Project	Lithium-ion battery’s life cycle: safety risks and risk management at workplaces
Work package	WP 3: Critical occupational risk factors
Task	T. 3.1 Hazard assessment of materials
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Abstract

The aim of this report is to identify the hazard potential of the materials used during the production of the selected NMC 811 Lithium-ion battery (LIB), throughout the production value chain: the mining of raw materials; the production of cathodes, anodes, and electrolytes; and the use and end of life of the batteries.

It also considers accidents that are relevant to this type of battery. Battery failure can be caused by physical factors, electrical factors, thermal factors, manufacturing defects, or ageing. All these factors can lead to a thermal runaway (TR) with consequent exothermic reactions and the release of hazardous gases. The report also covers leaks during the recycling process.

A hazard classification of the materials is included, based on the EU Classification, Labelling and Packaging (CLP) system (EU regulation No1272/2008) and the Joint Research Centre's (JRC) 'Safe and Sustainable by design chemicals and materials' document.

Finally, new materials that have recently been applied in the production of LIBs, such as CNTs and graphene, are also considered, and a short review of their issues related to human health is provided.

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Glossary

Abbreviations

AH	Ampere/Hour
ARC	Accelerated Rate Calorimetry
CNT	Carbon Nanotubes
CNT OELs	Carbon Nanotubes Occupational Exposure Limits
CNFs	Carbon Nanofibers
COPs	Combustion of Organic Products
DNA	Deoxyribonucleic Acid
DNEL	Derived No Effect Level
ECHA	European Chemical Agency
FTIR	Fourier Transform Infrared Spectrometry
GC	Gas Chromatography
HAPSITE	Hazardous Air Pollutants on site
HMLD	Hard Metal Lung Disease
IARC	International Agency for Research on Cancer
IC	Ion Chromatography
INSST	Instituto Nacional de Salud y Seguridad en el Trabajo
LIBs	Lithium-ion Batteries
LFP	Lithium-Iron-Phosphate Battery
LOAEC	Lowest Adverse Effect Concentration
LOAEL	Lowest Adverse Effect Level
MS	Mass Spectrometry
MWCNT	Multi Walled Carbon Nanotubes
NCA	Lithium Nickel Cobalt Aluminium Oxide Battery
NIOSH	National Institute for the Occupational Health and Security
Nis	Number of Identifications
NMC	Nickel-Manganese-Cobalt
NMC 811	Nickel-Manganese-Cobalt 811
NOAEC	No Observed Adverse Effect Concentration
NOAEL	No Observed Adverse Effect Level
PCNA	Proliferating Cell Nuclear Antigen
PD	Parkinson Disease
PDE	Permitted Daily Exposure
PE	Polyethylene
PG-DSC-EI-MS	Electronic Ionization
PP	Polypropylene
QEPAS	Quartz-Enhanced Photoacoustic Spectrometry
QMS	Quadrupole Mass Spectrometry
$R_{i\Omega}$	Internal Ohmic Resistance
SEI	Solid Electrolyte Interface
SEM	Scanning electron microscopy
SOC	State of Charge
SWCNT	Single Walled Carbon Nanotubes
T	Temperature
TG	Thermogravimetry
TG-DSC	Scanning calorimetry
TR	Thermal Runaway
WT%	Percentage By Weight
XRD	X-ray diffraction

Chemicals

C	Carbon
Cu	Copper
Co	Cobalt
CH_4	Methane
C_2H_2	Ethine
C_2H_6	Ethane
C_4H_{10}	Butane
C_5H_8	Isoprene
C_5H_{10}	Cyclopentene
CO	Carbon monoxide
CO_2	Carbon dioxide
CO_2^+	Carbon dioxide ion
CO_3^{2-}	Carbonate ion
C_3H_4O	Acrolein
$C_3H_4O_3^+$	Acrolein ion
$C_3H_2N_2$	Isocyanoacetonitrile
C_5H_9NO	1-methyl-2pyrrolidine
$COSO_4$	Cobalt (II) sulphate
DEC	Diethyl carbonate
EC	Ethylene carbonate
EMC	Ethyl methyl carbonate
F	Fluor
F^+	Fluor cation
F^{1-}	Fluor anion
H_2	Hydrogen
HCl	Chlorohydric acid
HF	Fluorohydrin acid
H_2O	Water
H_2O^+	Water ion
H_2SO_4	Sulphuric acid
Li	Lithium
LiH	Lithium hydride
LiF	Lithium fluoride
LiO	Lithium oxide
$LiCoO_2$	Lithium cobalt oxide
Li_2CO_3	Lithium carbonate
$LiPF_6$	Lithium Hexafluorophosphate
$LiFePO_4$	Lithium ferrophosphate
$Li_4Ti_5O_{12}$	Lithium titanate
Mn	Manganese
$MnSO_4$	Manganese (II) sulphate
NaOH	Sodium hydroxide
NH_4OH	Ammonium hydroxide
Ni	Nickel
$NiSO_4$	Nickel sulphate
NMP	N-methyl-2-pyrrolidine
O_2	Oxygen
P	Phosphorus
PCl_5	Phosphorus pentachloride

PF_5	Phosphorus pentafluoride
PF_2^+	Phosphenium ion
PO_4^{3-}	Phosphate anion
POF_3	Phosphoryl fluoride
PVDF	Poly(vinylidene fluoride)

1 Methods

1.1 Identification of hazards

A literature review was carried out to identify the hazard potential of the materials used throughout the value chain and identified in T1.3, the different failure factors, the gases that can be emitted in these circumstances, and which of the gases may be hazardous to human health.

The literature review also focused on the hazard review of new materials recently applied in LIB production.

The information used was taken from:

- Literature: papers, reviews, books, safety data sheets (SDS)
- Patents search: patents related to main materials identified

1.2 Hazard classification of the materials

The CLP hazard statements were used as the basis for the hazard classification of the chemicals used in the production of the LIBs. These statements determine the nature and the relative severity of the hazard of a chemical substance or mixture. The hazard codes and hazard statements according to CLP are shown in Table 1.

Table 1. Hazard codes and hazard statements according to CLP.

Hazard Code	Hazard statement	Hazard Category
H200	Unstable explosive substances/mixtures	Unstable Explosive
H201	Explosive; mass explosion hazard	Division 1.1
H202	Explosive; severe projection hazard	Division 1.2
H203	Explosive; fire, blast, or projection hazard	Division 1.3
H204	Fire or projection hazard	Division 1.4
H205	May mass explode in fire	Division 1.5
H220	Extremely flammable gas	Category 1A
H221	Flammable gases	Category 1B
H222	Extremely flammable aerosol	Category 1
H224	Extremely flammable liquid and vapour	Category 1
H225	Highly flammable liquid and vapour	Category 2
H226	Flammable liquid and vapour	Category 3
H227	Combustible liquid	Category 1
H228	Flammable Solid	Category 1
H230	Flammable gases (may react explosively even in the absence of air)	Category 1A
H231	Flammable gases (may react explosively even in the absence of air at elevated pressure or temperature)	Category 1A
H232	Flammable gases (may react explosively in contact with air)	Category 1A
H240	Self-reactive substances mixtures (Heating may cause an explosion)	Type A
H241	Self-reactive substances mixtures (Heating may cause a fire or explosion)	Type B
H242	Self-reactive substances mixtures (Heating may cause a fire)	Type C & D; Type E & F
H270	Oxidizing gases	Category 1
H272	Oxidizing liquids or solids	Category 2 & Category 3
H280	Contains gas under pressure; may explode if heated	Compressed gas
H281	Contains refrigerated gas; may cause cryogenic burns or injury	Refrigerated liquified gas
H300	Acute toxic substances/mixtures	Category 1 & Category 2
H301	Acute toxicity (Toxic if swallowed)	Category 3
H302	Acute toxicity (Harmful if swallowed)	Category 4
H304	Substances/mixtures with a risk of aspiration	Category 1
H310	Acute toxic substances/mixtures (Fatal in contact with skin)	Category 1 & Category 2
H311	Acute toxicity (Toxic in contact with skin)	Category 3
H312	Acute toxicity (Harmful in contact with skin)	Category 4
H314	Substances/mixtures corrosive to the skin	Category 1/1A/1B/1C
H315	Skin irritant substances/mixtures	Category 2
H317	Skin-sensitizing substances/mixtures	Skin sensitizers Category 1 & Sub-categories 1A & 1B
H318	Eye-damaging substances/mixtures	Category 1
H319	Eye irritant substances/mixtures	Category 2

Hazard Code	Hazard statement	Hazard Category
H330	Acute toxic substances/mixtures (Fatal if inhaled)	Category 1 & Category 2
H331	Acute toxicity (Toxic if inhaled)	Category 3
H332	Acute toxicity (Harmful if inhaled)	Category 4
H334	Substances/mixtures that sensitize the respiratory organs	Respiratory sensitizers Category 1 & Sub-categories 1A & 1B
H335	Substances/mixtures with specific target organ toxicity: irritation of the respiratory organs	Category 3
H336	Substances/mixtures with specific target organ toxicity: drowsiness, dizziness	Category 3
H340	May cause genetic defects	Category 1 & Sub-categories 1A & 1B
H341	Suspected of causing genetic defects	Category 2
H350	May cause cancer	Category 1 & Sub-categories 1A & 1B
H350i	May cause cancer by inhalation	Category 1 & Sub-categories 1A & 1B
H351	Suspected of causing cancer	Category 2
H360	May damage fertility or unborn child	Category 1 & Sub-categories 1A & 1B
H360F	May damage fertility	Category 1 & Sub-categories 1A & 1B
H360D	May damage unborn child	Category 1 & Sub-categories 1A & 1B
H360FD	May damage fertility; May damage unborn child	Category 1 & Sub-categories 1A & 1B
H360Fd	May damage fertility; Suspected of damaging unborn child	Category 1 & Sub-categories 1A & 1B
H360Df	May damage unborn child; Suspected of damaging fertility	Category 1 & Sub-categories 1A & 1B
H361	Suspected of damaging fertility or unborn child	Category 2
H361f	Suspected of damaging fertility	Category 2
H361d	Suspected of damaging unborn child	Category 2
H361fd	Suspected of damaging fertility; Suspected of damaging unborn child	Category 2
EUH029	Substance/mixtures which, in contact with water, release toxic gases	No data
EUH031	Substance/mixtures which, in contact with acids, release toxic gases	No data
EUH032	Chemical mixtures which, in contact with acids, release highly toxic gases	No data
EUH066	Skin-damaging substances/mixtures	No data
EUH070	Substances/mixtures toxic in contact with eyes	No data
EUH071	Substances/mixtures with corrosive effect on respiratory organs	No data

Table 2 shows the most relevant parameters in the categorization of the chemicals used in the LIBs' value chain.

Table 2. Relevant parameters in categorization of different chemicals' hazards.

