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Original Research Article

Process Safety Challenges in Lithium-ion Battery Recycling

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Abstract

The rapid development of lithium-ion battery (LiB) recycling highlights its potential for addressing resource scarcity and environmental sustainability. Yet, the lack of systematic, process-specific safety frameworks means that critical hazards are often overlooked. Unlike existing studies that primarily emphasize technological advances, this study explores the process safety of LiB recycling through a struc-tured methodology. We conduct a review to map recycling processes (pretreatment, pyrometallurgy, and hydrometallurgy) and to uniquely identify and categorize the hazards arising from physical and chemical factors in these processes. In this regard, risk analysis was conducted to correlate hazards with potential accident scenarios, supported by accident case studies and industrial safety standards. To address these risks, this paper presents a comprehensive risk mitigation framework that utilizes the hierarchy of controls theory (elimination, substitution, engineering controls, administrative controls, and PPE). This methodology provides actionable recommendations for policymakers and industry practitioners to address existing technological and regulatory gaps to promote safe and sustainable LiB recycling practices. These insights offer new perspectives to the evolving discussion of sustainable energy systems, emphasizing safety as a cornerstone of innovation and implementation.

Keywords: Hazard; Lithium-ion battery; Process safety; Recycling; Risk mitigation.

1. Introduction

1.1 General

Lithium-ion batteries (LiBs) play a crucial role in modern energy storage, powering everything from smartphones and laptops to electric vehicles and renewable energy grids. Their high energy density, long lifespan, and fast charging capabilities make them superior to traditional battery technologies. LiBs have significantly contributed to reducing reliance on fossil fuels by enabling the widespread adoption of electric transportation and efficient renewable energy storage. As the demand for clean and sustainable energy solutions grows, advancements in lithium-ion battery technology continue to drive innovation, improving performance, safety, and environmental impact. Their versatility and efficiency make them a cornerstone of the transition toward a more sustainable and electrified future.

However, their rapid global deployment has introduced a critical challenge: managing the significant volume of waste generated by end-of-life batteries. By 2030, over 11 million tons of LiB waste are expected to accumulate worldwide, creating an urgent need for sustainable recycling solutions [1]. Due to their unique material composition, less than 6% of used lithium batteries are recycled, with the majority ending up in landfills, posing a particular environmental problem [2]. At the same time, the economic potential is substantial, with each ton of LiB waste valued at \$7708 [3]. Moreover, the recycling market is projected to grow to \$23.72 billion by 2030 [4]. The market revenue prospect is very considerable and thus drives the rise of the lithium battery recycling industry.

Current LiB recycling processes, including pretreatment, pyrometallurgy, and hydrometallurgy, have achieved significant advancements in recovery efficiency and cost-effectiveness [5]. However, Lithium-ion batteries pose a unique safety hazard at end-of-life due to their high stored electrochemical energy

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[6]. Even minor mechanical damage or residual charge can trigger thermal runaway, resulting in a dramatic temperature increase, fire, or outright explosion [7]. Exposure of active electrode materials to air and moisture during disassembly and pulverization can generate toxic and flammable gases (e.g., HF, CO_2) [8], and unintentional short-circuiting of the sorting line can initiate electrical arcing, resulting in severe burns and fire risk [9]. However, in the rush to maximize recovery rates and reduce costs, safety considerations are often an afterthought, leaving a serious gap in both academic research and industrial practice. This neglected and dangerous situation is a direct motivation to put process safety front and center in lithium battery recycling [10]. Field reports repeatedly document worker injuries, equipment damage, and environmental emissions—particularly during the pretreatment stage—yet safety measures remain treated as secondary to yield and cost considerations. This critical neglect of process safety directly motivates our study.

To address this gap, this study will deliver three primary outputs:

- Identify and analyze the physical and chemical hazards: A detailed mapping of pretreatment, pyrometallurgical, and hydrometallurgical workflows; A catalog of physical (e.g., thermal runaway, short-circuit) and chemical (e.g., HF, CO_2) hazards.
- Develop a robust safety framework based on the hierarchy of controls: Engineering-level measures (e.g., automated discharge stations, fire-resistant barriers); Administrative controls (e.g., inspection protocols, operator training curricula); PPE specifications tied to each identified hazard, with implementation templates and cost–benefit notes.
- Provide practical recommendations for policymakers and industry practitioners: Standardized "on-site" safety and safety facilities; Targeted policy proposals to integrate process safety into national and industry recycling standards.

To achieve these objectives, this study employs a comprehensive literature review and hazard identification approach. Analyzed to correlate hazards with potential accident scenarios. A systematic framework is proposed to address identified risks and address a critical gap in the existing literature by prioritizing process safety in LiB recycling. It provides actionable insights and a structured safety framework to reduce risks, enabling safer and more sustainable recycling practices. Additionally, the findings have practical implications for industry regulations and policy development, contributing to resource conservation and environmental protection.

1.2 Methodology

The overall research workflow is summarized in Figure 1. First, a comprehensive literature review was conducted to collect existing process data and risk assessment practices. Next, all identified process routes - pretreatment, pyrometallurgy, and hydrometallurgy - were mapped and tabulated for comparison as shown in Figure 2. The mapped processes then proceeded to the hazard identification phase: primary and secondary hazards were extracted and linked to potential accident scenarios following the steps in Figure 3. In the subsequent risk control phase, we develop targeted measures based on the established engineering control levels, as shown in Figure 4. Finally, we synthesize these results into a set of actionable recommendations.

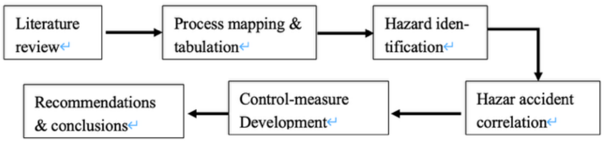

Figure 1. Overall methodology flowchart

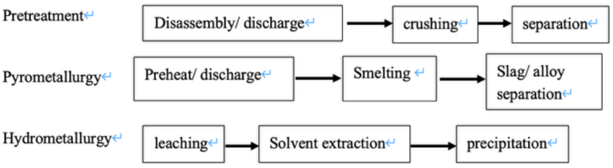

Figure 2. Three-Technique process overview

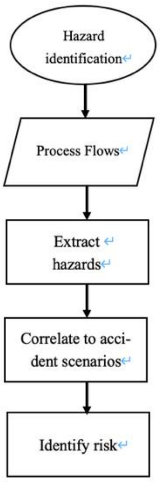

Figure 3. Hazard identification workflow

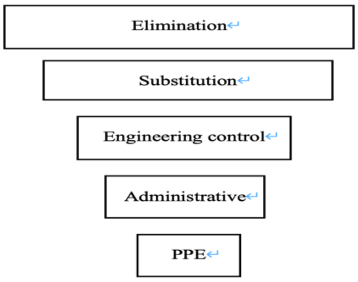

Figure 4. Hierarchy of control measures

Each of the three main processes is described in detail at the beginning of the corresponding subsection. Section 3.1 (Pretreatment) opens with the detailed flowchart in Fig. 5, guiding the reader through the disassembly, pulverization, and separation steps. Section 3.2 (Pyrometallurgy) begins with Figure 6, showing the furnace zone, reagent addition points, and product separation. Section 3.3 (Hydrometallurgy) begins with Figure 7, which shows leaching, solvent extraction, and precipitation, including key reagents and phase separation operations. By embedding these visualizations at each stage, the reader is provided with high-level structure (Figures 1-4) and fine-grained process details (Figures 5-7).

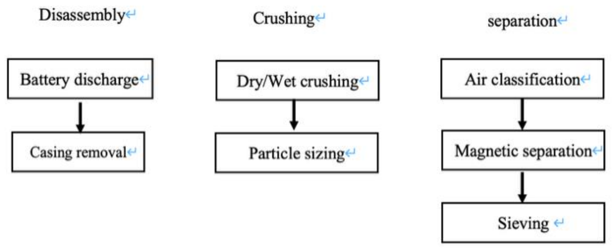

Figure 5. Pretreatment detailed flow

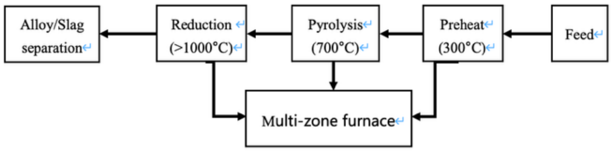

Figure 6. Pyrometallurgy detailed flow

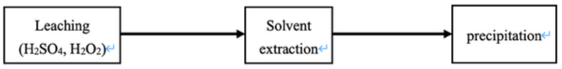

Figure 7. Hydrometallurgy detailed flow

1.3 Results and Discuss

1.3.1 Process and Risk Identification

During recycling, the hazards themselves can be divided into three categories: electrical, fire and explosion, and chemical [11]. Electrical hazards are divided into external short circuits and internal short circuits. The former occurs when charged electrodes are bridged by a conductor, forming a DC circuit that can cause electric shock (severity depends on remaining charge) [12]. The latter arises if the separator is breached by mechanical damage or dendrite growth-bringing electrodes into contact and unleashing the cell's stored energy as thermal runaway [13]. Thermal runaway triggers rapid, self-accelerating exothermic reactions that culminate in fire or explosion (see Figure 8).

