqueous solution, which can cause water pollution in industrial plants [28]. LIS have great potential in recovering Li from solutions, but they are not yet commercially available products. Another disadvantage of LIS is their sorption capacity, based on which it is possible to use LIS only in diluted solutions. When the H^+ ion is exchanged for Li^+ from the solution, the solution is gradually acidified, which reduces the efficiency of the LIS, which decreases with decreasing pH. For this reason, it can be argued that LIS as a sorbent is suitable for recovering Li from primary raw materials (brine, seawater). However, the production of ion-selective membranes can be a progressive method of using LIS, which would make it possible to process solutions of higher concentrations [16,117–120].

4. Lithium Losses in Hydrometallurgical Processes

This part is devoted to issues concerning lithium losses in individual processing steps. The primary sources of lithium include brines and spodumene. Lithium is found in brine in the form of the LiCl solution, while in spodumene, it is present as LiAlSiO_4 . These primary raw materials do not contain significant amounts of impurities, which could affect the purity of the obtained lithium.

Brines typically contain low concentrations of lithium, ranging from 0.2 to 0.7 g/L. Lithium is precipitated from the solution by using Na_2CO_3 , resulting in the formation of

Li_2CO_3 . However, such low concentrations hinder the precipitation of lithium due to the Li_2CO_3 concentration being below its solubility limit. As a result, concentrating lithium through solution evaporation becomes a necessary step. By evaporating the solution, it is possible to achieve a concentration of 20 g/L of Li^+ , which is sufficient for the precipitation process. The solutions after lithium precipitation typically contain an average of 1.5 g/L of Li^+ , which corresponds to the solubility of Li_2CO_3 .

When extracting lithium from minerals, the first step is to convert lithium into a solution, which is achieved through high-pressure leaching or roasting followed by leaching in water. After lithium is converted into a solution, refinement methods are necessary to remove the impurities and concentrate the solution to achieve the desired lithium concentration. Standard procedures, such as crystallization or precipitation, are employed to extract lithium from the solution. In both cases of processing primary raw materials, a significant step is the concentration of lithium in the solutions to enable its subsequent efficient extraction.

In the case of extracting lithium from secondary raw materials, such as spent LIBs, the process becomes more complicated. In the recycling process, it is necessary to utilize pretreatment methods to recover the cathode material from other parts of the LIBs. The cathode material contains a wide range of other elements in comparison to primary raw materials, such as Co, Ni, Mn, Cu, Al, Fe, and others. These metals can be recovered through both pyrometallurgical and hydrometallurgical processes; however, in the case of lithium, it can only be recovered through hydrometallurgical treatment. The leaching of the cathode material is a relatively straightforward process, which shares similarity with lithium primary production. The most commonly used leaching agent is 2M H_2SO_4 with addition of H_2O_2 . Effective leaching is typically carried out at higher temperatures from 40 to 90 °C. The leaching of the cathode material is non-selective, resulting in the dissolution of not only lithium but also of other metals. High leaching efficiencies of over 95% are achieved in this step. Unlike cobalt, nickel, manganese, and other metals, lithium is leached within the first few minutes of the leaching process (60% Li and 5% Co) at low concentrations and temperatures, without the need for an oxidizing agent. This characteristic enables potential for the selective leaching of lithium [121].

A significant number of research articles focus on the detailed study of leaching conditions. However, these studies are conducted using high K:P ratios (10–40), which, on the one hand, contribute to understanding the lithium leaching mechanism and are suitable for achieving high lithium leaching efficiencies, but leach solutions with low lithium concentration are produced. These solutions are not suitable for direct lithium extraction, and it is necessary to include the economically demanding process of lithium concentration increase. This creates an opportunity for further investigation of the counter-current multistage leaching process at lower L/S ratios, where lower leaching efficiencies are achieved in a single leaching step on the one hand, but the concentrations of the obtained solutions would be sufficient for the following direct lithium extraction. The alternative methods for lithium concentration increase are cooling crystallization, antisolvent crystallization, and eutectic freeze crystallization [96].

The extraction of Li from the leach solution is performed as the final step after the recovery of other metals present, such as Co, Ni, Fe, Mn, Al, and Cu. Each extraction can lead to losses of lithium through adsorption or co-precipitation of lithium. The leach solutions have a pH usually ranging from 0 to 2, while lithium intermediates precipitate at high pH values. Lithium hydroxide precipitates at pH values above 13, while lithium carbonate has a wide precipitation range and starts to precipitate at pH 4. Higher precipitation efficiencies ($\pm 75\%$) of lithium carbonates can be achieved at pH values above 8. This is advantageous in terms of lower consumption of pH adjustment agents, such as NaOH. On the other hand, to prevent co-precipitation and contamination of the obtained lithium carbonate, precipitation is suitable to be carried out after the removal of other metals present.

The overall efficiency of lithium precipitation is greatly influenced by its initial concentration in the LIBs leach solution. Authors often report the percentage efficiency of the

precipitation step, but in the case of LIBs recycling, the lithium concentrations, volume changes, and specific pH at the end of precipitation are also important. Lithium carbonate obtained by precipitation may contain a small amount of impurities up to 0.5% [97], but authors often do not mention previous losses of lithium during the precipitation of other elements present, which can reach up to 30%.