Physicochemical	Human Toxicity
	AT-Acute toxicity
	C-Carcinogenicity
	EI/C-Eye Irritation/corrosivity
	G-Genotoxicity
	M-Mutagenicity
C-Corrosivity	OEL-Occupational exposure limits
Ex-Explosivity	R-Reproductive toxicity
F/FP-Flammability/flash point	RSn-Respiratory sensitivity
O-Oxidizing	SI-Skin irritation
R-Reactivity	SnS-Skin sensitivity

The criteria for the categorization of the hazards of the different materials were determined on the basis of the most harmful parameters described in the document issued by the JRC – 'Safe and Sustainable by design chemicals and materials' (Caldeira, et al., 2022) (Jacobs, Malloy, Tickner, & Edwards, 2016). Five categories of risk were colour labelled for easy identification and comparison and are described below:

- Very high-risk (RED):
  - Hazard Endpoint: If the substance has any of the following hazards it is considered a very high hazard:
    - Acute toxic substances/mixtures (H300, H310, H330)
    - Chemical mixtures which, in contact with acids, release highly toxic gases (EUH032)
    - Carcinogenicity (H350, H350i)
    - Mutagenicity (H340)
    - Reproductive toxicity (Reprotoxic defects in animals and/or suspected or proven in humans; H360).
    - Respiratory sensitization (H334).
    - Specific target organ toxicity – repeated exposure (STOT-RE) (H370).
    - Unstable explosive substances/mixtures (H200)
    - Explosive substances/mixtures/articles (H201-H205).
    - Flammable gases, (H220, H230, H231, H232) and (H221)
    - Flammable liquids (H224).
    - Self-reactive substances/mixtures. (H240 and H241).
- High risk (ORANGE):
  - Hazard Endpoint: If the substance has any of the following hazards it is considered a high hazard:
    - Carcinogenicity (H351).
    - Mutagenicity (H341).
    - Reproductive toxicity (Reprotoxic defects in animals and/or suspected or proved in humans; Repr. H361).
    - Acute toxicity (H301, H311, H331)
    - Substances/mixtures toxic in contact with eyes (EUH070)
    - Substance/mixtures which, in contact with water or acids, release toxic gases (EUH029, EUH031)

        - Skin sensitizing substances/mixtures (H317)
        - Substances/mixtures that sensitize the respiratory organs (H334)
        - Substances/mixtures corrosive to the skin. (H314)
        - Flammable liquids (H225).
        - Flammable solids (H228).
        - Self-reactive substances/mixtures (H242).
        - Oxidizing gases (H270).
        - Oxidizing liquids or solids (H272).
- Medium risk (YELLOW):
    - criteria: If the substance has any of the following hazards it is considered a moderate hazard:
        - Acute toxicity substances /mixtures (H302, H312, H332)
        - Substances/mixtures with specific target organ toxicity (single exposure), possible organ damage (H371).
        - Substances/mixtures corrosive to the skin (H314)
        - Eye-damaging substances/mixtures (H318)
        - Substances/mixtures with corrosive effect on respiratory organs (EUH071)
        - Nontoxic gases that can cause suffocation by displacing air (e.g., nitrogen).
        - Flammable liquids (H226)
        - Flammable solids (H228)
        - Self-reactive substances/mixtures (H242)
        - Oxidizing liquids or solids (H272)
        - Gases under pressure (H280, H281)
- Low risk (GREEN):
    - criteria: substance has few hazard statements and is a low concern.
        - Skin-irritant substances/mixtures (H315)
        - Eye-irritant substances/mixtures (H319)
        - Skin damage when working in moisture.
        - Substances/mixtures with a risk of aspiration (H304)
        - Skin-damaging substances/mixtures (EUH066)
        - Substances/mixtures with specific target organ toxicity (single exposure): irritation of the respiratory organs (H335)
        - Substances/mixtures with specific target organ toxicity (single exposure): drowsiness, dizziness (H336)
        - Substances chronically harmful in other ways (no H-phrase).
        - Not readily flammable substances/mixtures (flash point > 60…100ºC, no H-phrase)
        - Self-reactive substances/mixtures (no H-phrase).
- No hazard (BLUE).

The hazard data for the chemicals were obtained from the ECHA website and the SDSs.

The ECHA website also provides the Occupational Exposure Levels (OELs). This parameter indicates the level of admissible exposure, for a specific length of time (usually 8 hours), to a chemical or physical hazard that is not likely to affect the health of a worker. It also provides the Permitted Daily Exposure (PDE) and the Short-term Exposure Limit (STEL) for some chemicals. The

PDE represents the substance-specific dose that is unlikely to cause an adverse effect if an individual is exposed to this dose or below every day throughout their lifetime, whereas the STEL is the acceptable average exposure over a short period of time, usually 15 minutes. The PDEs for Spain were obtained from the National Institute of Safety and Health in Workplaces (2019).

These values are also presented in the tables, when available, as they are important parameters for the development of the occupational hazard guidelines of Task 4.1 (Assessment of workers' exposure to chemicals).

2 Results and discussion

2.1 Battery production hazards

Figure 1 shows a schematic representation of the LIB production's value chain.

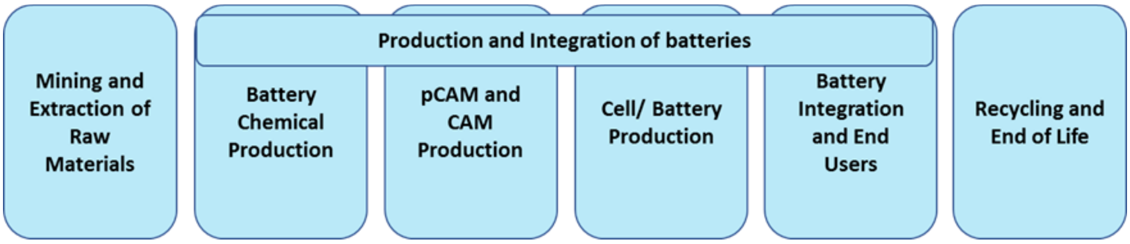

Figure 1. Scheme of LIB production's value chain. (pCAM-Precursor cathode and anode materials; CAM-cathode and anode materials)

T.1.3 identified the key materials used throughout the value chain in the production of LIBs (Table 3). This task (T.3.1) identified the hazard potential of these materials and classified the materials as described in the methodology section. During battery integration and end use, no chemicals are needed, but it is important to consider the cases of accidents in which several hazardous gases may be produced and emitted.

These accidents can also occur during the recycling step. Section 3.2 gives a description of how they can occur and the emissions they produce.

Table 3. Chemicals used for each step of LIB production's value chain

	Value Chain					
Chemicals	**Mining and extraction of raw materials**	**Production of battery chemical**	**Production of pCAM and CAM**	**Production of cell battery**	**Battery integration and end use**	**Recycling and end of life**
Cobalt	X					
Lithium	X					
Nickel	X	X				
Manganese	X					
Aluminium	X			X		
Copper	X			X		
Hydrogen peroxide		X				
Sulphuric acid		X				X
Sodium sulphate		X				
Nickel hydroxide		X				X
Manganese oxide		X				
Trimanganese tetroxide		X				
Manganese hydroxide		X				
Lithium sulphate		X				

	Value Chain					
Chemicals	**Mining and extraction of raw materials**	**Production of battery chemical**	**Production of pCAM and CAM**	**Production of cell battery**	**Battery integration and end use**	**Recycling and end of life**
Cobalt hydroxide		X				
Sodium hydroxide		X				X
Nickel sulphate		X	X			X
Cobalt sulphate		X	X			
Manganese sulphate		X	X			
Lithium carbonate			X			
Lithium hydroxide		X	X			
Ammonium hydroxide			X			
Carbon black				x		
PVDF				X		
N-methyl-2-pyrrolidine				X		
Graphite			X	X		
Lithium hexafluorophosphate				X		
Ethylene carbonate				X		
Dimethyl carbonate				X		
Vinyl carbonate				X		
Polypropylene				X		
Polyethylene				X		
Steel				X		
Polyethylene terephthalate				X		
Lime						X
Hard coal						X
Cobalt chloride						X
Oxygen						X
Co_3O_4						X
$LiCoO_2$						X

The next sections describe the materials' hazards in each production step.

2.2 Mining and extraction of raw materials

The main raw materials needed to produce LIBs are cobalt (Co), lithium (Li), nickel (Ni), manganese (Mn), aluminium (AL), and Copper (Cu). The main hazards of these materials were identified for different exposure routes: inhalation, dermal and ocular. Any existing derived no-effect levels (DNEL) were included. All the values included were obtained from the ECHA website (ECHA, Classification of substances and mixtures, s.f.).

Table 4. Hazards of raw materials via various exposure routes

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statement
Cobalt	Systemic effects → No hazard identified (long- and acute/short-term exposure) Local effects → DNEL = 40 μg/m^3 (long-term exposure)	Systemic effects → No hazard identified (long- and acute/short-term exposure) Local effects → Medium hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → low hazard, no threshold derived	**H341** **H350** **H360F**
Lithium	Systemic effects → DNEL = 4.2 mg/m^3, NOAEC = 4.2 mg/m^3 (long-term exposure); no hazard identified (acute/short-term exposure) Local effects → low hazard, no threshold derived (long- and acute/short-term exposure)	Systemic effects → DNEL = 12 mg/kg bw/day, NOAEL = 12 mg/kg bw/day (long-term exposure); no hazard identified (acute/short-term exposure) Local effects → medium hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → medium hazard, no threshold derived	**H314**
Nickel	Systemic effects → DNEL = 0.05 mg/m3 (long-term exposure); no hazard identified (acute/short-term exposure) Local effects → DNEL = 0.05 mg/m3 (long-term exposure); DNEL = 11.9 mg/m3 (acute/short-term exposure)	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → DNEL = 0.035 mg/cm2 (long-term exposure); no hazard identified (acute/short-term exposure)	Local effects → no hazard identified	**H351**
Manganese	Systemic effects → DNEL = 10.1 μg/m3 (long-term exposure) and no hazard identified (acute/short-term exposure) Local effects → no hazard identified (long- and acute/short-term exposure)	Systemic effects → DNEL = 0.256 mg/kg bw/day (long-term exposure) and no hazard identified (acute/short-term exposure) Local effects → no hazard identified (long- and acute/short-term-exposure)	Local effects → no hazard identified	**H228**

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statement
Aluminium	Systemic effects → DNEL = 3.72 mg/m3 (long-term exposure); no hazard identified (acute/short-term exposure) Local effects → DNEL = 3.72 mg/m3 (long-term exposure); no hazard identified (acute/short-term exposure)	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → no hazard identified (long- and acute/short-term exposure)	Local effects → no hazard identified	**H250**
Copper	Systemic effects → No hazard identified (long-term exposure); LOAEC = 1240 mg/m^3 Local effects → No hazard identified (long- and acute/short-term exposure)	Systemic effects → DNEL = 137 mg/kg bw/day (long-term exposure); DNEL = 237 mg/kg bw/day (acute/short-term exposure) Local effects → No hazard identified (long- and acute/short-term exposure)	Local effects → no hazard identified	No hazard identified

Using the criteria established in the methodology section, the chemicals were classified into different hazard levels. Table 5 shows the hazard levels for the different hazard parameters for LIBs, and Table 6 indicates the classification of the chemicals according to the criteria described in the methodology section.