In addition, chemical hazards resulting from chemical or physical behaviour changes in the chemicals inside the battery are another significant source of risk throughout the lithium-ion battery recovery process, including in Table 1:

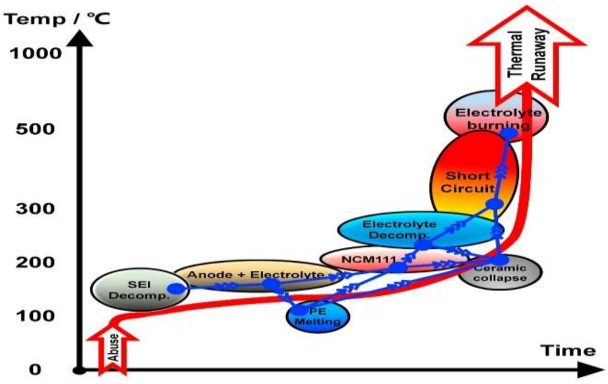

Figure 8. Thermal Runaway pathway (Feng, et al., 2018)

In the current recycling processes, pretreatment begins with discharging spent batteries and dismantling modules. Discharge methods include incineration or controlled thermal treatment [14]. Subsequent steps involve mechanical separation and targeted chemical processes-such as flotation or ultrasonic delamination isolate cell components [15]. Global LiB recycling operations typically follow one of two routes: the first is pretreatment (mechanical or physical) + hydrometallurgy[16]; The second category is pyrometallurgical + hydrometallurgical [17]. Although both end in hydrometallurgical recovery, their upstream technologies and associated hazards are poles apart. Therefore, our risk analysis is organized by sequential process stages: mechanical (or thermal) pretreatment, pyrometallurgy, and hydrometallurgy, ensuring each route's unique safety profile is fully evaluated.

1.3.2 Process of Pretreatments

Experimental data show that a 1-ton LiB pack holds about 7MJ at full charge [16], falling to 5.62MJ when the state-of-charge drops to 80%. This residual energy can still trigger thermal runaway or explosion during recycling. While cascade reuse of LiB is possible under strict integrity criteria, most facilities must first neutralize the remaining charge. Typical approaches include controlled thermal treatment or incineration (e.g, Umicore's shaft-furnace process); Inert-atmosphere heating to release energy safely; and Electrochemical discharge systems for gradual energy bleed-off.

Only after complete discharge do operators dismantle and separate modules—mechanically or via flotation and delamination—into cathode, anode, electrolyte, and casing. These pretreatment steps often overlap and are customized to optimize both safety and material recovery.

1.3.2.1 Discharge (Inactivate or Stabilize)

Salt solution discharge leverages the ionic conductivity of an aqueous NaCl bath to safely bleed residual charge from LiB cells [18, 19]. By submerging batteries in a ~10 wt% NaCl solution for 24h, the electrolytes short-circuit.

Table 1. Components hazardous to LiBs

Parts	Components	Details		References
Cathode	LiCoO2	React strongly with water, acid, or oxidant, burn or decompose by heat, and produce toxic lithium, cobalt oxides, etc.	Cobalt pollution changes the pH of the environment	[20]
Anode	Graphite	Combustion produces CO and CO2, and toner explodes when exposed to an open flame.	Dust pollution and fire risk	
Separator	Polypropylene, Polyethylene	It reacts with fluorine, strong acids, and strong bases to form HF	Fluorine pollution	[21]
Binder	Polyvinylidene fluoride (PVDF)	Combustion produces CO2， aldehyde, and so on	Organic pollution	[22]
Electrolyte	LiPF6	Highly corrosive, decomposes into HF in contact with water, reacts with strong oxidants, and burns into P2O5	Fluoride contaminates and alters the pH of the environment	[23]
Organic solvent	Ethyl carbonate (EC)	Reacting with acids, bases, strong oxidants, and reducing agents, the hydrolysates form aldehydes and acids, which are burned to form CO and CO2	Aldehyde, organic acid pollution	[24]
	Propylene carbonate (PC)	It reacts with water, air, and strong oxidants, and burns to form CO and CO2. Heat decomposition will produce aldehydes, ketones, and other harmful gases. Ignite can cause an explosion.	Organic pollution of aldehydes and ketones	
	Dimethyl carbonate (DC)	React violently with water, strong oxidants, strong acids, strong bases, and strong reducing substances. Hydrolysis yields methanol, and combustion yields CO and CO2	Methanol and other organic pollutants	
	Diethyl carbonate	reacts violently with water, strong oxidant, strong acid, strong base, and strong reducing agent	Organic contaminants such as alcohol	

Current is divert the electrolyte's is diverted into the brine, which absorbs heat and prevents thermal runaway [12, 25]. However, scaling this approach demands large salt volumes and prolonged immersion times—an obstacle for high-throughput recycling.

Alternatively, some facilities (e.g., Retriev, Mitsubishi) employ cryogenic passivation: freezing cells in liquid nitrogen (≈-195 °C) to immobilize the electrolyte and halt electrochemical reactions during disassembly [26]. While effective at quenching charge, this method faces practical hurdles: rapid LN_2 boil‑off at ambient temperature, high LN_2 consumption, and the need for cryo-rated handling equipment.

Both strategies—chemical discharge and cryogenic passivation—highlight trade-offs between safety, speed, and operational complexity in pretreatment, underscoring the need for optimized protocols that balance throughput with hazard mitigation.

1.3.2.1.1 Risk Identification and Analysis

Electric shock

LiB modules can retain dangerously high voltage even at 80% state of charge, posing serious shock hazards during disassembly. If insulation is compromised—by wear or mechanical damage—contact between a charged terminal (anode or shell) and an operator can complete a circuit and deliver a harmful electric shock. While small consumer cells carry minimal risk, EV packs—typically ~1,000 cells in series and over 7,000 in some Tesla models—can produce residual voltages far exceeding the human safety threshold of ~36 V [27].

Moreover, even after deliberate discharge, LiBs exhibit "voltage bounce," rebounding to ~1.5–2 V [28]. Though below lethal levels, this rebound can still deliver perceptible shocks, trigger involuntary muscle contractions, and precipitate secondary injuries—such as falls—when operators lose balance [29]. Rigorous voltage isolation, continuous monitoring, and strict handling protocols are therefore essential during mechanical removal.

Thermal runaway

Salt-solution discharge leverages a galvanic cell in brine to safely bleed residual charge as heat via controlled short-circuiting [12]. Although thermal runaway can occur in a single cell under these conditions, the surrounding salt bath rapidly absorbs and dissipates the heat, preventing propagation to neighboring cells. Furthermore, the oxygen-depleted environment of the solution inhibits fire or explosion, making salt-solution discharge a robust pretreatment method for large-scale LiB handling.

Leakage of electrolyte

A LiB requires up to 24 hours of immersion in sodium chloride solution. During this period: Galvanic corrosion occurs as Cl^- attacks the steel casing and Al foil electrodes, causing metal leaching "Eq. (1)" and reducing recovered metal precipitation "Eq. (2)," [28]; Chlorine evolution "Eq. (3)" produces a pungent, irritant gas, posing respiratory hazards; Water electrolysis may also generate H_2 "Eq. (4)", introducing an explosion risk in confined spaces [28].

$$Fe - 2e^- \rightarrow Fe^{2+}\ ;\ Al - 3e^- \rightarrow Al^{3+}\ ; \tag{1}$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \downarrow\ ;\ Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \downarrow \tag{2}$$

$$2Cl^- + 2e^- \rightarrow Cl_2 \uparrow;\ \ 2Fe(OH)_2 + Cl_2 + 2H_2O \rightarrow 2Fe(OH)_3 \downarrow +2HCl \tag{3}$$

$$2H_2O + 2e^- \rightarrow H_2 \uparrow +2OH^-\ ;\ 2H_2O - 4e^- \rightarrow 2O_2 \uparrow +4H^+ \tag{4}$$

On the other hand, Leaked LiB electrolyte—rich in volatile lithium salts—rapidly hydrolyses on contact with water to form highly toxic fluorides "Eq. (5)" [30]. Notably, phosphoryl fluoride (OPF_3) generated in this reaction can be more harmful than HF and itself hydrolyses into corrosive nitric acid and additional HF. Meanwhile, organic solvent components undergo hydrolysis to produce CO_2 and toxic or combustible by-products such as aldehydes and alcohols "Eq. (6-7)" [1].

$$LiPF_6 + H_2O \rightarrow HF\ + OPF_3 + LiF\ ;\ \ OPF_3 + H_2O \rightarrow H_3PO_4 + HF \tag{5}$$

$$(C_2H_5O)_2CO + H_2O \rightarrow CO_2 + C_2H_5OH\ ; \tag{6}$$

$$(CH_3O)_2CO + H_2O \rightarrow CO_2 + 2CH_3OH \tag{7}$$

Salt-solution discharge can create a highly corrosive and toxic environment if not carefully managed. Leaked electrolyte and galvanic corrosion produce fluorinated compounds alongside strong acids (HF, HCl, HNO_3), which attack equipment linings and accelerate casing degradation. Meanwhile, water-induced hydrolysis of organic solvents releases CO_2, methanol, ethanol, and irritating vapors such as formaldehyde—further compounding chemical hazards.

These by-products present multiple operational risks; Corrosion of tanks, pipes, and seals, leading to leaks and mechanical failures; Pressure buildup from undissolved gases, which can trigger overpressure explosions; Airborne hazards in open or poorly ventilated areas—HF inhalation can be life-threatening, CO_2 can cause localized asphyxiation, and flammable vapors may ignite or explode if they reach their lower flammability limits.

Mitigation requires corrosion-resistant materials, robust ventilation, continuous gas monitoring, and pressure-relief systems to ensure safe salt-solution pretreatment.

