Project	Lithium-ion battery’s life cycle: safety risks and risk management at workplaces
Work package	WP3: Critical occupational risk factors
Task	T.3.2 Assessment of workers’ exposure to chemicals
Responsible organisation	FIOH
Authors	Anneli Kangas, Tiina Santonen, Arto Säämänen

Abstract

This task report describes the assessment of workers’ exposure to chemicals and is part of the ‘Lithium-ion battery’s life cycle: safety risks and risk management at workplaces’ project. In this report, workers’ exposure to chemicals distinguished in the value chain is assessed on the basis of measurement data collected from Finnish workplaces and the literature. Biomonitoring and air concentration data were used to evaluate the magnitude of the exposure. The exposure levels were compared to the current Finnish Occupational Exposure Limit (OEL) values and when available, to the corresponding indicative limit values for biological exposure indicators.

This study identified hazardous substances and workers’ exposure at different stages of the lithium-ion battery (LIB) value chain. Information about nickel and cobalt exposure was produced in relation to LIB value chain in Finnish workplaces. High potential exposure related almost to all life cycle stages of the value chain. The OEL values were exceeded in several cases, although not in all workplaces. Concentrations of impurities and even substances vary in individual workplaces and processes, which makes a general risk assessment in a value chain difficult. Exposure also varies among different work groups. Therefore, exposure assessment here does not represent exposure in individual workplaces or individual workers.

Several data gaps relating to LIB production were observed. Overall, further studies of exposures in the LIB value chain are needed, especially in precursor materials (pCAM) and lithium-ion cathode active battery materials (CAM), cell and battery production, and in recycling.

Table of contents

1 Methods

The Safe and Sustainable by Design (SSbD) is a pre-market approach to chemical and material design that focuses on providing a function (or service), while avoiding volumes and chemical and material properties that may be harmful to human health or the environment, in particular groups of chemicals likely to be (eco)toxic, persistent, bio-accumulative or mobile. Its main aim is the exclusion of the most harmful chemicals and materials in the early R&D phase of new chemical or material development, and the substitution of existing chemicals or materials with these properties. Based on the hazard classification of the chemicals of the EU Classification, Labelling and Packaging of substances and mixtures (CLP) regulation, the Joint Research Centre (JRC) defines criteria for classifying the inherent hazard potential of a substance into three categories (Caldeira et al., 2022). Using these categories can help identify compounds which that should not be included in consumer products or that may need to be substituted in the future. In our assessment, we used this JRC classification and the substances with an inherent hazardous potential were classified according to the same criteria. Table 1 presents these criteria. Substances that may cause a health risk at workplaces were identified by gathering the available information on lithium-ion battery (LIB) processes in the literature, or company interviews of occupational safety and health personnel, or observations made in work environments.

For the exposure assessment, we developed and applied three-category evaluation criteria to assess the monitoring data of chemical impurities in the air or in biological samples (Table 2). The exposure levels were compared to the current Finnish Occupational Exposure Limit (OEL) values, which have been confirmed by the Finnish Ministry of Social Affairs and Health (2020). These limit values are set for air levels and specifically defined for the evaluation of workers' exposure levels. OELs are mainly the smallest concentrations that can harm the safety, health or reproductive health of a worker. Effects on sensitive workers, mild effects, and severe effects when the probability of their occurrence is low are generally not taken into consideration when setting these OEL values. When available, corresponding indicative limit values for biological exposure indicators were also considered. These were available for cobalt (Co) and nickel (Ni), for example. In addition, recent evaluations by the EU authoritative bodies were taken into account. These included the European Chemicals Agency's (ECHA) Risk Assessment Committee's (RAC) evaluations of Ni and Co salts, which led to recommendations on health-based limit values. These evaluations are expected to result in the current Finnish OELs and biological limit values (BLVs) being lowered.

The Finnish Institute of Occupational Health utilises a laboratory information management system (LIMS) to retain measurement data. This database contains information on the concentrations of air impurities measured at Finnish workplaces. The registry of biomonitoring measurements also contains data on all biomonitoring measurements made by the Finnish Institute of Occupational Health. We used these registers to gather information on exposure in the different phases of Li-ion battery (LIB) manufacturing. Biomonitoring and air concentrations from 2012 to 2019 generated the data for the exposure assessment. We also received pseudonymised biomonitoring data directly from companies producing chemicals for LIBs. The EASC-IHSTAT tool (AIHA 2022) was used to calculate exposure statistics on workers’ breathing zone samples and stationary measuring points.

Table 1. Hazard categorisation based on JRC (2020) proposal.