Table 5. Classification of materials in mining and extraction steps. (C- Corrosivity, Ex- Explosion, F/FP- Flammability/Flash Point, O- Oxidizing, R- Reactivity, WP- Vapor Pressure, WS- Water solubility, AT- Acute Toxicity, C- Cancerogenicity, D- Developmental, ED- Endocrine Disruption, EI/C- Eye Irritation/Corrosivity, G- Genotoxicity, M- Mutagenicity, N- Neurotoxicity, OEL- Occupational Exposure Limit, R- Reproductive toxicity, RSn- Respiratory Sensitization, SI- Skin Irritation, SnS- Skin Sensitivity) (VH- very high risk, H- High risk, M- Medium risk, L- Low risk, -- No risk and/or No data)

		Copper	**Aluminium**	**Lithium**	**Manganese**	**Nickel**	**Cobalt**
Physicochemical	**C**	--	--	--	--	--	--
	Ex	--	--	--	--	--	--
	F/FP	--	VH	--	H	--	--
	O	--	--	--	--	--	--
	R	--	H	VH	--	--	--
	WP	--	--	--	--	--	--
	WS	--	--	--	--	--	--
Human Toxicity	**AT**	--	--	--	--	--	M
	C	--	--	--	--	H	VH
	D	--	--	--	--	--	--
	ED	--	--	--	--	--	--
	EI/C	--	--	--	M	--	--
	G	--	--	--	--	--	--
	M	--	--	--	--	--	H
	N	--	--	--	--	--	--
	OEL	--	--	--	--	--	--
	R	--	--	--	--	--	VH
	RSn	--	--	--	--	--	--
	SI	--	--	M	--	--	--
	SnS	--	--	--	--	H	M

Table 6. Classification of hazards of raw materials obtained in mining and extraction steps.

Hazard	Production of battery chemicals
Cobalt	🟥
Lithium	🟧
Nickel	🟥
Manganese	🟧
Aluminium	🟨
Copper	🟦

As indicated earlier, the PDE is also an important parameter. Table 7 presents the PDE for some of the raw materials.

Table 7. Permitted Daily Exposure for some raw materials in Spain

	Nickel	Manganese	Aluminium	Copper
PDE (Permitted Daily Exposure) (mg/m^3)	1	0.2 (Inhalable fraction) 0.05 (Respirable fraction)	10 (Aluminium, dust) 5 (Aluminium, welding fumes)	0.1 (Respirable fraction)

2.3 Production of battery chemicals

This section discusses the production of the chemicals to be used in the batteries.

The materials used in this step are nickel, hydrogen peroxide, sulphuric acid, sodium sulphate, nickel hydroxide, manganese oxide, trimanganese tetroxide, manganese hydroxide, lithium sulphate, cobalt hydroxide, sodium hydroxide, nickel sulphate, cobalt sulphate, manganese sulphate and lithium hydroxide.

As nickel is also used in the mining step, its hazard assessment is given in Tables 4, 5 and 6.

The hazards for the rest of the materials: hydrogen peroxide, sulphuric acid, sodium sulphate, nickel hydroxide, manganese oxide, trimanganese tetroxide, manganese hydroxide, lithium sulphate, cobalt hydroxide, sodium hydroxide, nickel sulphate, cobalt sulphate, manganese sulphate, and lithium hydroxide are presented in the tables below.

Table 8. Hazards of materials from production of battery chemicals via various exposure routes

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
Nickel sulphate	Systemic effects → DNEL = 0.05 mg/m^3 (long-term exposure); DNEL = 104 mg/m^3 (acute/short-term exposure) Local effects → DNEL = 0.05 mg/m^3 (long-term exposure); DNEL = 1.6 mg/m^3 (acute/short-term exposure)	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → DNEL = 0 mg/cm^2(long-term exposure); no hazard identified (acute/short-term exposure)	Local effects → no hazard identified	**H314** **H271**
Hydrogen peroxide	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H314**
Sulphuric acid	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → other toxicological threshold = 0.05 mg/m3 (long-term exposure); other toxicological threshold = 0.1 mg/m3 (acute/short-term exposure)	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → high hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → high hazard, no threshold derived	**H314** **H319**
Sodium hydroxide	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → DNEL = 1 mg/m^3 (long-term exposure); no hazard identified (acute/short-term exposure)	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → high hazard, no threshold derived (long- and acute/short-exposure)	Local effects → high hazard, no threshold derived	No Hazards identified
Sodium sulphate	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H315**

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
Manganese oxide	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	No Hazards identified
Trimanganese tetroxide	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H315**
Manganese sulphate	Systemic effects → Other toxicological threshold = 0.2 mg/m^3 (long-term exposure); no-threshold effect and/or no dose-response information available (acute/short-term exposure) Local effects → Other toxicological threshold = 0.2 mg/m^3 (long-term exposure); no hazard identified (acute/short-term exposure)	Systemics effects → DNEL = 0.004 mg/kg bw/day (long-term exposure); no-threshold effect and/or no dose-response information available (acute/short-term exposure) Local effects → no-threshold effect and/or no dose-response information available (long- and acute/short-term exposure)	Local effects → no hazard identified	**No hazards identified**
Manganese hydroxide	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**No identified Hazards**
Cobalt sulphate	Systemic effects → No hazard identified (long- and acute/short-term exposure) Local effects → DNEL = 105.2 µg/m^3 (long-term exposure)	Systemic effects → No hazard identified (long- and acute/short-term exposure) Local effects → Medium hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → low hazard, no threshold derived	**No identified Hazards**

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
Lithium sulphate	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H350** **H360**
Cobalt hydroxide	Systemic effects → No hazard identified (long- and acute/short-term exposure) Local effects → DNEL = 63.1 µg/m^3 (long-term exposure); High hazard (no threshold derived) (acute/short-term exposure)	Systemic effects → No hazard identified Local effects → medium hazard (long- and acute/short-term exposure)	Local effects → low hazard	**H314**
Lithium hydroxide	Systemic effects → DNEL = 10 mg/m^3 (long-term exposure); DNEL = 30 mg/m^3 (acute/short-term exposure) Local effects → low hazard, no threshold derived (long- and acute/short-term exposure)	Systemic effects → DNEL = 41.35 mg/kg bw/day (long-term exposure); DNEL = 100 mg/kg bw/day (acute/short-term exposure) Local effects → medium hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → medium hazard, no threshold derived	

As described in the methodology section, the chemicals were ranked according to their hazards. Tables 9 and 10 show the hazard level for the different parameters considered, as well as a ranking based on the criteria established in the methodology.

Table 9. Hazard level for different parameters.

		Manganese oxide	**Sulphuric acid**	**Hydrogen peroxide**	**Cobalt hydroxide**	**Nickel hydroxide**	**Nickel sulphate**	**Sodium hydroxide**	**Lithium hydroxide**	**Manganese sulphate**	**Cobalt sulphate**	**Sodium sulphate**	**Trimanganese tetroxide**	**Manganese hydroxide**	**Lithium sulphate**
Physico-chemical	**C**	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	Ex	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	F/FP	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	O	--	--	**VH**	--	--	--	--	--	--	--	--	--	--	--
	R	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	WP	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	WS	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Human Toxicity	**AT**	**M**	--	**M**	**VH**	**M**	**M**	--	**M**	--	**M**	--	--	--	**M**
	C	--	--	--	**VH**	**VH**	**VH**	--	--	--	**VH**	--	--	--	--
	D	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	ED	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	EI/C	--	**H**	--	**L**	--	--	**L**	--	**M**	**L**	**L**	**L**	--	**L**
	G	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	M	--	--	--	**VH**	**H**	**VH**	--	--	--	**H**	--	--	--	--
	N	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	OEL	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	R	--	--	--	--	**VH**	**VH**	--	--	--	**VH**	--	--	--	--
	RSn	--	--	--	**H**	**H**	--	--	--	--	**H**	--	--	--	--
	SI	--	--	**M**	--	**L**	**L**	**L**	**M**	--	--	**L**	**L**	--	--
	SnS	--	--	--	**H**	**H**	**H**	--	--	--	**H**	--	--	--	--

Table 10. Classification of hazards of materials used in chemical production step.

Hazard	Production of battery chemicals
Nickel sulphate	🟥
Hydrogen peroxide	🟧
Sulphuric acid	🟧
Sodium hydroxide	🟩
Sodium sulphate	🟩
Nickel hydroxide	🟥
Manganese oxide	🟨
Trimanganese tetroxide	🟩
Manganese sulphate	🟨
Manganese hydroxide	🟦
Cobalt sulphate	🟥
Lithium sulphate	🟨
Cobalt hydroxide	🟥
Lithium hydroxide	🟨

As indicated earlier, the PDE and STEL are also important parameters. Table 11 shows them in the chemical production step.

Table 11. Permitted Daily Exposure for some materials in chemical production step in Spain.

	PDE (Permitted Daily Exposure) (mg/m^3)
Nickel sulphate	0.1
Sulphuric acid	0.05 (fog)
Nickel sulphate	0.1
Manganese sulphate	0.2 (inhalable fraction) / 0.05 (respirable fraction)
Sodium hydroxide	STEL (short-term exposure limit) = 2 mg/m^3
Sodium hydroxide	STEL (short-term exposure limit) = 2 mg/m^3
Manganese sulphate	0.2 (inhalable fraction) / 0.05 (respirable fraction)

2.4 Production of pCAM and CAM

In this section, we look at the production of the chemicals to be used in the production of cathode active material.

The chemicals used in this step are lithium carbonate, ammonium hydroxide, graphite, nickel sulphate, cobalt sulphate, manganese sulphate, and lithium hydroxide.

Although nickel sulphate, cobalt sulphate, manganese sulphate, and lithium hydroxide are used in this step, they are also used in the previous step, and thus their hazard assessment is given in Tables 8, 9 and 10.

Table 12 presents the hazards for the rest of the materials: lithium carbonate, ammonium hydroxide, and graphite.