Liquid nitrogen

While liquid nitrogen pretreatment is effective in passivating lithium batteries, it also carries significant operational risks:

High cryogenic demand - freezing 1 kg of lithium batteries requires approximately 4.3 kilograms of liquid nitrogen, thus requiring large-scale production, storage, and recirculation systems.

Over-pressure hazard - any leakage, increase in ambient heat, or seal failure can lead to rapid vaporization of LN_2. A liquid-gas expansion ratio of 1:694 can cause a sudden rise in vessel or piping pressure. If venting is delayed or obstructed, there is a risk of over-pressure explosion.

Material embrittlement - Continued exposure to -196 °C can cause steel and seals to become embrittle, increasing the likelihood of brittle fracture under mechanical stress.

Frostbite Hazard - Direct contact with LN_2 or supercooled surfaces can cause severe cold burns to personnel.

Reducing these hazards requires the use of robust containment, automatic pressure-relief systems, cryogenic materials, and rigorous personal protective equipment and training programs.

1.3.2.2 Disassembly

A LiB whose terminal voltage has been brought and held below 1 V is deemed sufficiently discharged for safe handling [25]. At this point, specialized mechanical equipment applies calibrated force at the battery's positive and negative ends to strip away the outer casing—without breaching internal cell architecture. Most facilities stop at shell removal, leaving electrodes intact to minimize handling risks.

1.3.2.2.1 Risk Identification and Analysis

Mechanical damage and loss of control

Removing electrode sheets demands precise force control: too little force won't detach the active material, while too much can fracture cells and trigger electrolyte leaks. As a result, robust mechanical regulation—calibrated actuators, force sensors, and guarded feed systems—is essential. Additionally, manual interaction during loading exposes workers to moving parts and sharp cell fragments, highlighting the need for interlocks, protective shields, and, where feasible, automated handling.

Thermal Runaway

It is a relatively small risk, but it is still there. Module movement during disassembly can still cause positive and negative terminals to touch, creating an external short circuit; the heat generated may vaporize electrolyte and—even without full thermal runaway—spark fire or small explosions. Unlike controlled discharge, these mechanical-contact incidents seldom cascade into true thermal runaway, so they do not typify the major fire/explosion hazards in LiB recycling.

1.3.2.3 Crushing (Open Battery)

1.3.2.3.1 Mechanical treatment

In LiB pretreatment, crushing is the central operation once the residual charge has been fully neutralized. The primary goal is to fragment the battery modules and liberate internal components—cathode, anode, electrolyte, and casing—while simultaneously venting trapped liquids and solvents to mitigate pressure buildup and fire risks. Different vendors employ either dry or wet crushing under inert atmospheres to achieve these ends. Recupyl's two‑step dry method first uses a low‑speed (≈10 rpm) shear crusher in Ar/CO_2 to mince modules and release electrolyte, then a high‑speed (≈90 rpm) impact mill to reduce fragments to under 75 mm [31, 32]. Duesenfeld's LithoRec process similarly operates in N_2 at 100–140 °C but uses a single, high‑speed (≥300 rpm) rotary shear crusher to yield powder <500 µm once dry [31]. In Finland, Akkuser chains two airtight cutters (100–400 rpm) to a hammer mill (1,000–1,200 rpm) to achieve particles <6 µm [31].

By contrast, BatRec (Switzerland) and some U.S. facilities employ wet crushing: modules are submerged in deoxygenated water/N_2, and blade and impact crushers fracture the cells. At the same time, the water flow washes away debris and controls temperature, preventing additional heat generation during mechanical disruption [33]. Each approach balances throughput, safety, and material recovery, underscoring the need to select and optimize crushing protocols based on facility capabilities, desired particle size, and hazard mitigation requirements.

1.3.2.3.2 Thermal treatment

In addition to mechanical module opening, many recyclers employ thermal decomposition to fracture cells and liberate electrolytes [34]. In this approach, battery modules are incrementally heated above the melting points of internal components—such as the separator, current-collector foils, and polymer binders—so that each material layer softens or volatilizes in sequence. Sony–Sumitomo Electronics (Japan) applies this stepwise heating in ambient or inert atmospheres. Accurec (Germany) performs the same thermal profile under vacuum to reduce oxidation and gas-phase side reactions. By precisely controlling temperature ramps, both methods achieve clean separation of casings, electrodes, and electrolyte without mechanical shear, offering an alternative pretreatment path that minimizes dust generation and particulate release.

1.3.2.3.3 Risk Identification and Analysis

Thermal Runaway [13]

Thermal runaway in LiBs is not driven by a single material but by a cascade of exothermic events: a violent mechanical impact converts kinetic energy into heat, external heating conducts thermal energy into the cell, or a rapid internal/external short circuit generates intensive Joule heating. This initial heat triggers decomposition reactions of electrode materials and separator polymers, releasing combustible gases and further accelerating temperature rise. The resulting self-propagating chain of reactions—thermal runaway—carries a high risk of fire or explosion. In the crushing stage, the combination of mechanical energy input, separator breach, electrode contact, and any applied heat treatment makes the cell-opening process particularly susceptible to initiating thermal runaway.

Although thermal runaway triggers an average temperature of 198.6 ℃ (when the battery capacity is 50%), if the lithium battery discharge or stability fails it can produce voltage recovery, and can also cause the battery to be mechanically crushed, with a local temperature rise when the battery has 10% remaining power; the crushing process will cause stress near the point of a local temperature rise of up to 75 ℃, and even with 2% charge remaining it can produce heat that raises the temperature by 27 degrees Celsius.

Above 90 °C, the anode's solid–electrolyte interphase (SEI) film begins to break down. The SEI—composed of inorganic salts (Li_2CO_3, LiF) and organic species ($ROCO_2Li$, $(CH_2OCO_2Li)_2$)—normally passivates the graphite surface and permits only Li^+ transport. Once it decomposes, fresh graphite is exposed to the electrolyte, prompting continuous SEI re-formation and self-accelerating heat release. Critically, SEI decomposition also evolves explosive ethylene (C_2H_4) and oxygen (O_2), according to "Eq. (8)". These exothermic reactions produce both combustible and oxidizing gases, driving thermal runaway even in oxygen-limited environments.

$$(CH_2OCO_2Li)_2 \rightarrow Li_2CO_3 + C_2H_4 \uparrow + CO_2 \uparrow + O_2 \uparrow \tag{8}$$

At around 130 °C, the polyolefin and polycarbonate separators begin to melt and fracture, destroying ionic isolation and triggering internal short circuits that generate additional Joule heat. Simultaneously, separator breakdown releases toxic volatiles—most notably formaldehyde and benzene. As temperatures climb to 200 °C, the electrolyte itself undergoes pyrolysis "Eq. (9)" or, in wet-crushing scenarios, reacts with water "Eq. (5)" to form highly corrosive HF and phosphoryl fluoride

(POF_3), compounding both thermal and chemical hazards.

$$LiPF_6 \rightarrow LiF + PF_5 \tag{9}$$

PF_5 is highly reactive and readily attacks organic carbonate solvents-such as diethyl carbonate (DC), to form HF and ethylene "Eq. (10)", and the resulting products will also decompose "Eq. (11)".

$$C_2H_5OCOOC_2H_5 + PF_5 \rightarrow C_2H_5OCOOPF_4 + HF\uparrow + C_2H_4\uparrow \tag{10}$$

$$C_2H_5OCOOPF_4 \rightarrow OPF_3 + HF\uparrow + C_2H_4\uparrow + CO_2\uparrow \tag{11}$$

Then, when the decomposition reaction continues, exothermic heat continues to increase the temperature to 300℃. Still, the battery's cathode material has already decomposed at about 200℃ (decomposition "Eq. (12)"), providing conditions for combustion reaction under anaerobic conditions.

$$Li_xCoO_2 \rightarrow CoO + O_2\uparrow + LiCoO_2 \tag{12}$$

At around 500 °C, the cathode binder polyvinylidene fluoride (PVDF) undergoes exothermic decomposition "Eq. (13)", releasing further heat that sustains the runaway chain. Importantly, even without external heating, this step alone can maintain high temperatures; any added thermal input will not only accelerate PVDF breakdown but may also cause its onset to overlap with earlier decomposition reactions, compounding the severity of thermal runaway.

$$n(CH_2 - CF_2) \rightarrow n(CH = CF) + HF\uparrow \tag{13}$$

These decomposition reactions release large volumes of gas, which can rapidly elevate internal pressures and trigger overpressure explosions. In addition, any oxygen ingress can ignite the combustible pyrolysis or hydrolysis products—under residual heat or mechanical sparks—leading to fires or detonations.

Thermal runaway further generates significant quantities of hydrofluoric acid (HF), not only from Li-salt breakdown but also from PVDF binder decomposition. Aqueous HF aggressively permeates and corrodes equipment liners, thinning structural walls and increasing the risk of catastrophic failure. Escaped HF vapor and liquid can attack adjacent machinery and pose acute inhalation and skin-contact hazards to workers, underscoring the need for robust acid-resistant materials, continuous pressure relief, and protective measures.

Mechanical damage

During the crushing stage, LiB modules are fragmented by both reciprocating and rotary machinery, rendering high-speed moving parts and their couplings critical mechanical hazards. Wuschke (2019) reports that crushing requires a specific energy input of over 4.5 kWh t^{-1}, equivalent to a continuous power of 4,500 W. Assuming a 1 m stroke operating at 1 Hz, this corresponds to a force of approximately 4,500 N—on par with the weight of a 450 kg mass under gravity. Rotary cutters running at up to 1,200 rpm deliver substantial shearing action but also generate localized low-pressure zones (Bernoulli effect), which can draw in thin materials and create severe entanglement risks [35].