There are several alternative methods for lithium losses reduction during the extraction of present metals. The most extensively studied method is solvent extraction, but other methods, such as adsorption, membrane processes, and electromembrane processes like electro dialysis, are also studied.

From the overview, it is evident that the combined method of precipitation of Al, Fe, and Cu followed by solvent extraction of the remaining components can still lead to high lithium losses exceeding 25%. Therefore, it is appropriate to also apply solvent extraction to Al, Fe, and Cu.

Aluminum can be effectively removed from the leach solution with an efficiency of 99.5% at pH 3 using CYANEX 272. Copper and nickel can be extracted from the solution using LIX84-IC (PC-88A) + Kerosene at pH 3 and 4.6, respectively, with lithium losses below 1% in the case of copper extraction and a loss of 1.7% in the case of nickel extraction. For the separation of Co from Ni, it is also possible to use Cyanex 272. With properly set conditions, in a solution with a concentration of 8.32 g/L Co and 1.95 g/L Ni, it is possible to separate 98% of cobalt in a single step while maintaining a low nickel extraction of up to 5%. Manganese can be extracted from the leachate using 10% D2EHPA at pH 3, but lithium losses reach 3%. In the case of a combination of several stages of solvent extraction, the total lithium losses can reach up to 15%.

In comparison to precipitation and solvent extraction methods, the method of ion exchange for lithium extraction is not extensively studied. This method is suitable for solutions with lower lithium concentrations below 2 g/L, and the presence of other metal ions at higher concentrations may not affect the selectivity of lithium sorption. The application of ion exchange offers the advantage of obtaining lithium during the primary stage of leachate processing, but it comes with the drawback of lower sorption capacities.

The application of the K2629 resin is not suitable for solutions containing both lithium and sodium. However, when the sodium content is low, it can retain lithium with an efficiency of up to 95%. Therefore, this ion exchanger is well suited for lithium extraction from LIBs leachates.

In terms of practical feasibility, precipitation is the easiest method; however, it can result in lithium losses of up to 30%. Solvent extraction and ion exchange are multistep and more complex processes, but they offer greater advantages in terms of lithium losses and the ability to obtain purer intermediates.

5. Conclusions

The increasing demand for portable devices, electric transportation, and battery storage has led to a growing need for lithium, making it a sought-after resource. As the production of lithium-ion batteries continues to rise, so does the quantity of generated waste, requiring appropriate processing. Although research into the treatment of lithium batteries receives significant attention, it cannot be claimed that the issue of their processing is fully resolved.

If physical–mechanical pretreatment is used during LIBs recycling, it is advisable to discharge the batteries prior to shredding and grinding, or to utilize grinding in an internal atmosphere or cryogenic grinding.

The recycling of LIBs is commonly carried out through large-scale pyrometallurgical processing. The advantages of these processes include lower requirements for mechanical pretreatment, the ability to process larger cell blocks, the absence of fire-related issues, and the presence of graphite acting as a reducing agent.

From the point of view of LIB recycling through hydrometallurgical processes, it is appropriate to ensure the classification of spent LIBs by chemical composition, as hy-

drometallurgical processes are sensitive to changes in the chemical composition of the input material. For the extraction of lithium from LIBs, the following aspects are associated with hydrometallurgical processing:

- Sulfuric acid with hydrogen peroxide appear to be the most promising agents for leaching.
- When considering optimal leaching conditions, the efficiency of leaching should not be the only determining factor. The resulting lithium concentration in the solution has a significant impact, as it affects the subsequent processing step. For instance, if a high L/S ratio is chosen, the resulting solution cannot be directly used for precipitation, and a solution concentration step is necessary.
- Lithium concentration increase can be achieved by evaporative, cooling, antisolvent, or eutectic freeze crystallizations, but these methods are economically unfavorable.
- The recovery of elements from a leach solution is mostly carried out by precipitation, solvent extraction, or ion exchange.
- Precipitation enables the extraction of compounds from solutions mainly in the form of hydroxides, carbonates, oxalates, sulfides, and phosphates.
- The use of precipitation can lead to total lithium losses of up to 30%.
- Solvent extraction is a more selective and efficient method, with lithium losses under 3% per individual step. The overall lithium losses in the whole process using SX could be up to 15%.
- In the case of both precipitation and SX, lithium is recovered last, after the recovery of the other elements from the solution.
- The process of ion exchange offers a high level of selectivity in lithium recovery, is suitable for low lithium concentrations, and does not necessitate the preliminary removal of other elements present in the solution. However, the disadvantage lies in the relatively low sorption capacity of ion exchangers.

The reduction in primary lithium raw material mining and import dependency can be accomplished by developing technologies for the valorization of secondary resources. Recycling of the LIBs allows the recovery of relatively pure lithium compounds, which can be reused in the production of new LIBs. However, the challenge remains in the relatively high losses of lithium, which creates the need for further research and process optimization.

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