Table 12. Hazards of chemicals used in pCAM and CAM production via various exposure routes

	Hazard via inhalation route	**Hazard via dermal route**	**Hazard to the eyes**	**Hazard statements**
Lithium carbonate	Systemic effects → DNEL = 10 mg/m^3 (long-term exposure); DNEL = 30 mg/m^3 (acute/short-term exposure) Local effects → Low hazard (long- and acute/short-term exposure)	Systemic effects → DNEL = 30 µg/kg bw/day (long-term exposure); DNEL = 100 mg/kg bw/day (acute/short-term exposure) Local effects →no hazard identified (long- and acute/short-term exposure)	Local effects → medium hazard, no threshold derived	**H319**
Ammonium hydroxide	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H314**
Graphite	Systemic effects → DNEL = 1.2 mg/m^3 (long-term exposure); no hazard identified (acute/short-term exposure) Local effects → DNEL = 1.2 mg/m^3 (long-term exposure); no hazard identified (acute/short-term exposure)	Systemic effects → No hazard identified (long- and acute/short-term exposure) Local effects → No hazard identified (long- and acute/short-term exposure)	Local effects → no hazard identified	No hazards identified

As described in the methodology section, the chemicals were ranked according to their hazard. Table 13 and Table 14 show all the different hazards and their levels for the chemicals used in this step, as well as their ranking based on the criteria established in the methodology.

Table 13. Qualification of chemicals in pCAM and CAM production step. (C- Corrosivity, Ex-Explosion, F/FP- Flammability/Flash Point, O- Oxidizing, R- Reactivity, WP- Vapor Pressure, WS-Water Solubility, AT- Acute Toxicity, C- Carcinogenicity, D- Developmental, ED- Endocrine Disruption, EI/C- Eye Irritation/Corrosivity, G- Genotoxicity, M- Mutagenicity, N- Neurotoxicity, OEL-Occupational Exposure Limit, R- Reproductive Toxicity, RSn- Respiratory Sensitization, SI- Skin Irritation, SnS- Skin Sensitivity) (VH- Very High risk process, H- High risk process, M- Medium risk process, L- Low risk process, -- No hazard and/or No data).

COMPOUNDS		**Lithium carbonate**	**Ammonium hydroxide**	**Graphite**
Physicochemical	**C**	--	--	--
	Ex	--	--	--
	F/FP	--	--	--
	O	--	--	--
	R	--	--	--
	WP	--	--	--
	WS	--	--	--
Human Toxicity	**AT**	**M**	**M**	--
	C	--	--	--
	D	--	--	--
	ED	--	--	--
	EI/C	**L**	**M**	--
	G	--	--	--
	M	--	--	--
	N	--	--	--
	OEL	--	--	--
	R	--	--	--
	RSn	--	--	--
	SI	--	**M**	--
	SnS	--	--	--

Table 14. Hazards of materials in pCAM and CAM production step.

Hazard	Production of battery chemicals
Lithium carbonate	🟨
Ammonium hydroxide	🟥
Graphite	🟦

Table 15 presents the PDE and STEL for one of the chemicals used in the production of pCAM and CAM.

Table 15. Permitted Daily Exposure for some materials in pCam and Cam formation in Spain

	PDE (Permitted Daily Exposure) (mg/m^3)
Ammonium hydroxide	PDE = 14 mg/m^3 STEL = 36 mg/m^3

2.4.1 Production of cells/batteries

This section examines the chemicals to be used in the production of the cell or the battery.

The following materials are used in this step: aluminium, copper, carbon black, PVDF, N-methyl-2-pyrrolidine, graphite, lithium hexafluorophosphate, ethylene carbonate, dimethyl carbonate, vinyl carbonate, PP, PE, steel, and polyethylene terephthalate.

As aluminium and copper are also used in the mining step, their hazard assessment is presented in Tables 4, 5 and 6. Graphite is also used in the pCam and Cam step, so its hazard assessment is presented in Tables 12, 13 and 14.

The hazards for the rest of the materials: carbon black, PVDF, N-methyl-2-pyrrolidine, lithium hexafluorophosphate, ethylene carbonate, dimethyl carbonate, vinyl carbonate, PP, PE, steel, and polyethylene terephthalate are presented in the tables below.

Table 16. Hazards of materials used in production of cells and batteries via various exposure routes.

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
Carbon black	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H350**
Polyvinylidene fluoride (PVDF)	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H315**
N-methyl-2-pyrrolidone	Systemic effects → DNEL = 14.4 mg/m^3 (long-term exposure); no hazard identified (acute/short-term exposure) Local effects → 40 mg/m^3 (long-term exposure); medium hazard (acute/short-term exposure)	Systemic effects → DNEL = 4.8mg/kg bw/day (long-term exposure) no hazard identified (acute/short-term exposure) Local effects → medium hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → medium hazard, no threshold derived	**H360D** **H319**
Lithium hexafluorophosphate	Systemic effects → DNEL = 0.931 mg/m^3 (long-term exposure); High hazard, no threshold derived (acute/short-term exposure) Local effects → DNEL = High hazard, no threshold derived (long-term exposure); High hazard, no threshold derived (acute/short-term exposure)	Systemic effects → DNEL = 133 µg/kg bw/day (long-term exposure); High Hazard, no threshold derived (acute/short-term exposure) Local effects → High hazard (long- and acute/short-term exposure)	Local effects → high hazard, no threshold identified	No Hazards identified
Ethylene carbonate (EC)	Systemic effects → DNEL = 15 mg/m^3 (long-term exposure); No hazard identified (acute/short-term exposure) Local effects → No hazard identified (long-term exposure); No hazard identified (acute/short-term exposure)	Systemic effects → DNEL = 4.3 mg/kg bw/day (long-term exposure); No hazard identified (acute/short-term exposure) Local effects → No hazard identified (long- and acute/short-term exposure)	Local effects → low hazard, no threshold identified	No Hazards identified

	Hazard via inhalation route	**Hazard via dermal route**	**Hazard to the eyes**	**Hazard statements**
Dimethyl carbonate (DMC)	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	No Hazards identified
Vinyl carbonate (VC)	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H302**
Polypropylene (PP)	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H314**
Polyethylene (PE)	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	No Hazards identified
Steel	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	No Hazards identified
Polyethylene Terephthalate (PET)	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	No Hazards identified

As described in the methodology section, the chemicals were ranked according to their hazards.

Table 17 and 18 show all the different hazards and levels of hazards of the different chemicals, and classes them based on the criteria established in the methodology.

Table 17 Classification of chemicals in cell/battery production step. (C- Corrosivity, Ex- Explosion, F/FP- Flammability/Flash Point, O- Oxidizing, R- Reactivity, WP- Vapor Pressure, WS- Water Solubility, AT- Acute Toxicity, C- Cancerogenicity, D- Developmental, ED- Endocrine Disruption, EI/C- Eye Irritation/Corrosivity, G- Genotoxicity, M- Mutagenicity, N- Neurotoxicity, OEL- Occupational Exposure Limit, R- Reproductive Toxicity, RSn- Respiratory Sensitization, SI- Skin Irritation, SnS- Skin Sensitivity) (VH- Very High risk process, H- High risk process, M- Medium risk process, L- Low risk process, -- No hazard and/or No data).

		Carbon black	**PVDF**	**N-methyl-2-pyrrolidine**	**Lithium hexafluorophosphate**	**EC**	**DMC**	**VC**	**PP**	**PE**	**Steel**	**PET**
Physicochemical	**C**	--	--	--	--	--	--	--	--	--	--	--
	Ex	--	--	--	--	--	--	--	--	--	--	--
	F/FP	--	--	--	--	--	**H**	--	--	--	--	--
	O	--	--	--	--	--	--	--	--	--	--	--
	R	--	--	--	--	--	--	--	--	--	--	--
	WP	--	--	--	--	--	--	--	--	--	--	--
	WS	--	--	--	--	--	--	--	--	--	--	--
Human Toxicity	**AT**	--	--	--	**H**	**M**	--	**M**	--	--	--	--
	C	**H**	--	--	--	--	--	--	--	--	--	--
	D	--	--	--	--	--	--	--	--	--	--	--
	ED	--	--	--	--	--	--	--	--	--	--	--
	EI/C	--	**L**	**L**	**H**	**L**	--	**M**	--	--	--	--
	G	--	--	--	--	--	--	--	--	--	--	--
	M	--	--	--	--	--	--	--	--	--	--	--
	N	--	--	--	--	--	--	--	--	--	--	--
	OEL	--	--	--	--	--	--	--	--	--	--	--
	R	--	--	**VH**	--	--	--	--	--	--	--	--
	RSn	--	--	--	--	--	--	--	--	--	--	--
	SI	--	**L**	**L**	--	--	--	--	--	--	--	--
	SnS	--	--	--	--	--	--	**H**	--	--	--	--

Table 18 . Classification of hazards of materials in cell/battery production step.

	Hazard	Production of battery chemicals
Cathode production	Carbon black	🟧
	PVDF	🟨
	N-methyl-2-pyrrolidine	🟥
	PVDF	🟨
Electrolyte production	Lithium hexafluorophosphate	🟥
	EC	🟨
	DMC	🟧
	VC	🟧
Separator production	PP	🟦
	PE	🟦
Non-cell material production	Steel	🟦
	PET	🟦

Table 19 presents the PDE and/or the STEL for some materials used in cell/battery production.

Table 19 Permitted daily exposure for some materials in Cell/Battery production step in Spain.

	PDE (Permitted Daily Exposure) (mg/m^3)
PVDF	500 ppm
N-methyl-2-pyrrolidone	PDE = 40 STEL = 80

2.4.2 Battery integration and end users

This section focuses on battery integration and the use of LIBs. No chemicals are used in this part and the main concern is accidents, which can produce hazardous gases. This is described in detail in Section 3.2.

2.4.3 Recycling and end of life

This section examines the materials used and obtained at the battery's end of life, as well as its recycling.

The materials used in this step are sulphuric acid, nickel hydroxide, sodium hydroxide, nickel sulphate, lime, hard coal, cobalt chlorhyde, oxygen, Co_3O_4, and $LiCoO_2$.

As sulphuric acid, nickel hydroxide, sodium hydroxide and nickel sulphate are also used in the battery chemical production step, their hazard assessment is presented in Tables 8, 9 and 10.

The hazards for the rest of the materials: lime, hard coal, cobalt chlorhyde, oxygen, Co_3O_4, and $LiCoO_2$ are shown in the tables below.

Table 20. Hazards of chemicals used in recycling and end-of-life step via various exposure routes

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
Lime (calcium hydroxide)	Systemic effects → DNEL = no hazard (long-term exposure); no hazard (acute/short-term exposure) Local effects → 1 mg/m^3 (long-term exposure); 4 mg/m^3 (acute/short-term exposure)	Systemic effects → no hazard identified (long-term exposure) no hazard identified (acute/short-term exposure) Local effects → low hazard (no threshold derived) (long- and acute/short-term exposure)	Local effects → medium hazard (no threshold derived)	**H314**
Hard coal	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H341** **H35**
Cobalt chloride	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → other toxicological threshold = 88.1µg/m^3 (long-term exposure) high hazard (no threshold derived) (acute/short-term exposure)	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → medium hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → medium hazard, no threshold derived	**H350** **H341** **H360D**
Oxygen (O_2)	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H341** **H360D** **H350i**

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
Co_3O_4	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → other toxicological threshold = 50.9 µg/m^3 (long-term exposure) high hazard (no threshold derived) (acute/short-term exposure	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → medium hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → no hazard identified	**H350i**
$LiCoO_2$	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → other toxicological threshold = 66.4 µg/m^3 (long-term exposure) no hazard identified (acute/short-term exposure)	Systemic effects → no hazard identified (long- and acute/short-term exposure) Local effects → medium hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → no hazard identified	**H350**

As described in the methodology section, the chemicals were ranked according to their hazards.