Inert gases and dust

Inert-atmosphere crushing relies on a continuous purge of CO_2, N_2, or Ar to displace oxygen and suppress combustion of released electrolytes and reaction gases. However, any leak or intentional venting introduces large volumes of asphyxiant gas—often mixed with toxic vapors—into the work area, creating serious suffocation and inhalation hazards if oxygen levels fall below safe limits. Continuous O_2 and gas-phase contaminant monitoring, combined with dedicated exhaust and dilution ventilation, is therefore mandatory.

High-speed cutting and milling likewise generate metal dust—predominantly nickel and cobalt oxides—even when nominal fragment sizes exceed 75 µm. Finer respirable fractions can become airborne during feeding and airflow, risking pulmonary inflammation and long-term lung damage. Effective dust capture (e.g., local exhaust ventilation, cyclonic separators) and mandatory respiratory PPE are essential to protect worker health.

Vacuum equipment

High-temperature pyrolysis under reduced pressure offers two key safety benefits: it suppresses unwanted side reactions and contains volatile by-products within the closed system. However, maintaining even a moderate vacuum poses structural challenges—thin-walled reactors must withstand external atmospheric forces, and true high-vacuum conditions risk catastrophic collapse. Consequently, the most critical hazard is failure of the vacuum generation or sealing system, which would both compromise inerting and expose operators to high-temperature vapours and reaction gases.

1.3.2.3.4 Specialized treatment

Most recycling facilities suppress electrolyte decomposition and combustion during cell opening and crushing by operating under an inert atmosphere (e.g., N_2 or CO_2) and routing any released vapors through dedicated exhaust-gas treatment. In contrast, OnTo (USA) employs a supercritical CO_2 extraction process to recover electrolyte and minimize emissions. In this method, spent battery modules are first pressurized to 74 bar at 31 °C in a CO_2 environment, exploiting the fluid's polar miscibility to dissolve carbonate-based electrolytes [36]. Subsequent depressurization separates the recovered electrolyte from CO_2, which can be recycled for continuous operation, thereby reducing hazardous by-products and improving process safety.

1.3.2.3.5 Risk identification and analysis

The residue of lithium

Supercritical CO_2 readily dissolves polar organic solvents but cannot solvate the lithium salt used as a conductive additive. Consequently, residual lithium species may become entrained in the supercritical fluid or remain trapped in the extraction vessel. Upon depressurization and CO_2 recovery, these lithium residues can undergo the reactions detailed in "Eq. (16)", regenerating HF and recreating the corrosive acid hazard described above.

Asphyxiating gas

Supercritical CO_2 extraction operates at pressures well above the critical point of CO_2, meaning the fluid behaves like a dense, liquid‑phase medium. In the event of a seal failure or system breach, the sudden decompression produces high‑velocity CO_2 jets that rapidly expand and displace ambient air. This can generate a large, oxygen‑depleted cloud, creating an immediate and potentially life‑threatening asphyxiation hazard over a broad area.

Equally concerning are the mechanical stresses imposed by these extreme pressures. Pressure vessels, piping, and seals must withstand cyclic loading and constant high‑pressure operation, which accelerates metal fatigue, degrades gaskets, and can precipitate weld failures. Any compromise in containment—whether from material fatigue, manufacturing defects, or maintenance lapses—can trigger a catastrophic overpressure rupture, making robust design, regular inspection, and fail‑safe pressure‑relief systems essential.

Recovery and storage of organic solvents

Recovered organic solvents from supercritical CO_2 extraction are both highly volatile and flammable. When stored in on‑site vessels, even small leaks or cross‑contamination with other combustibles can generate a dense vapor cloud that poses a serious fire or explosion risk upon ignition. Moreover, continual solvent evaporation raises internal tank pressures, creating a secondary hazard of overpressure rupture. Robust, sealed storage, explosion‑proof ventilation, and reliable pressure‑relief systems are therefore essential to prevent both vapor cloud formation and catastrophic vessel failure.

1.3.2.4 Separation

After all active materials and casings have been removed, the remaining solids—comprising electrode powders, current-collector foils, and polymer fragments—are subjected to staged physical separation to recover recyclable fractions. First, an air-classification unit uses controlled airstream velocities to segregate particles by size and density, yielding coarse and fine fractions for independent collection (Figure 9) [37]. Next, a magnetic separator captures ferromagnetic components (e.g., steel casings, iron impurities) via a drum or magnetic-adsorption system. Finally, a vibrating screen sorts the non-magnetic residue into predefined size ranges, ensuring that each fraction is optimized for its respective recycling pathway (Figure 10).

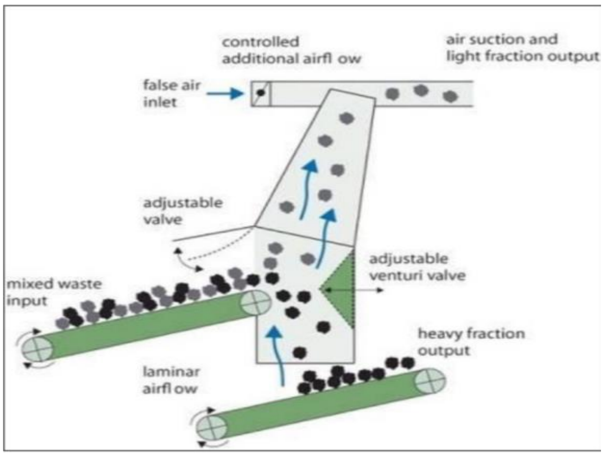

Figure 9. Air separation

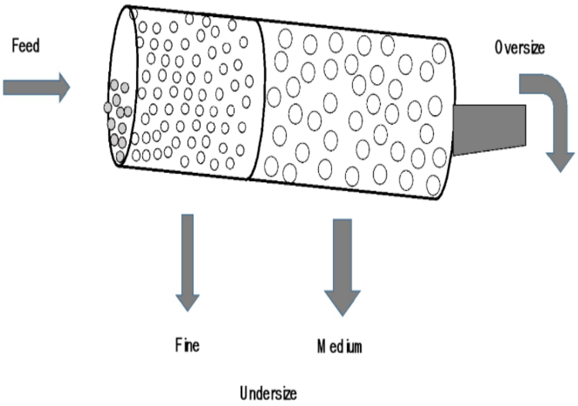

Figure 10. Vibrating screen

1.3.2.4.1 Risk Identification and Analysis

Dust

Vibratory screening can aerosolize metal fragments and graphite powder, creating inhalation hazards and dust explosion hazards like those encountered in the crushing stage.

Mechanical damage

Rotating transmission components in the separation stage present the same high-speed entanglement and mechanical impact hazards as those in the crushing process, requiring identical guarding and lockout/tagout controls.

1.3.3 Process of Pyrometallurgy

Revised Pyrometallurgy Section

Pyrometallurgical recycling harnesses high-temperature roasting or melting to recover valuable metals from LiB waste. Two principal architectures prevail:

Direct Smelting. Spent modules or individual cells are first disassembled [38] and then fed—together with a carbonaceous reductant (e.g. graphite) and slag-forming fluxes (e.g. SiO_2, FeO)—into a vertical shaft furnace partitioned into low-, mid-, and high-temperature zones. In each zone, cathode oxides (e.g., $LiCoO_2$) undergo carbothermic reduction to metal alloys, while the exothermic oxidation of graphite sustains furnace heat [39].

Multi-Step Smelting. After mechanical pretreatment, cells are melted in an electric-arc furnace at temperatures exceeding 1,000 °C. The intense heat reduces oxides and produces immiscible metal alloys—typically separating into a dense alloy phase and a lighter slag—facilitating downstream metal recovery [37, 40].

Complementary to these, pyrolysis (800 – 1,000 °C under inert gas) and incineration (~550 °C in oxidizing atmospheres) have become widespread for organic-binder removal[41, 42]. While effective at volatilizing polymeric binders and electrolytes, both routes emit CO, CO_2, and fluorinated by-products that require robust off-gas treatment.

Among emerging techniques, carbothermic reduction roasting (CRR)—operating at 650 – 1,000 °C—offers selective reduction of cathode materials with superior energy efficiency. Key reactions "Eq. (14-19)" and a comprehensive process flowchart are shown in Figure 11 [43].

Overall reaction:

$$4LiCoO_2 + 3C \rightarrow 2Li_2\mathrm{CO}_3 + 4\mathrm{Co} + CO_2; \qquad (14)$$

Process reaction:

$$4LiCoO_2 \rightarrow 2Li_2\mathrm{O} + 4\mathrm{CoO} + O_2 \qquad (15)$$

$$2CoO + C \rightarrow 2\mathrm{Co} + \mathrm{C}O_2 \qquad (16)$$

$$Li_2\mathrm{O} + \mathrm{C}O_2 \rightarrow 2Li_2CO_3 \qquad (17)$$

$$C + O_2 \rightarrow \mathrm{C}O_2 \qquad (18)$$

$$C + O_2 \rightarrow \mathrm{CO} \qquad (19)$$

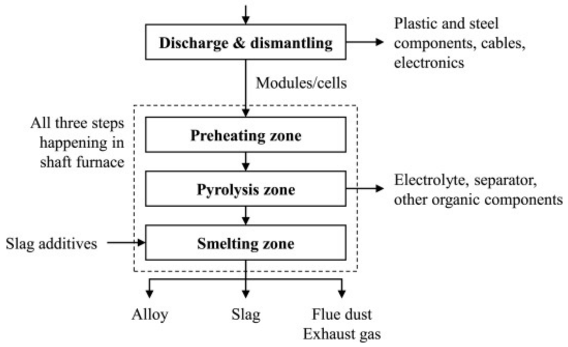

Figure 11. Direct smelting process [44]

In addition to carbothermic reduction, salt-assisted roasting has emerged as an alternative route to convert cathode oxides into low-melting, water-soluble metal salts. Laboratory-scale studies have explored sulfation and nitration roasting to produce metal sulfates and nitrates, respectively, but only chlorination roasting—using HCl, NH_4Cl, Cl_2, or $CaCl_2$—has been industrialized [45-48]. In this process, high-temperature treatment in the presence of chlorinating agents yields metal chloride salts that volatilize or dissolve at much lower temperatures than the parent oxides, greatly easing downstream separation [39].

Commercial pyrometallurgical operations—such as those run by Umicore (Belgium), Glencore (Switzerland), Accurec (Germany), and Inmetco (USA)—nonetheless rely predominantly on high-temperature smelting in rotary kilns or electric-arc furnaces, varying temperature profiles and residence times to optimize metal yield [38, 40].

As a result, the principal safety challenges mirror those of conventional carbothermic processes, centering on control of thermal gradients, reactive gas evolution, and material handling across sequential temperature zones.

1.3.3.1 Carbon Thermal Reduction （CTR）

In the shaft-furnace route, recovered LiB modules are first homogeneously mixed with a reductant charge—comprising a slag former (SiO_2, $CaCO_3$) and coke—and then fed into a vertical shaft furnace[19]. The thermal profile is divided into three zones:

Preheating Zone (<300 °C): Electrolyte evaporation and casing expansion facilitate safe cell opening without mechanical intervention.

Pyrolysis Zone (≤700 °C): Organic electrolytes volatilize and combust, supplying in-situ heat to maintain furnace temperature.

Smelting Zone (1,200–1,450 °C): Oxygen introduced at the furnace base reacts with the charge, reducing cathode oxides to form metal alloys and slag, which separate by density under gravity.

This staged heating strategy maximizes energy efficiency and metal recovery while controlling reactive gas evolution and ensuring structural integrity of the furnace lining.

1.3.3.2 High-Temperature Smelting

Different companies employ a range of furnace technologies for pyrometallurgical recovery: Glencore operates rotary kilns and converters, Sony–Sumitomo uses reverberatory furnaces, and JX Nippon favors fixed-bed furnaces. In each system, careful temperature control (typically ≥ 1,300 °C) ensures complete evaporation of residual organic electrolytes before reduction. Thereafter, carbon—often sourced from solvent residues—and aluminium inherent in LiB components serve as in-situ reductants, converting metal oxides into molten alloys. Fluxing agents are added to lower the melting point and promote slag formation, yielding cleaner metal and slag phases for downstream separation [49].

1.3.3.3 Risk Identification and Analysis

Thermal runaway

In pyrometallurgical operations, maintaining a stable furnace temperature is essential—but the risk of internal thermal runaway remains ever-present. If residual charge or hot spots trigger an uncontrolled exotherm, the ensuing spike in thermal radiation and convective heat can ignite nearby combustibles and inflict severe burns on personnel. Leaks, overflows, or tapping of molten alloys and slag may release streams of 450–1,200 °C fluid or solid droplets, whose radiant and conductive heat fluxes pose catastrophic injury hazards. High-temperature off-gas emissions—often rich in particulates and corrosive species—can overpressurize ductwork and erode lining materials, further compromising safety. Mitigation requires robust furnace containment, redundant pressure-relief systems, thermal shielding around tapping points, and strict operational protocols to safeguard workers and equipment.

Fire explosion

Under controlled heating, LiB cell casings begin to fracture below 200 °C, allowing liquid electrolyte to escape; above 200 °C, this electrolyte vaporizes rapidly [37]. If temperature continues to climb unchecked, sudden gas evolution can spike internal pressures—within intact cells or containment vessels—creating an imminent risk of overpressure rupture or explosion. At the same time, the released combustible vapors can ignite inside the furnace or upon venting into the workshop atmosphere, where even small leaks may trigger fire or deflagration.

Dioxins, furans

Lithium-ion separators commonly incorporate polyethylene, which under incomplete combustion (< 800 °C) can yield chlorobenzenes and ultimately dioxins[47]. Moreover, residual chlorine- and carbon-rich materials may directly catalyze dioxin synthesis in the presence of transition-metal electrodes (e.g., Co, Cu), bypassing chlorobenzene intermediates. Although separator pyrolysis during pretreatment (≥ 400 °C) releases chlorine-containing volatiles, its brief residence time and the lack of solid-phase metal catalysts (metals remain in ionic form) make significant dioxin formation unlikely in this stage.

HF and other fluorinated compounds, CO

In pyrometallurgical recycling of spent LiBs—when no prior pyrolysis pretreatment is applied—the thermal decomposition of LiF and polymeric binders liberates significant amounts of HF. Concurrently, at temperatures below 450 °C, incomplete combustion of graphite can generate CO, posing asphyxiation and explosion hazards. Moreover, side reactions produce SiF_4 "Eq. (20)", a highly corrosive gas that readily hydrolyzes to H_2SiF_6, exacerbating equipment corrosion and demanding robust off-gas scrubbing.

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O \tag{20}$$

1.3.4 Process of Hydrometallurgy

Hydrometallurgical recovery of LiB materials relies on aqueous-phase leaching followed by solvent extraction and precipitation [50, 51]. In the primary leaching step, cathode oxides (M–O) are dissolved using sulfuric acid—often with a reducing agent such as H_2O_2—to generate soluble metal ions [52, 53].

To boost dissolution rates and mass transfer, cavitation from ultrasonic treatment and mechanical stirring are applied, creating microjets and turbulence that enhance particle–liquid contact [1, 54].

The ensuing pregnant liquor is then subjected to solvent extraction—typically using organophosphorus or amine-based extractants—to concentrate target metals selectively. Finally, metals are recovered via chemical precipitation (e.g., as hydroxides or sulfates) in a second stage, yielding pure metal salts suitable for reuse [52, 53] (see Figure 12 for process flow).

Hydrochloric and sulfuric acid leaching proceed according to "Eq. (21)" and "Eq. (22)", respectively. To enhance cobalt recovery, H_2O_2 is added as a reductant, converting Co^{3+} to Co^{2+} "Eq. (23)"—a critical step since divalent cobalt salts exhibit substantially higher solubility. Additionally, Recupyl (France) implements a preliminary NaOH leach to selectively dissolve and recover aluminium before the main acid leach, as shown in "Eq. (24)" [27].

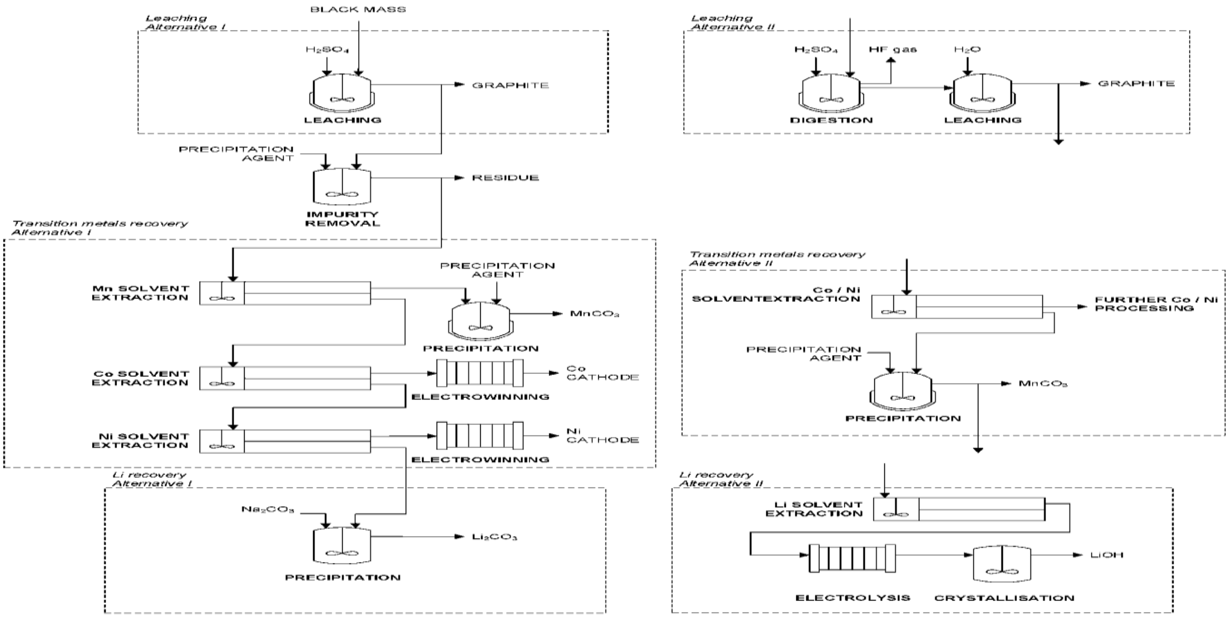

Figure 12. H_2SO_4 leaching and extraction process [55]

$$2LiCoO_2 + 8HCl \rightarrow 2CoCl_2 + Cl_2 \uparrow + 2LiCl + 5H_2O \tag{21}$$

$$4LiCoO_2 + 6H_2SO_4 \rightarrow 4CoSO_4 + O_2 \uparrow + 2Li_2SO_4 + 6H_2O \tag{22}$$

$$2LiCoO_2 + 3H_2SO_4 + H_2O_2 \rightarrow 2CoSO_4 + O_2 \uparrow + Li_2SO_4 + 4H_2O \tag{23}$$

$$H_2O + 2NaOH + Al \rightarrow 2NaAlO_2 + 3H_2 \uparrow \tag{24}$$

1.3.4.1 Risk Identification and Analysis

Chemical reagent

Hydrometallurgical recycling relies entirely on aqueous chemistry to dissolve and recover valuable metals from spent LiB materials. Beyond the redox leaching of cathode oxides, the process steps that follow—solvent extraction, chemical precipitation, and ion exchange—are governed by solubility and displacement reactions rather than further redox chemistry. As a result, the primary safety concerns stem from the reagents themselves.