Table 21 and Table 22 show all the hazard levels of the different parameters and the hazard classification of the chemicals in this step based on the criteria established in the methodology.

Table 21. Qualification of chemicals in recycling and end-of-life step. (C- Corrosivity, Ex- Explosion, F/FP- Flammability/Flash Point, O- Oxidizing, R- Reactivity, WP- Vapor Pressure, WS- Water Solubility, AT- Acute Toxicity, C- Carcinogenicity, D- Developmental, ED- Endocrine Disruption, EI/C- Eye Irritation/Corrosivity, G- Genotoxicity, M- Mutagenicity, N- Neurotoxicity, OEL- Occupational Exposure Limits, R- Reproductive Toxicity, RSn- Respiratory Sensitization, SI- Skin Irritation, SnS- Skin Sensitivity) (VH- Very High risk process, H- High risk process, M- Medium risk process, L- Low risk process, -- No hazard and/or No data).

		Lime (CaO)	**Hard Coal**	**$CoCl_2$**	**O_2**	**Co_3O_4**	**$LiCoO_2$**
Physicochemical	**C**	--	--	--	--	--	--
	Ex	--	--	--	VH	--	--
	F/FP	--	H	--	--	--	--
	O	--	--	--	VH	--	--
	R	--	--	--	--	--	--
	WP	--	--	--	--	--	--
	WS	--	--	--	--	--	--
Human Toxicity	**AT**	--	--	--	--	--	--
	C	H	--	H	--	VH	H
	D	--	--	--	--	--	--
	ED	--	--	--	--	--	--
	EI/C	--	--	--	--	--	--
	G	--	--	--	--	--	--
	M	--	--	H	--	--	VH
	N	--	--	--	--	--	--
	OEL	--	--	--	--	--	--
	R	--	--	--	--	--	--
	RSn	--	--	H	--	H	H
	SI	H	--	--	--	--	--
	SnS	H	--	H	--	--	--

Table 22. Classification of hazards of materials in recycling and end-of-life steps.

Hazard	Production of battery chemicals
CaO	🟧
Hard coal	🟩
$CoCl_2$	🟥
O_2	🟥
Co_3O_4	🟥
$LiCoO_2$	🟥

Table 23 shows the PDE and/or the STEL of the materials used in the recycling and end-of-life step.

Table 23. Permitted Daily Exposure of chemical used in recycling and end-of-life step in Spain

	PDE (Permitted Daily Exposure) (mg/m^3)
$LiCoO_2$	0.02

Table 24 presents a summary of the hazards of all the chemicals used in the value chain, categorized according to the methodology already described

Table 24. Categorization of hazards of chemicals used in LIBs' value chain. Red is very high risk, orange is high risk, yellow is medium risk, green is low risk, and blue is no risk

	Value Chain					
Chemicals	Mining and extraction of raw material	Production of battery chemicals	pCAM and CAM production	Production of cell/batteries	Battery integration and end users	Recycling and end of life
Cobalt	🟥					
Lithium	🟧					
Nickel	🟥	🟥				
Manganese	🟧					
Aluminium	🟨			🟨		
Copper	🟦			🟦		
Hydrogen peroxide		🟧				
Sulphuric acid		🟧				🟧
Sodium sulphate		🟩				
Nickel hydroxide		🟥				
Manganese oxide		🟨				
Trimanganese tetroxide		🟩				
Manganese hydroxide		🟩				
Lithium sulphate		🟩				
Cobalt hydroxide		🟥				
Sodium hydroxide		🟨				🟨
Nickel sulphate		🟥	🟥			
Cobalt sulphate		🟧	🟧			
Manganese sulphate		🟨	🟨			
Lithium carbonate			🟥			
Lithium hydroxide		🟨	🟨			

	Value Chain					
Chemicals	Mining and extraction of raw material	Production of battery chemicals	pCAM and CAM production	Production of cell/batteries	Battery integration and end users	Recycling and end of life
Ammonium hydroxide			🟨			
Carbon black			🟥			
PVDF				🟧		
N-methyl-2-pyrrolidine				🟨		
Graphite			🟥	🟥		
Lithium hexafluorophosphate				🟩		
Ethylene carbonate				🟨		
Dimethyl carbonate				🟥		
Vinyl carbonate				🟨		
Polypropylene				🟧		
Polyethylene				🟧		
Steel				🟦		
Polyethylene terephthalate				🟦		
Lime						🟧
Hard coal						🟩
Cobalt chloride						🟥
Oxygen						🟥
Co_3O_4						🟥
$LiCoO_2$						🟥

2.5 Accidents related to Li-ion batteries

As indicated in the previous section, one of the main hazards in the assembly, use and recycling of batteries is accidents. Table 25 presents some of the incidents that occurred in the last year.

Table 25. Most representative accidents related to LIBs around the world.

Classification	Date	Location	Accident Reply
Mobile phone	24.08.2016	Korea	First explosion of a Note 7 in the world
	18.09.2016	China	First explosion of a Note 7 in China
	10.10.2016	China	iPhone 7 exploded, injuring user
	14.10.2016	China	Huawei P9 exploded while charging
	17.10.2016	Australia	iPhone 7 caught fire, burning a car
	09.01.2018	Switzerland	iPhone exploded during battery replacement, causing injury and poisonings
	10.01.2018	Spain	iPhone exploded inside a store
	2018.12.30	America	iphone XS Max self-ignited and burned the user
Electrical vehicles	01.01.2016	Norway	Tesla Model S caught fire while charging
	14.05.2016	China	EV bus caught fire due to a battery pack short circuit
	07.09.2016	the Netherlands	Tesla ModelS crashed into a tree, causing battery to catch fire
	15.01.2016	China	EV bus self-ignited while being driven
	18.02.2017	China	Tesla Model X caught fire after crashing
	01.05.2017	China	EV bus self-ignited while charging
	24.03.2018	America	Tesla Model S caught fire while stationary
	21.05.2018	China	EV bus self-ignited while being driven
Airplane	03.09.2010	United Arab Emirates	Boeing 787 crashed due to battery catching fire
	07.01.2013	America	Battery pack caught fire in a Boeing 787
	16.01.2013	Japan	Battery pack caught fire during a Boeing 787 flight
	04.2014	Australia	Boeing 737 caught fire due to a short-circuit in a battery inside a trunk

Source: Table modified from (Ouyang, et al., 2019).

These incidents may be due to abusive factors that damage the original stable structure of LIBs, generating thermal hazards. These factors can be classified as physical, electrical, and thermal, but may also be due to manufacturing defects and battery ageing. Most of these factors lead to a TR, a process that is accelerated by increased temperature, which releases energy that even further increases the temperature. Each of the factors that can produce the accidents are described below.

Physical factors

The battery is deformed due to an applied force. One of the most common causes is a vehicle collision/crash and the battery being penetrated by a sharp object. The volume expansion of electrode materials and stress generation within the battery may also lead to physical failure.

This deformation may have dangerous consequences because:

(1) The electrodes may come into contact, causing an internal short circuit

(2) The flammable electrolyte may leak and induce a fire (Ouyang, et al., 2019). As indicated in Section 3.1.2, the electrolytes used in batteries usually contain organic solvents, such as ethyl carbonate, which in turn contain solvated ions provided by salts, commonly Lithium hexafluorophosphate ($LiPF_6$). These organic solvents are often highly volatile and flammable, and their decomposition can lead to a significant temperature increase.

Another important contributor to the heat generated during a fire is the separator (often made of PE, PP or a combination of both), which is highly combustible (Pfrang, Kriston, Ruiz, Lebedeva, & di Persio, 2017).

Another physical factor is the penetration mentioned above, which may occur when a battery comes into contact with a sharp object. Compared with a collision or a crash, penetration may result in more severe consequences due to the severity of an internal short circuit. In this case, a severe short circuit of the battery will occur quickly, increasing the internal temperature and facilitating the decomposition of the lithium salt, which can cause combustion or even an explosion (Ouyang, et al., 2019).

Finally, the compressive stress reached during lithiation, and the tensile stress reached during de-lithiation will lead to fatigue damage, leaving battery materials susceptible to fracture and pulverization (Ouyang, et al., 2019).

Electrical factors

External short circuit, overcharge and over-discharge are common conditions of electrical failure.

The external short circuit of a battery occurs when electrodes with a voltage difference are connected by conductors. This usually results from battery deformation, water immersion, conductor ageing, improper use, or prolonged charging.

Overcharge occurs when the open circuit voltage of a battery is charged above the cut-off voltage (Ouyang, et al., 2019), the charging of the battery may continuously increase the internal pressure and deform the battery, which in turn can cause the electrolyte to leak. Extra or unwanted Li+ moves from the cathode to the anode, changing the atomic structure of the cathode side and causing it to collapse and release oxygen (Gandoman, et al., 2019). This oxygen accelerates decomposition.

Finally, and similarly to overcharge, over-discharge can occur when the open circuit voltage of a battery is discharged below the cut-off voltage (Ouyang, et al., 2019). Over-discharge may not cause TR directly, but if the cell is discharged to zero voltage, it will start an electrochemically irreversible solid-state amorphization process, resulting in the destruction of its structure (Gandoman, et al., 2019). Gases such as CO and CO_2 may also be generated, resulting in battery swelling. Over-discharge will also cause the dissolution of copper collector, piercing the separator and causing a short circuit (Ouyang, et al., 2019).

Thermal factors

Thermal failure can also be triggered by external high temperature and overheating, resulting in a substantial increase in battery temperature and leading to the melting of the separator, the decomposition of electrodes/electrolytes, and numerous side reactions, finally causing a TR. Both physical and electrical factors can ultimately cause a TR. (Ouyang, et al., 2019).

Manufacturing defect and ageing

In addition to external factors, batteries' internal defects due to poor manufacturing (low-quality separators, material contaminants, and improperly arranged constituents) can also result in thermally hazardous conditions.

Finally, the aged battery will lose quantities of lithium and active materials, increasing its thermal hazards due to Li plating on the electrodes and even the separator, ultimately generating a dendrite. The dendrite may form a bridge between the electrodes, causing micro-shorting inside the battery, which may lead to its failure. At the same time, the ageing of the battery can thicken the solid electrolyte interface (SEI), leading to increase battery resistance, heat generation, and thermal hazards (Ouyang, et al., 2019).

Inherently, NMC 811 cathode batteries are not very stable, due to:

- High nickel content. The fully oxidized Ni^{4+} produced after charging is reactive and an excessive amount increases the possibility of unwanted side reactions with the electrolyte (Manthiram, 2017), (Schipper, et al., 2017).