The initial leaching stage uses hydrochloric acid or sulfuric acid, typically heated in an 80 °C water bath to accelerate dissolution. These strong acids generate dense acid mists and fumes during storage, handling, and especially when warmed, posing serious corrosion risks to piping and equipment and chemical-burn hazards to exposed skin and eyes.

Next comes alkaline leaching or pH adjustment with sodium hydroxide (or sometimes calcium carbonate to form Na_2CO_3 in situ). These highly caustic solutions release significant heat upon mixing and neutralization, producing hot, corrosive aerosols that can degrade seals and vessels—and inflict permanent chemical burns or vision loss on contact.

During solvent extraction, common reagents (Cyanex 272, PC88A, DEHPA) are generally regarded as low toxicity, but their organic diluents can volatilize under process conditions. Without proper containment and vapor-capture systems, these vapors can irritate respiratory tracts and, in worst-case scenarios, contribute to fire hazards.

The final precipitation and neutralization steps—using sodium carbonate or sodium hypochlorite—are relatively low-risk chemically. However, preparing sodium carbonate from NaOH and $CaCO_3$ can be highly exothermic, generating corrosive steam that threatens both operator safety and equipment integrity. Any leaks or seal failures during handling of strong bases will accelerate corrosion and environmental contamination.

Above all, the single greatest risk in wet-chemical recycling is waste‑stream management. Improper capture, neutralization, or disposal of spent acids, bases, and metal-laden effluents can lead to severe soil, water, and ecosystem pollution. Robust wastewater treatment—incorporating neutralization, heavy-metal removal, and polishing filtration—is therefore essential to safeguard both human health and the environment.

Gas

Depending on the choice of leaching solvent, acid treatments can evolve toxic gases—most notably chlorine (Cl_2) and sulfur dioxide (SO_2). Both inhalation hazards and, upon contact with moisture, form strongly corrosive acids that threaten equipment and personnel.

Similarly, alkaline leaching liberates hydrogen gas, which can accumulate in confined or poorly ventilated areas and, upon encountering an ignition source, trigger flash fires or full-scale explosions.

1.3.5 Summary of Risk Analysis

1.3.5.1 Summary risk

The safety issues in the whole process of lithium-ion battery recycling are summarized in the following table 2 after the above analysis:

Table 2. Three-process risk details

Process	Risk	Risk details
Pretreatment	Electric shock	1. Residual internal power 2. The risk of the voltage relaxation effect is difficult to eliminate 3. Electric shock
	Thermal Runaway （High Temperature)	1. Can be excited by external or internal short-circuit power release 2. Violent disassembly, mechanical energy into heat 3. External heat source leads to an uncontrollable pyrolysis chain reaction
	Release of Electrolyte	1. Lithium salt solution in the electrolyte is decomposed to generate highly toxic and corrosive HF 2. Electrolysis of discharge salt solution generates toxic chlorine gas, flammable hydrogen, and oxygen as combustion support, even if the closed environment is flammable, fire and explosion can occur 3. Organic solvent components are hydrolyzed to generate many gases and more flammable alcohols, aldehydes, etc
	Cold Injury	Liquid nitrogen, frequent heat convection equipment, pipeline brittle fracture failure; Cold frostbite; Overpressure; Suffocation
	Mechanical damage	High-speed moving, protruding, or sharp parts
	Substance Hazardous	1. Decomposition of combustible gas released, combustion-supporting gas, causing fire and explosion 2. Pyrolysis products of lithium electrolyte salt, highly toxic HF, and combustible gas 3. Decomposition of positive electrode materials, gas combustibles 4. Binder decomposition, HF 5. Process conditions: inert gas environment causes asphyxiation
	Dust	1. Metal dust, which can affect lung health if inhaled. 2. Graphite dust, explosion risk
	Others	1. Supercritical carbon dioxide, ultra-high pressure, asphyxia 2. In a vacuum environment, high vacuum will seriously damage the equipment 3. Inert gases
Pyrometallurgy	Thermal Runaway （and High Temperature)	Without pretreatment, the risk is consistent with the risk of the pretreatment process. After pretreatment, thermal runaway is reflected in the furnace temperature control loss or alloy fluid, slag leakage, and thermal impact on the surrounding environment.
	dioxins	Special product of the pyrometallurgical process, high toxicity
	Fire explosion	The temperature rises out of control, and rapid evaporation of the electrolyte generates many combustible, toxic gases, causing overpressure explosions and fires.
	HF	Pyrolysis product
Hydrometallurgy	Chemical reagent	The causticity of strong acids and alkali, and the harmfulness of acid fog to people
	Gas	REDOX reactions, chlorine, sulfur oxides, and hydrogen hazards

Throughout the recycling workflow, three hazard categories are mainly analyzed with the most possible causes: thermal runaway, fire/explosion, and chemical/physical risks. Thermal runaway is triggered by the exothermic interaction between the SEI layer of the anode, the trapped electrolyte, and the separator material. While simple overpressure explosions or fires in electrolyte vaporization are not themselves out-of-control events, they can easily provide the required external heat to trigger a complete out-of-control sequence. At the same time, each stage depends on a wide range of chemical reactions and treatment of aggressive reagents (acid, caustic, flammable, or toxic), so the reaction by-products, as well as the inherent physical hazards of powders, sharp debris, and high-speed machinery, represent the dangers of the entire LIB regeneration.

1.3.5.2 Risk Mitigation

1.3.5.2.1 Thermal runaway

The fundamental driver of thermal runaway in Li-ion cells is a self-sustaining exothermic chain reaction: once heat generation outpaces dissipation, cell temperature—and thus reaction rate—accelerates uncontrollably. Consequently, any effective mitigation strategy must focus on interrupting this heat accumulation.

First, real-time temperature monitoring is essential. Infrared thermography or embedded fiber-optic sensors can detect localized “hot spots” before they escalate.

Automated interlocks tied to these sensors should immediately halt material feed and isolate the affected zone, limiting the spread of runaway to neighboring cells or modules.

Second, forced-cooling systems can arrest rising temperatures if applied swiftly. Timed injections of cryogenic fluids (e.g., liquid nitrogen) or cold inert gas can quench developing hot spots but must be engineered to avoid thermal shock to equipment—excessive cooling rates can embrittle linings and mechanical components. Cooling protocols, therefore, require controlled ramp-down rates and mechanically robust vessels.

Finally, once a cell enters full runaway—where temperatures climb at hundreds of degrees per second—only rapid quenching with water-spray deluge or foam can reliably terminate the reaction. Housing pretreatment and crushing equipment in dedicated quench chambers or remote, thermally shielded enclosures further protects personnel and adjacent systems. Water curtains or heat-absorbing barriers around high-risk areas will intercept radiant heat and contain any fire or explosion, ensuring that even the most violent runaways can be managed safely.

1.3.5.2.2 Electric Shock

Electrical hazards in LiB pretreatment go beyond the familiar shocks from mains or live machinery. The primary risk arises when residual charge remains in battery modules: an operator who inadvertently contacts both the positive and negative terminals at once—during dismantling or handling—can receive a harmful electric shock. To guard against this, all personnel must wear insulated gloves and fully rated PPE whenever they interact with spent cells, and tools must be insulated to the highest expected residual voltage.

Equally important is work-practice control: no one should supervise or manipulate live components while standing on ladders or elevated platforms, since a shock can cause involuntary muscle contractions or nerve impairment and precipitate a fall. By enforcing strict “no-height” rules during pretreatment and mandating lockout of residual energy before any disassembly, facilities can dramatically reduce both shock and secondary fall-related injuries.

1.3.5.2.3 Chemical Hazardous

Liquid nitrogen, supercritical carbon dioxide

Inert-gas atmospheres inherently carry a significant asphyxiation hazard, since any oxygen displacement within the work area can render even brief exposures life-threatening. To minimize leakage, all process vessels, piping, and valves must be engineered for high sealing performance and routinely inspected for integrity. Continuous pressure monitoring—capable of detecting both under-pressure (indicative of a leak) and over-pressure (suggesting blockage or runaway vaporization)—should be tied to an automated alarm and isolation system that can promptly halt operations and evacuate the affected zone.

Ventilation systems must be capable of both normal and emergency duty, converting the facility to negative pressure during a gas release and safely routing exhaust well away from occupied areas. Fixed gas-detection sensors, together with personal respiratory protection, ensure early warning and individual safety. When cryogenic fluids such as liquid nitrogen or supercritical CO_2 are employed, all vessels and transfer lines require insulation and materials rated to withstand rapid temperature swings without embrittlement. Automated pressure-relief valves should be installed on all cryogenic storage and reaction vessels to prevent over-pressure events, and their set-points must be calibrated to the lowest fault-tolerant threshold. Together, these measures create layered defenses that protect personnel and equipment from the dual threats of asphyxiation and pressure-induced failures.