- Less Mn and Co than in other NMC batteries. Co and Mn hold the NMC-layered oxide structure together, so their content reduction reduces the structural stability of the material (Kim, Lee, Cha, Yoon, & Cho, 2017), (Hou, Yin, Ding, Huang, & Xu, 2017).

- The very high capacity to which NMC batteries can be charged. However, residual lithium compounds may decompose at high voltages, producing dangerous gases and swelling of the cell (Konarov, Myung, & Sun, 2017), (Ma, Nie, Xia, & Dahn, 2016).

Furthermore, elevated temperatures increase chemical and structural instability, as they increase degradation, cell swelling, and the likelihood of TR.

Researchers are already investigating multiple strategies to address this stability problem (Myung, et al., 2017), (Hou, Yin, Ding, Huang, & Xu, 2017), (Kim, Lee, Cha, Yoon, & Cho, 2017)

Emissions of gases in cases of accidents and classification of their hazards

As already mentioned, the uncontrollable exothermic reactions that take place during a TR are caused in cases of abuse such as short circuit, overcharge, nail penetration, and crushing.

In recent years, many authors have reported chain reactions following a TR. The TR starts with the decomposition of SEI and involves the reaction of the cathode, the anode, and the electrolyte (Diaz, Wang, Weyhe, & Friedrich, 2018).

The ideal operating temperature range for lithium batteries is between 20 °C and 40 °C. At low temperatures (< 0 °C), lithium might become irreversibly damaged in its charge state, when it is deposited on the negative electrode. In the worst case, an internal short circuit may occur. At high temperatures, the pressure inside the battery increases, flammable gases are released, and cells may combust (Jung Park, Kook Kim, Sik Kim, & Mu Lee, 2019).

Thus, many authors have simulated TR processes with different triggers and measured the gases emitted using different techniques.

(Essl, Golubkox, Thaler, & Fuchs, 2020) carried out several experiments on an unused NMC pouch cell, using three different TR triggers (overtemperature, overcharge and nail penetration) to study thermal behaviour and the production of vent gases and their composition.

Vent gas composition was measured using a FTIR spectrometer and GC in parallel after the TR. The pipes from the reactor to gas analysis were closed during the TR experiment and reopened after the TR.

Firstly, in the TR triggered by overtemperature, the first and second venting were identified at temperatures of $T_{cell}^{v1} = (121 \pm 1)°C$ and $T_{cell}^{v2} = (204 \pm 1)°C$, the cell released a significant amount of gas, and the pressure inside the sealed reactor increased within seconds up to the maximum value.

Table 26. Gases released due to overtemperature

Gases	First cell components (%)	Second cell components
CO2	30	21
CO	26	30
H2	15	15
C_2H_4	10	5
CH_4	5	5
H_2O	4	4
EMC	3	-
DMC	-	2
C_4H_{10}	<1	2
C_6H_{14}	-	<1
C_2H_6	<1	<1
C_2H_2	<1	<1

At 240 seconds before the overcharge-triggered TR, the first venting could be observed at $T_{cell}^{v1} = (82 \pm 17)°C$. The cell produced significantly more gas in total during the overcharge than during overtemperature. Despite this, in regards to the main gas compounds produced during the TR, the cell produced higher volume percentage values of CO (33%) and H_2 (26%), and lower volume percentage values of CO_2 (20%) than was produced in the overtemperature triggered cell.

Finally, in the nail-triggered TR, the cell released a significant amount of gas immediately after the nail penetrated the cell. The pressure inside the sealed reactor increased up to the maximum value and produced less gas than that produced in the overcharge-triggered TR, but more than that in the overtemperature-triggered TR. In this case, the cell produced the lowest CO volume percentage values and the highest C_2H_4 value of all three triggers. The H_2 values were lower than those in the overcharged cells, but higher than those in the overtemperatured cells. The same values were achieved by Diaz et al., with the exception that they referred to gas results without TR.

The authors suggest that the gases produced during the TR may be explained by SEI decomposition, electrolyte decomposition, NMC cathode degradation, and the reaction of the solvent with the cathode.

As shown in the presented results, no HF was identified, probably due to the low concentration and high reactivity with materials inside the test reactor, the analysis pipes, and the ejected particles.

(Golubkov, et al., 2014) investigated the influence of three different cathode-material chemistries on the safety of commercial graphite-based 18650 cells in terms of their thermal stability. The NMC (Li $(Ni_{0.5}Mn_{0.25}Co_{0.25})$ O_2) batteries were included in the LIBs.

The compositions of the sampled gas were analysed using a gas chromatograph, which was calibrated for H_2, O_2, N_2, CO, CO_2, CH_4, C_2H_4, and C_2H_6.

The molar percentages of the produced gases for the **NMC battery were: 41.2% CO_2, 30.8% H_2, 13% CO, 8.2% C_2H_4 and 6.8% CH_4.** Again HF, which can be a major source of toxicity, was not detected.

(Chen, et al., 2019) investigated the solid products that remained after thermolysis at different temperatures and the relationship between the gas emission and the thermal behaviour of the cathodes, using spent NMC LIBs from electric vehicles.

Figure 2 shows the chemical analysis of the solid products that remained after thermolysis at different temperatures. An increase in the temperature of the thermolysis process thus produces an increase in the contents of Ni, Co, Mn, and Li, and a decrease in C, P, and F.

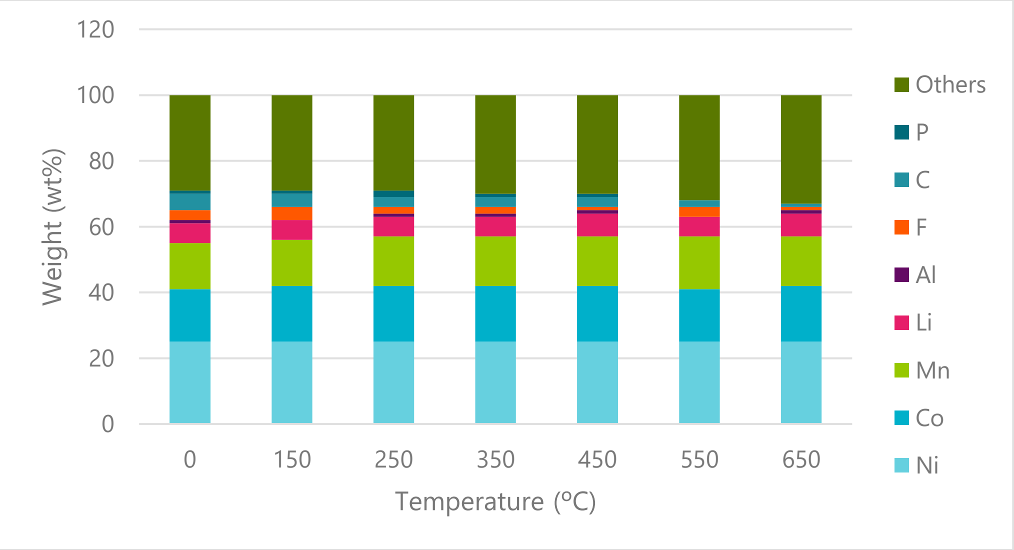

Figure 2. Chemical analysis of solid thermolysis products at different temperatures. Modified from (Chen, et al., 2019).

The results of the study on the relationship between the emission of the identified gaseous species and the thermal behaviour of the cathodes highlighted that the thermolysis process included a series of chain reactions which occurred sequentially as the temperature increased. Thus, the solvent EC/EMC volatilized and decomposed into gaseous hydrocarbons, CO_2, and H_2O, at around 177 °C. Fluoride-containing gases, mainly POF3 and PF, were released from the electrolyte over the same temperature range. The PVDF binder decomposed as H_2O, CO_2, and fluoride-containing gases with maximum emission peaks at 522 °C, and the generation of CO_2 above 600 °C may have been due to the oxidation of acetylene black.

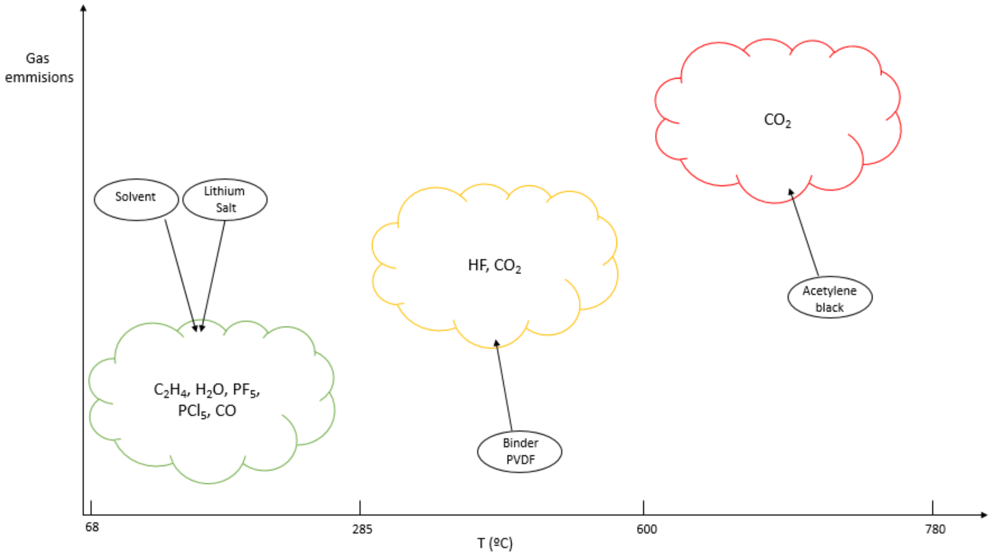

Figure 3. Relationship between emission characteristics, off-gas, and thermolysis behaviours of the cathodes. Modified from (Chen, et al., 2019).

Sun, et al. (2016) analysed the toxicity of combustion products from commercialized LIBs at different states of charge (SOC). They identified more than 100 emitted gaseous products, most of which are hazardous to human beings and the environment. The number of combustion products was highly dependent on the SOC.

They found that the number of identifications (Nis) of the COPs were strongly dependent on the batteries' SOC. It increased as the SOC increased from 0% to 100%, but decreased when the SOC increased from 100% to 150% (overcharge). The decreases may have been due to Li deposition and the consumption of solvent-based electrolytes, leading to relatively less species being left in the subsequent combustion.

In the case of the NMC111 cell, some of the COPs detected were: C_3H_4O and $C_{10}H_8$ at 0% SOC; C_3H_4O at 50% SOC; $C_3H_2N_2$, $C_{10}H_8$, Butane, C_5H_9NO, C_5H_8 and C_5H_{10} at 100% SOC; and $C_{10}H_8$ and C_5H_{10} at 150% SOC.

Sun, et al. (2016) found that the concentrations of the gas emissions of the second scenarios were higher for the selected species. The reason for this behaviour may be that the first scenario was chosen to represent the event of a battery failure without any further security measures. In this case, the cell expands until it bursts open and catches fire. As the outgassing of the cell within the barrel occurs abruptly, it is assumed that the available quantity of O_2 is insufficient for the oxidation of all the components, because the gas from the cell displaces the environmental air in the barrel. Therefore, only some of the volatile organic compounds fed the combustion, whereas a considerable amount still emerged as fume. This fume mainly consisted of the electrolyte's main constituents EMC and EC, with traces of DEC, benzene, toluene, styrene, and biphenyl.

As burning cells must be strictly avoided because of the cascaded inflammation of neighbouring cells, which is most likely to occur, the first security measure is to suppress the inflammation of the emission gases, thus drastically reducing the amount of energy released. This was achieved by using a textile composite material to enclose the cell, thereby prohibiting flying sparks while remaining permeable for the emission gases. In this case (Scenario 2), almost no oxidation took place. Consequently, a larger amount and a respectively higher quantity of unburned organic substances were expected and could be verified by the analytical methods.

In the work of Cristensen, et al., (2021) some gas was expelled from accidents in the use phase of the battery as fire or electronic problems, of which the most harmful consequences are the release of HF from the hydrolysis of POF_3, which forms from $LiPF_6$ at high temperatures. Cristensen et al. also exposed some incidents related to the end-of-life phase in which HCN was released from an explosion, causing great damage to humans and the environment.

Lastly, Amano et al. (2022) studied the gas release of NMC Li-ion pouch batteries during a TR. They tested pouch cells with nominal capacities of 10 Ah and 32 Ah, but they also used a battery stack consisting of four assembled cells. Table 27 shows the concentrations of the gas components released:

Table 27. Gas components released during thermal runaway.

Test	**SOC, %**	**CO, ppm**	**CH_4, ppm**	**H_2O, ppm**	**HF, ppm**	**HCN, ppm**	**C_2H_6, ppm**	**C_2H_4, ppm**	**NH_3, ppm**
Test series 1									
#01–#03	80–89	45–500	14,370	36,660	7	50	2040	5960	0
#04	90–100[α]	238,240	88,430	40,000	10	48	2490	167,420	5650
Test series 2									
#01–#03	30–50	7970	2740	50,000	0	130	6450	6410	3
#01–#03	80–89	12,650	3040	53,000	0	166	4880	10,350	0
#01–#03	90–100	33,970	9030	53,500	0	147	5090	9110	3
#01–#03	90–100[β]	101,290	23,980	56,670	0	137	5440	30,790	0
#01–#03	90–100[γ]	136,120	60,810	46,670	0	287	10,030	71,040	0

[α], 4-cell stack; [β], double cells; [γ], 32 Ah cells.

Source: Table modified from (Amano, Hahn, Tschirschwitz, Rappsilber, & Krause, 2022).

2.5.1 Hazards of gases released in accidents

This section identifies the hazard potential of the gases emitted in the accident simulation studies previously described. Table 28 provides a summary of the materials and their effects on health via the three potential exposure routes, as well as the hazards statements described in the methodology section.

Table 28. Hazards of gases identified in accident simulation studies via various exposure routes.

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
LiF	Systemic effects → DNEL = 10 mg/m^3 (long-term exposure); no hazard (acute/short-term exposure) Local effects → low hazard (long-term exposure); low hazard (acute/short-term exposure)	Systemic effects → DNEL = 44.8mg/kg bw/day (long-term exposure) no hazard identified (acute/short-term exposure) Local effects → no hazard identified (long- and acute/short-term exposure)	Local effects → low hazard, no threshold derived	**H319** **H315**
PF_5	Systemic effects → DNEL = 0.931 mg/m^3 (long-term exposure); high hazard (acute/short-term exposure) Local effects → high hazard (long- and acute/short-term exposure)	Systemic effects → DNEL = 133 µg/kg bw/day (long-term exposure) high hazard (acute/short-term exposure) Local effects → high hazard (long- and acute/short-term exposure)	Local effects → high hazard	**H280** **H314**
PCl_5	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	No hazard identified
CO_2	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H280**
CO	Systemic effects → DNEL = 23 mg/m^3 (long-term exposure); no hazard identified (acute/short-term exposure) Local effects → no hazard identified (long-term exposure); no hazard identified (acute/short-term exposure)	Systemic effects → hazard unknown but no further hazard information necessary as no exposure expected (long-term exposure and acute/short-term exposure) Local effects → hazard unknown but no further hazard information necessary as no exposure expected (long-term exposure and acute/short-term exposure)	Local effects → medium hazard, no threshold derived	**H360D** **H220**
H_2	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H220**
CH_4	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H220**
C_2H_4	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H220**
H_2O	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	No hazard identified

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
EMC	Systemic effects → DNEL = 12.2 mg/m^3 (long-term exposure); no hazard identified (acute/short-term exposure) Local effects → no hazard identified (long-term exposure); no hazard identified (acute/short-term exposure)	Systemic effects → 12.2 mg/kg (long-term exposure) no hazard identified (acute/short-term exposure) Local effects → no hazard identified (long-term exposure and acute/short-term exposure)	Local effects → no hazard identified	**H225** **H319**
C_4H_{10}	Systemic effects → DNEL = no threshold effect and/or no dose-response information available (long-term exposure and acute/short-term exposure) Local effects → no threshold effect and/or no dose-response information available (long-term exposure and acute/short-term exposure).	Systemic effects → no data available: testing technically not feasible (long-term exposure and acute/short-term exposure) Local effects → no data available: testing technically not feasible (long-term exposure and acute/short-term exposure)	Local effects → no hazard identified	**H220** **H231**
C_2H_6	Systemic effects → DNEL = no threshold effect and/or no dose-response information available (long-term exposure and acute/short-term exposure) Local effects → no threshold effect and/or no dose-response information available (long-term exposure and acute/short-term exposure).	Systemic effects → no data available: testing technically not feasible (long-term exposure and acute/short-term exposure) Local effects → no data available: testing technically not feasible (long-term exposure and acute/short-term exposure)	Local effects → hazard unknown	**H220**
C_2H_2	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H220** **H231**
HCN	Systemic effects → DNEL = 0.78 mg/m^3 (long-term exposure and acute/short-term exposure) Local effects → 0.2 mg/m^3 (long-term exposure); 1.25 mg/m^3 (acute/short-term exposure)	Systemic effects → 0.054 mg/kg (long-term exposure) acute toxicity (acute/short-term exposure)	Local effects → no hazard identified	**H310** **H300** **H314** **H330**
HF	Systemic effects → DNEL = 0.03 mg/m^3 (long-term exposure and acute/short-term exposure)	Systemic effects → no-threshold effect and/or no dose-response information available (long-term exposure and acute/short-term exposure) Local effects → no-threshold effect and/or no dose-response information available (long- and acute/short-term exposure)	Local effects → medium hazard, no threshold derived	**H314**

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
HCl	Systemic effects → no hazard identified (long-term exposure and acute/short-term exposure) Local effects → 8 mg/m^3 (long-term exposure); 15 mg/m^3 (acute/short-term exposure)	Systemic effects → no hazard identified (long-term exposure and acute/short-term exposure) Local effects → high hazard, no threshold derived (long- and acute/short-term exposure)	Local effects → medium hazard, no threshold derived	**H224** **H330**
CH_3F	Systemic effects → DNEL = 7.035 mg/m^3 (long-term exposure and acute/short-term exposure) Local effects → no hazard identified (long-term exposure and acute/short-term exposure)	Systemic effects → no hazard identified (long-term exposure and acute/short-term exposure) Local effects → no hazard identified (long- and acute/short-term exposure)	Local effects → no hazard identified	**H220** **H280**
CF_4	Systemic effects → DNEL = 16.341 mg/m^3 (long-term exposure and acute/short-term exposure) Local effects → 8 mg/m^3 (long-term exposure); 15 mg/m^3 (acute/short-term exposure)	Systemic effects → 3.3 mg/kg (long-term exposure) acute toxicity (acute/short-term exposure)	Local effects → no hazard identified	**H280**
CHF	No data for this substance	No data for this substance	No data for this substance	**H280***
COF_2	No data for this substance	No data for this substance	No data for this substance	**H280 *** **H330**
POF_3	No data for this substance	No data for this substance	No data for this substance	**H280*** **H330**
$(CN)_2$	No data for this substance	No data for this substance	No data for this substance	**H280*** **H314**
NO	No data for this substance	No data for this substance	No data for this substance	**H225***
H_3	Systemic effects → DNEL = 47.6 mg/m^3 (long-term exposure and acute/short-term exposure) Local effects → 14 mg/m^3 (long-term exposure); 36 mg/m^3 (acute/short-term exposure	Systemic effects → 6.8 mg/kg (long-term exposure) acute toxicity→ no-threshold effect and/or no dose-response information available (acute/short-term exposure)	Local effects → no data	**H318** **H335**
DMC	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → No hazard identified Local effects → No hazard identified	Local effects → no hazard identified	**H225**
EC	Systemic effects → DNEL = 15 mg/m^3 (long-term exposure and acute/short-term exposure) Local effects → no hazard identified (long-term exposure and acute/short-term exposure)	Systemic effects → 4.3 mg/kg (long-term exposure) acute toxicity→ no hazard identified (acute/short-term exposure)	Local effects → low hazard	**H315** **H319**

	Hazard via inhalation route	Hazard via dermal route	Hazard to the eyes	Hazard statements
EMC	Systemic effects → DNEL = 10.3 mg/m^3 (long-term exposure and acute/short-term exposure) Local effects → no-threshold effect and/or no dose-response information available (long-term exposure and acute/short-term exposure)	Systemic effects → 2.92 mg/kg (long-term exposure) acute toxicity→ 417 mg/kg (acute/short-term exposure)	Local effects → no-threshold effect and/or no dose-response information available	**H311** **H318**
DEC	Systemic effects → DNEL = 69.792 mg/m^3 (long-term exposure) low hazard (acute/short-term exposure) Local effects → low hazard (long-term exposure) no hazard identified (acute/short-term exposure)	Systemic effects → 10 mg/kg (long-term exposure) acute toxicity→ low hazard (acute/short-term exposure) Local effects → low hazard (long-term exposure and acute/short-term exposure)	Local effects → low hazard (no threshold derived)	No hazard identified
VC	Systemic effects → No hazard identified Local effects → No hazard identified	Systemic effects → 0.21 mg/kg (long-term exposure) acute toxicity→ no DNEL information (acute/short-term exposure) Local effects → 0.04 mg/kg (long-term exposure) acute toxicity→ no DNEL information (acute/short-term exposure)	Local effects → medium hazard (no threshold derived)	No hazard identified

[*] Data gathered from safety data sheet

As described in the methodology section, the chemicals were ranked according to their hazards. Table 29 shows the hazard level for the different parameters considered, and Table 30 shows the classification made for the identified gases.