Electrolytes, adhesives, and other decomposition products HF (fluorine compounds), organic combustibles

In LiB recycling, two categories of off-gas and condensate must be managed: (1) high-temperature decomposition products and (2) hydrolysis by-products, some of which volatilize, and others dissolve in water to form corrosive, flammable liquids.

For high-temperature decomposition gases, a closed-loop condensation system should recover vapors for subsequent treatment in a dedicated incinerator. Integrity of the condenser and ductwork must be monitored continuously, and fixed gas detectors must be deployed to alert on any leaks. Because hydrogen fluoride (HF) is non-combustible yet acutely corrosive and toxic, all personnel working in these areas must wear acid-resistant clothing, neoprene gloves, chemical splash goggles, and cartridge respirators rated for HF. Ventilation must support at least three air changes per hour under normal conditions and six during an incident, exhausting well away from occupied or traffic zones. A water-spray dilution system should be installed to suppress accidental HF releases, and all process wastewaters must be routed to a dedicated holding tank—never into common drains—before neutralization. Emergency eyewash stations and safety showers must be positioned adjacent to any HF-generation or condensate-handling equipment.

Recovered HF and related fluorides are to be stored in compatible plastic containers, and all piping, valves, and tank linings exposed to HF must undergo regular inspection for corrosion and integrity testing of protective coatings.

Volatile organic solvents liberated during hydrolysis or pyrolysis pose fire and explosion hazards. Flammable-gas detectors, explosion-proof ventilation, and intrinsically safe electrical fixtures are therefore mandatory wherever solvent vapors may accumulate.

Operators must don antistatic, acid-resistant clothing with non-sparking footwear, and floors and walls should be smooth and grounded to prevent vapor pockets and static discharges.

Finally, incomplete combustion below 800 °C can generate dioxins, which must be captured by the same condensation and incineration infrastructure used for HF. All dioxin-laden condensates are channeled to the high-temperature exhaust incinerator, and any residual off-gas controls mirror the HF management measures described above.

Hydrometallurgical solvent

Storage and handling of strong acids and bases demand rigorous containment and environmental controls:

- Closed, double-contained systems. All tanks, piping, and transfer lines are fully sealed and double-contained, with dry-break quick-connects and double-isolation-and-bleed (DIB) valves at transfer points to prevent fugitive vapours and drips.
- Negative-pressure bays and dedicated off-gas. Storage/transfer areas operate under slight negative pressure and vent to a dedicated off-gas header (not general HVAC).
- Off-gas capture/treatment train. Headspace is routed through quench/condense → alkaline packed-bed scrubber → high-efficiency mist eliminator, sized for peak gas rates; add WESP where sub-micron acid aerosols are expected.
- Materials of construction. For HF/strong acids use PTFE/PFA-lined steel, PVDF/PP vessels, or vinyl-ester FRP; for chloride/oxidant service upgrade 316L to 904L/C-276 at nozzles and wear points.
- Closed sampling. Replace open dipping with closed sample loops and quick-disconnect bottles.
- Secondary containment & drainage. Floor trenching drains to an isolated emergency collection basin (not the municipal sewer); curbs and lined sumps include level alarms.
- Deluge and spill control. Install water-spray deluge adjacent to storage/transfer to rapidly dilute accidental acid/alkali releases and limit corrosion/exposure.
- Heat management. Provide temperature control/shading to avoid heat input from nearby pyrometallurgical/pyrolysis equipment that could increase reagent volatilization.
- Monitoring and interlocks. Fixed $HF/HCl/Cl_2/SO_2$ (as applicable) and LEL/CO_2 detectors in storage bays and at scrubber outlets; excursions interlock to stop transfers and divert to standby scrubbing.
- PPE and emergency fixtures. Personnel wear chemical-resistant garments, gloves, face/eye protection; eyewash and safety showers are located immediately adjacent to handling areas.

Together, these measures ensure acids and bases are handled in closed, monitored, and recoverable systems; any spills or leaks are promptly contained, scrubbed, and neutralized without endangering workers, equipment, or the environment.

1.3.6 Discussion

1.3.6.1 Process of Recycling

Recycling end-of-life Li-ion batteries has become an essential pillar of sustainable electrification, yet today's dominant industrial practices still carry a heavy environmental and energetic penalty. In Europe and Japan, pyrometallurgical processes reign supreme: Umicore's proprietary shaft-furnace technique consumes roughly 5,000 MJ to process one tonne of batteries, and even Sony-Sumitomo's unitized smelter requires around 1,000 MJ per ton[56]. By contrast, China's hydrometallurgical industry—though far less energy-intensive—relies on vast quantities of aggressive chemicals, generating large volumes of acidic and alkaline effluents whose treatment can itself negate many of the gains from material recovery. This paradox—high energy use or high chemical load—runs counter to the very goals of carbon neutrality and pollution reduction that drive battery recycling, underscoring the urgent need for truly green, low-impact alternatives.

Unfortunately, the commercial confidentiality surrounding many recycling processes further complicates efforts to assess safety and scalability. Patented workflows are rarely disclosed in full, forcing researchers to extrapolate from lab-scale reports and reagent lists rather than actual plant-level data. As a result, novel hazards that emerge only at industrial throughput are often overlooked in safety analyses, and the true acceptability of any single technology remains tied to the strategic interests of individual firms or subsidiaries.

Nevertheless, promising routes are emerging. In the pyrometallurgical sector, salt-assisted roasting has matured to the point where metal recoveries exceed 97 % without the need for 1,400–1,500 °C smelters—catalyzing chloride or sulfate formation at much lower temperatures and streamlining downstream separation. Meanwhile, the wet-chemistry domain is seeing steady progress in bio- and plant-based leaching, where microbial metabolites or naturally derived organic acids (e.g., tartaric, citric) achieve comparable or superior recovery efficiencies to conventional mineral acids. Should these approaches prove economically viable at scale—and should patent barriers be navigated or relaxed—they offer a clear path to slashing both the carbon and chemical footprints of Li-ion battery recycling. Yet even as technology advances, the perennial challenge of incomplete process disclosure will demand ever more creative safety-analysis methods and cross-sector collaboration.

1.3.6.2 Process Safety of Recycling

In contrast to processes that treat a single, well-characterized feedstock, lithium-ion batteries present a unique challenge: they are complex assemblies of metals, polymers, electrolytes, and stored electrical energy, all of which must be separated and recovered. Choice of separation techniques, therefore, hinges on the precise material mix and the physicochemical behavior of each component. In practice, different recyclers develop proprietary pretreatment and separation workflows—driven by factors such as patent protection, available equipment, and feedstock variability—so no single, unified description of cell-component behavior applies across the industry. This heterogeneity makes rigorous process control the only reliable means of ensuring operator safety and consistent recovery performance.

Two factors undermine traditional safety paradigms. First, battery chemistries continue to evolve rapidly: new cathode formulations, solid-state electrolytes, and higher-energy designs emerge under the cloak of intellectual-property confidentiality, leaving recyclers to extrapolate performance and degradation characteristics from limited data. Second, the rush to scale—from pilot to commercial throughput—often outpaces the development of bespoke safety standards, creating regulatory and engineering gaps that can precipitate accidents. Just as the oil and chemical industries update their safety regimes in lockstep with technological advances, Li-ion battery recycling must embrace a dynamic, continuously revised framework of hazard analysis and process control if it is to keep pace with the ever-accelerating cycle of battery innovation and end-of-life volumes.

1.3.7 Evidence-based Adaptive Overly for Evolving Chemistries

Battery chemistries evolve faster than fixed, chemistry-by-name prescriptions. Our goal is not to expand the chemical list, but to retain safety controls for any feed by adding evidence-based overlays at the existing stage. The principle is simple: see the cue, apply the control. Whenever a specific hazard cue is observed or measured, the corresponding control already defined in this paper is activated for that stage.

Rather than enumerate every new cell design, we select two contrastive chemistries—Ni-rich NMC (oxygen-releasing layered oxide) (table 4) and LMFP (phosphate olivine with Mn) (table 3). We then attach an evidence-based overlay to our existing stages (Pretreatment, Pyrometallurgy, Hydrometallurgy): observe a hazard cue → activate the matching control that is already defined in the framework