Table 29. Identified hazards of the gases emitted during accidents.

(C- Corrosivity, Ex- Explosion, F/FP- Flammability/Flash Point, O- Oxidizing, R- Reactivity, WP- Vapor Pressure, WS- Water solubility, AT- Acute Toxicity, C- Cancerogenicity, D- Developmental, ED- Endocrine Disruption, EI/C- Eye Irritation/Corrosivity, G- Genotoxicity, M- Mutagenicity, N- Neurotoxicity, OEL- Occupational Exposure Limit, R- Reproductive Toxicity, RSn- Respiratory Sensitization, SI- Skin Irritation, SnS- Skin Sensitivity) (VH- Very High risk process, H- High risk process, M- Medium risk process, L- Low risk process, -- No hazard and/or No data).

		CO_2	CO	H_2	CH_4	C_2H_4	EMC	C_4H_1	C_2H_6	C_2H_2	HF	HCN	LiF	PF_5	PCl_5	HCl	CH_3F	CF_4	CHF	COF_2	POF_3	(CN)	NO	NH_3	EC	DMC	EMC	DEC	VC
Physicochemical	**C**	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	Ex	**H**	--	--	**H**	--	--	**H**	**H**	**H**	--	--	--	**H**	--	--	**H**	**M**	**M**	**M**	**M**	**M**	**M**	--	--	--	--	--	--
	F/ FP	--	**VH**	**VH**	**VH**	**VH**	**VH**	**VH**	**VH**	**VH**	--	**VH**	--	--	--	--	**VH**	--	--	--	--	--	--	**VH**	--	**H**	**VH**	--	--
	O	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	**H**	--	--	--	--	--	--
	R	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	WP	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	WS	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Human Toxicity	**AT**	--	**M**	--	**M**	--	--	--	--	--	**VH**	**VH**	**VH**	**VH**		--	--	**L**	--	**VH**	**VH**	--	**L**	**H**	--	--	**VH**	**H**	**M**
	C	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	D	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	ED	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	EI/C	--	--	--	--	--	**VH**	--	--	--	**M**	--	**H**	**H**	--	**H**	--	--	--	--	--	--	--	--	**L**	--	--	**M**	**M**
	G	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	M	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	N	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	OEL	--	**H**	--	--	**M**	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	R	--	**VH**	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
	RSn	--	--	--	--	--	**M**	--	--	--	--	--	**M**	--	--	**L**	--	--	--	--	--	--	--	--	--	--	--	--	--
	SI	--	--	--	--	--	**H**	--	--	--	**VH**	--	**H**	**M**	--	--	--	--	--	--	--	**H**	--	**H**	**L**	--	--	--	--
	SnS	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	**H**

Table 30. Hazards of gases emitted during simulation of accidents.

Hazard	Production of battery chemicals
LiF	🟧
PF_5	🟧
PCl_5	🟦
CO_2	🟧
CO	🟥
H_2	🟥
CH_4	🟥
C_2H_4	🟥
H_2O	🟦
EMC	🟥
C_4H_{10}	🟥
C_2H_6	🟥
C_2H_2	🟥
HF	🟥
HCN	🟥
HCl	🟧
CH3F	🟥
CF4	🟨
CHF	🟨
COF2	🟥
POF3	🟥
(CN)2	🟧
NO	🟧
NH3	🟥
DMC	🟧
EC	🟩
EMC	🟥
DEC	🟧
VC	🟧

Table 31 contains the PDE and/or the STEL for some of the materials used in the recycling and end-of-life step.

Table 31. Permitted Daily Exposure for some of the gases released in accidents in Spain.

	PDE (Permitted Daily Exposure) (mg/m^3)
LiF	2.5
PF_5	2.5
PCl_5	1
CO_2	PDE = 1.5 STEL = 2.5
CO	PDE = 23 STEL = 117
CH_4	1000 ppm
C_2H_4	200 ppm
C_4H_{10}	1000 ppm
C_2H_6	1000 ppm
HF	PDE = 1.5 STEL = 4.7
HCN	PEL = 11 STEL = 5
HCl	STEL= 10 ppm
PF_5	2.5
NH3	PEL = 25 STEL = 35

2.6 New Materials (CNTs/Graphene)

2.6.1 CNTs

Carbon nanotubes (CNTs) are new nanomaterials which, as indicated in the T1.3 report, have great potential for use in LIBs due to their high conductivity and good mechanical properties. This will increase the electronic conductivity of the cathode electrode, increase the charge/discharge rate, and increase structural flexibility. They also have low flammability, which reduces the probability of accidents. However, some harmful effects on the human body have been reported.

Kobayashi et al. ()2017 published a comprehensive review of the health effects of CNTs. Some of their results are summarized in Table 32. Summary of toxicity studies of CNTs:

*Table 32. Summary of toxicity studies of CNTs reported in Kobayashi et al. (2017)***.**

Evaluated endpoint	Result
Inflammation in respiratory system	Both SWCNTs and MWCNTs are considered to induce persistent pulmonary inflammation in experimental animals, although short fibres tend to induce less persistent inflammation than long ones.
Injury in respiratory system	After inhalation and instillation studies of CNTs, the evidence on persistent hyperplasia of bronchoalveolar epithelial cells was not sufficient.
Fibrosis in respiratory system	Most inhalation and intratracheal instillation studies showed pulmonary fibrosis. Long, needle-like fibres induced most fibrotic responses.
Biopersistence of CNTs in the lung	Biopersistence depends on length, flexibility, and durability. Long, insoluble fibres are biopersistent. Shorter, more soluble ones are efficiently cleared and have lost persistence.
Gene damage in the lung	MWCNTs can induce mutation, and on the other hand, SWCNTs can induce DNA breakage, form micronuclei, and produce ROS in human peripheral bool lymphocytes
Malignant tumour in respiratory system	Several studies conducted on long, thin fibres demonstrate the formation of malignant tumours in the respiratory system. No studies have followed the long-term inhalation of short-length CNTs

In conclusion, Kobayashi, et al. (2017) indicated that CNTs may be considered carcinogenic and can cause lung tumours. These effects depend on whether the fibre length is more attenuated in shorter fibres.

However, there is still some uncertainty regarding the potential toxicity of these innovative raw materials. According to the information provided by industries to ECHA in REACH registrations, no hazards have been classified.

2.6.2 Graphene

As indicated in the Task 1.3 report, graphene has high electrical and thermal conductivities, and a unique electronic structure, in which charge carriers behave as particles and every atom in graphene can be considered as a surface atom. Graphene gives the batteries a higher power density, energy density, and cycle life. The large surface areas can provide more electrochemical reaction-active sites for energy storage. Another advantage is its flexibility, which is beneficial for flexible energy storage devices (Wu, et al., 2012).

However, as in the case of CNTs, some health and safety concerns have been raised, and many studies have been performed to determine the toxicity of graphene, as regulatory agencies require these studies to register the use of the materials.

Extensive research has been carried out, particularly on the interaction between graphene-related materials (GRM) and the lung barrier. Contradictory results have been obtained due to different types of GRMs and the lack of standardization in toxicological screening methods.

Some studies have indicated that certain forms of graphene may be cytotoxic (Wang K. , et al., 2011). Achawi et al. (2021) studied data from the literature on the structure–activity relationship of Graphene materials and concluded that the largest few layers of graphene tend to show higher oxidative stress and may be classified as highly cytotoxic and oxidant. The thickest are classified as nontoxic, and the thinnest are moderately or highly toxic and do not appear to affect oxidative stress.

In vivo toxicity research has also been carried out in recent years, but the toxicity of GRM remains unclear due to the variations in the sample quality, diversity of GN, and difficulty interpreting the *in vivo* studies due to limitations in the methodologies e.g., graphite does not have a strong Raman signal that can be tracked *in vivo*.

Graphene is registered in REACH under EC number 801-282-5 and CAS number 1034343-98-0. No hazard statements have been raised in this register.

3 Conclusions

This report presents the study of the hazards of the chemical materials used in the different stages of the value chain to produce LIBs. Data were obtained from the bibliography and the ECHA and GSH website, and the materials were classified according to their potential hazards.

Categorization used a system based on the CLP/GHS hazard statements and considered the JRC criteria in the 'Safe and Sustainable by design chemicals and materials' document. Figure 4 presents a summary of the conclusions regarding the chemicals along the value chain.

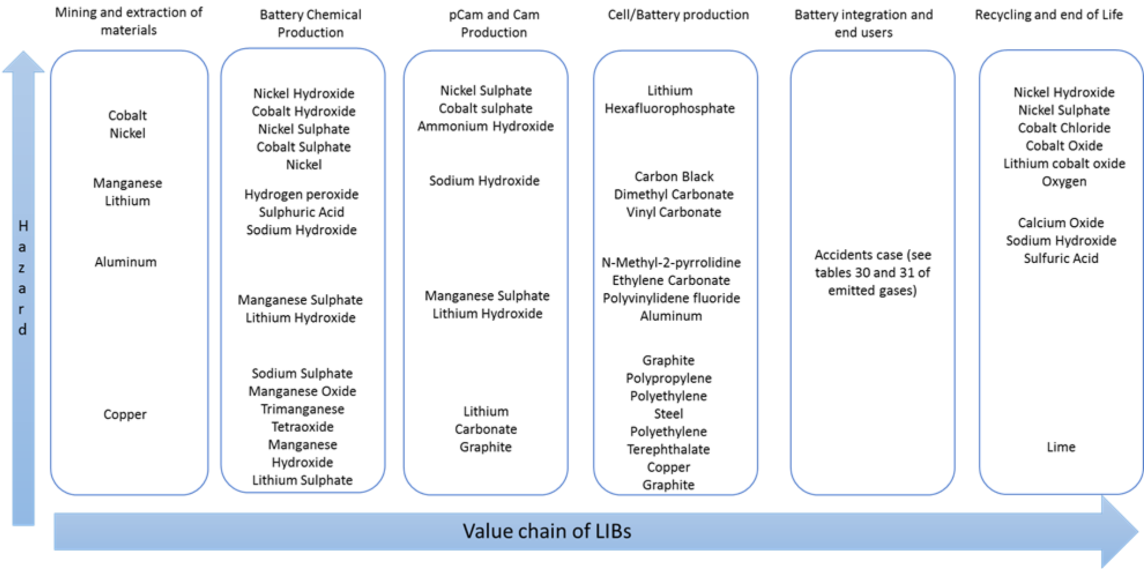

Figure 4. Classification of chemicals' hazards along the value chain

For the stage of battery integration and end use, the chemical hazards were mainly due to accidents in which misuse of the battery or errors in fabrication may lead, as explained in Section 3.2, to TR and the emission of gases that can be harmful to human beings. Simulation experiments, the results of which were found in the literature, have identified the emitted gases. The gases were also characterized in this work according to their health hazards, and their categorization is shown in Table 30 of the present report.

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