Table 3. LMFP cell and its representative reactions

Component	Representative reactions	Typical condition/scene	Reference
Electrolyte (1.2 M $LiPF_6$ in FEC: DMC 1:4)	1. $LiPF_6 \rightleftharpoons LiF + PF_5$; $PF_5 + H_2O \rightarrow POF_3 + 2\,HF$ (hydrolysis LMFP cell and its representative reaction chain). 2. Carbonate side reactions on abuse: $2\,EC + 2\,Li^+ + 2\,e^- \rightarrow Li_2EDC + C_2H_4\uparrow$; thermal cracking $\rightarrow CO_2/CO$/hydrocarbons.	Opening, draining, cutting; low-temperature warm-up; early furnace ramp.	[57, 58]
Binder/solvent (PVDF / NMP)	PVDF dehydrofluorination/pyrolysis (schematic): $-(CH_2-CF_2)-_n \rightarrow HF\uparrow +$ unsaturated fragments; NMP volatilization/oxidation → $VOC/NO_x/CO$.	Drying, de-slurry, crushing, thermal treatment.	
Conductive phase & carbon coating (Super-S, SWCNT, ~2 wt% carbon coat)	$C + O_2 \rightarrow CO_2$; $2\,C + O_2 \rightarrow 2\,CO$ (incomplete combustion); dust cloud deflagration (physical combustion).	Crushing, sieving, transfer; pre-burn/oxidizing zones.	
Cathode active (LMFP, $LiMnyFe1-yPO_4$)	Acid leach (oxidative): $LiMnyFe_1-yPO_4 + 2\,H^+ + H_2O_2 \rightarrow Li^+ + y\,Mn^{2+} + (1-y)\,Fe^{2+} + H_2PO_4^- + H_2O$; impurity/precursor on heating: $MnCO_3 \rightarrow MnO + CO_2\uparrow$; Li recovery: $2\,Li^+ + CO_3^{2-} \rightarrow Li_2CO_3\downarrow$.	Oxidative leach; thermal regeneration; neutralization/precipitation.	
Current collector (Al foil)	$Al + 3\,H^+ \rightarrow Al^{3+} + 3/2\,H_2\uparrow$ (e.g., $Al + 3\,HCl \rightarrow AlCl_3 + 3/2\,H_2$); $2\,Al + 2\,NaOH + 6\,H_2O \rightarrow 2\,Na[Al(OH)_4] + 3\,H_2\uparrow$.	Acid/alkali pretreatment, Al removal.	
Separator (Celgard 2320, PP/PE multilayer)	Thermal shrink/closure (pores close ~135 °C); further heating → cracking to light hydrocarbons/olefins; combustion → CO/smoke.	Local overheating/hot spots; furnace ramp.	
Lithium metal (counter electrode in half-cells)	$2\,Li + 2\,H_2O \rightarrow 2\,LiOH + H_2\uparrow$; $2\,Li + 2\,HF \rightarrow 2\,LiF + H_2\uparrow$; $Li + O_2 \rightarrow Li_2O / Li_2O_2$.	Moisture ingress; HF presence; air exposure.	

Compared with the Ni-rich NMC chemical reaction shows in Table 4:

Table 4. Ni-rich NMC battery recycling reaction

Process	Reaction	Reference
Pretreatment/Dismantling	$LiPF_6 \rightarrow LiF + PF_5$; $PF_5 + H_2O \rightarrow POF_3 + 2\ HF$ $2\ EC + 2\ Li^+ + 2\ e^- \rightarrow Li_2EDC + C_2H_4\uparrow$ (SEI/solvent side-gas) $MO_2 \rightarrow MO_2{-}\delta + (\delta/2)\ O_2\uparrow$ (high SOC / temperature) $2\ RCO_3Li + LiPF_6 \rightarrow 2\ LiF + 2\ RF + LiPO_2F_2 + 2\ CO_2$; $LiPF_6 \rightarrow 2\ LiF + RF + POF_3 + CO_2$	[59, 60]
Pyrometallurgy	Rising T accelerates $LiPF_6$ routes; O_2 release from layered MO_2 intensifies solvent oxidation (no single stoichiometric equation)	
Hydrometallurgy	HF-promoted TM dissolution (Ni/Mn/Co) → M^{2+}; residual Li_2CO_3 / $LiPF_6 \rightarrow HF/POF_3/CO_2$ (secondary).	
Storage / Handling / Humidity exposure	Air/humidity drives surface Li_2CO_3/LiOH on NMC; later heating re-releases CO_2/HF via the routes above.	

These two cases demonstrate the mechanism: as chemistries evolve away from LiCoO2, operators do not redesign the framework- they toggle and escalate controls according to the observed cue set. Shows below:

- Fluoride tips: $LIPF_6$/PVDF identified in the material list, or HF detected in a gentle warm-up/ventilator. →Wet-inert opening/electrolyte drain; local exhaust to an alkaline scrubber (with demister/condense as needed); corrosion-resistant materials; HF PPE; two-stage defluoridation in hydromet; dedicated fluoride liquor collection/neutralization.
- Early gas tips: When the small sample is heated to < ~ 400°C, the visible discharge or pressure rise is increased. →Staged slow ramp; limit batch size; inert sweep; off-gas through oxidizer → alkaline scrubber; pressure-relief/over-pressure protection; continuous CO_2/CO monitoring.
- High Reactivity/Oxygen Release Tips: Identify Ni-rich oxides, or low emission heat in fast DSC/ARC scans. →Verified discharge before opening; N_2/inert enclosure for dismantling; hot-work ban in pretreatment bay; more conservative ramp in thermal steps; continuous off-gas monitoring.
- Leach Reactive Tips: Foam/foam or temperature will increase when the acid contacts the powder in the beaker test. →Closed leach reactor; ORP/pH interlocks; segmented oxidant dosing; condenser + mist scrubbing on vents; wastewater neutralization using your existing train.
- Carbon content tips: dusty, carbon-rich electrodes (visible carryover or increased dust reading). →Dust capture/housekeeping; area inerting (e.g., O_2 < 8%); EX-rated electricals and ventilation; avoid dust clouds during transfer/sieving.
- Sulfide Tips (if related to feed): Sulfide solid electrolyte present, or readings when opened. →Water/acid exclusion; H_2S/SO_x capture and scrubbing; corrosion-resistant ducting; fixed H_2S monitors in the opening/pretreatment area.

Thus, for each observed cue, we activate only the corresponding measures already defined; if a cue is absent, those measures are not applied.

1.4 Conclusion and Recommendations

The safety risk of the LIBs recycling process is reflected in the three technological processes: pretreatment, pyrometallurgy, and hydrometallurgy.

(1) There are two main safety challenges posed by the pretreatment stage in lithium-ion battery recycling. First, residual electrical and chemical energy within spent cells can interact under mechanical or thermal stress to initiate self-accelerating reactions. Second, opening and dismantling fully expose reactive components—electrolyte, electrodes, separators—each of which may undergo rapid chemical or physical transformations, releasing a variety of toxic, corrosive, and flammable by-products.

The dominant hazard mechanisms are as follows. Spontaneous thermal runaway can occur at temperatures as low as 69–100 °C and, once initiated, cannot be quenched by conventional fire-suppression techniques, because it generates its own oxidizer and combustible gases. Chemical hazards arise both from hydrolysis—liberating hydrogen fluoride and other corrosive fluorinated compounds—and from heat-driven decomposition of organic solvents, which emits flammable vapors. Finally, the rapid evolution of gases during these processes can produce sudden overpressure explosions. If released gas is not ignited immediately, the internal pressure surge may fragment cell casings and propel combustible materials into the air, triggering secondary fires. Collectively, these intertwined thermal, chemical, and overpressure risks make pretreatment the most accident-prone phase of the recycling workflow.

(2) In the pyrometallurgical stage, most residual electrical and chemical energy has already been dissipated during pretreatment, yet the high-temperature environment itself introduces distinct hazards. Uncontrolled temperature excursions can subject nearby equipment and materials—particularly those with low ignition points—to intense radiant and convective heat, risking secondary fires. Simultaneously, thermal decomposition of residual electrode components,

polymer binders, and electrolyte produces corrosive and toxic gases such as HF and chlorine-bearing species, which must be captured and neutralized to protect both personnel and infrastructure.

Beyond these shared risks, pyrometallurgy carries an additional, uniquely severe chemical threat: the potential generation of dioxins and furans. Formed under industrial-scale smelting conditions when chlorine-containing organics decompose, these highly toxic by-products demand specialized off-gas treatment and destruction systems. Proper design and control of furnace atmospheres, temperatures, and residence times are therefore essential to prevent their formation and to ensure that any inadvertent emissions are rendered harmless before release.

(3) Wet-chemical (hydrometallurgical) recovery is conducted at near-ambient temperature, but it still demands engineered controls for acids, caustics, and gas-evolving reactions. In our design, leach, neutralization, and SX operations run in fully enclosed vessels under slight negative pressure. Headspace is treated by a peak-rate-sized train of quench/condense, alkaline packed-bed scrubbing, and high-efficiency mist elimination; an emergency diversion header allows automatic switch-over to a standby scrubber. Reagent additions are segmented and hard interlocked to ORP, pH, and temperature to prevent runaway foaming or gas surges. Where alkaline leach can liberate hydrogen, tanks are N_2-blanketed with fixed H_2/LEL detection, flame arrestors, and relief devices discharging into the scrubber train rather than to

Transfers and sampling are closed and double-contained, and materials of construction are selected for service—PTFE/PFA-lined steel, PVDF/PP or vinylester FRP for HF/strong acids. Condensates and wash waters are routed to segregated tankage (acidic, caustic, fluoride-bearing, metal-laden) for two-stage defluoridation and pH-controlled neutralization, governed by a fluoride mass balance and divert-to-hold logic. Fixed HF/HCl/Cl_2/SO_2 (as applicable) and LEL/CO_2 monitors, impervious curbs and alarmed sumps, and water-spray deluge at transfer areas complete a closed, monitored, and recoverable hydromet configuration that proactively manages toxic gases and corrosive reagents.

This study assumes $LiCoO_2$ as the cathode feedstock. Although modern batteries also employ NCM (Ni-Co-Mn) cathodes or lithium iron phosphate, all of these materials share a metal-oxide backbone that behaves similarly in acid- or base-leaching processes; accordingly, their safety profiles in hydrometallurgy can be treated as functionally equivalent and are not considered separately here.

Looking ahead, any robust safety analysis must be grounded in real-world operating data: actual plant flow diagrams, reagent dosages, temperature and pH setpoints, and off-gas compositions. As recycling throughput scales up—and as next-generation solid electrolytes, high-nickel cathodes, and novel cell formats enter the waste stream—process-safety models will need continual revision. Only by integrating field data, failure-mode statistics, and emerging battery chemistries can we maintain a dynamic, up-to-date safety framework capable of protecting workers, communities, and the environment.

Conflict of Interests

No conflict of interest has been expressed by the authors.

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