	HUMAN HEALTH HAZARD CRITERIA
CRITERION 1 **MOST HARMFUL SUBSTANCES. (SUBSTANCES OF VERY HIGH CONCERN, SVHC)**	Carcinogenicity Cat. 1A and 1B Germ cell mutagenicity Cat. 1A and 1B Reproductive/developmental toxicity Cat. 1A and 1B Endocrine disruption Cat. 1 (human health) Respiratory sensitisation Cat 1 Specific target organ toxicity – repeated exposure (STOT-RE) Cat. 1, including immunotoxicity and neurotoxicity
CRITERION 2 **SUBSTANCES OF CONCERN. CHRONIC EFFECTS**	Skin sensitisation Cat 1 Carcinogenicity Cat. 2 Germ cell mutagenicity Cat. 2 Reproductive/developmental toxicity Cat. 1 and 2 Specific target organ toxicity – repeated exposure (STOT-RE) Cat. 2 Specific target organ toxicity – single exposure (STOT-SE) Cat. 1 and 2 Endocrine disruption Cat. 2 (human health)
CRITERION 3 **OTHER HAZARD**	Acute toxicity Skin corrosion Skin irritation Serious eye damage/eye irritation Aspiration hazard (Cat. 1) Specific target organ toxicity – single exposure (STOT-SE) Cat. 3
NOT CLASSIFIED	

Table 2. Criteria created to assess the magnitude of exposure.

Air sampling criteria	**BM criteria**
>100% OEL	5% > Action level
10–100% OEL	Non-exposed < BM < Action level
<10% OEL	75% < Non-exposed

2 Results

2.1 Identification of substances with inherent hazard potential

Several compounds are involved in the production chain of LIBs. Table 1 presents the compounds relevant for the manufacturing of LIBs that may pose health risks during the LIB life cycle. The inherent hazard potential was based on current EU harmonised classification and labelling, unless otherwise stated. The hazard categorisation for risk assessment based on the JRC (2020) proposal introduced in the Methods section is based on the available health hazard information (Table 3).

For lithium compounds, the recent classification proposal by the ECHA RAC suggests classifying specific Li salts as reproductive toxicants in Category 1B (ECHA 2020). Lithium hydroxide is used in the manufacturing of cathode materials, such as lithium cobalt (or manganese or nickel) oxide (LiCoO2) and lithium iron phosphate for LIBs. Solutions of lithium hexafluorophosphate are used as electrolytes in LIBs. The potential reproductive toxicity of lithium compounds is related to the lithium ion but is dependent on the solubility and bioavailability of the exact lithium compound. Lithium iron phosphate has no health hazard classification, but LiCoO2 has been classified for its carcinogenicity, reproductive toxicity and sensitising properties, due to the properties of soluble Co ion. Lithium hexafluorophosphate is classified for its toxicity and skin corrosion.

Currently, Ni compounds have no harmonised classification or hazards notified by manufacturers (ECHA, 2022a). The primary hazard of Ni compounds relates to carcinogenicity in the respiratory tract. However, metallic Ni has shown no clear carcinogenic effects. Ni compounds can have genotoxic effects via different indirect mechanisms (ECHA 2018). In addition, nickel hydroxide has a harmonised classification. It may cause cancer by inhalation, may damage an unborn child (Carc.1A, Muta.2 Repr. 1B), causes damage to organs through prolonged or repeated exposure (STOT RE 1), is harmful if swallowed, is harmful if swallowed or inhaled (Acute Tox. 4), is suspected of causing genetic defects, causes skin irritation, may cause an allergic skin reaction and may cause allergy or asthma symptoms or breathing difficulties if inhaled (Skin Irrit. 2 Resp. Sens.1, Skin Sens. 1).

Co has a harmonised classification. It is classified for its skin and respiratory sensitisation (Skin Sens. 1, Resp. sens. 1), germ cell mutagenicity (Muta. 2) and environmental effects. It is suspected of causing genetic defects, may cause an allergic skin reaction and may cause allergy or asthma symptoms or breathing difficulties if inhaled (ECHA, 2022b). Other hazards of cobalt relate to that it may cause cancer and may damage fertility (Repr.1B). The carcinogenicity and mutagenicity of Co compounds presumably relates to the Co (II) ions (ECHA 2020). Cobalt dihydroxide has no harmonised classification. Its hazardous effects relate to its skin and respiratory sensitisation, acute toxicity, reproductive toxicity 1B, carcinogenicity 1A or 1B and environmental effects.

Manganese (Mn) compounds currently have no harmonised classification for long-term health effects (STOT RE), but depending on the compound, some industries have self-classified manganese compounds as either STOT RE 1 or 2. This is because occupational exposure to fine manganese dust or fumes cause neurological effects in humans. In the past, this has even led to a clinical syndrome named manganism (SCOEL, 2011).

Sulphuric acid has harmonised classification due to that it causes severe skin burns and eye damage (Skin Corr. 1A). Additionally, industry has self-classified it toxic if inhaled.

LIBs also contain the fluoropolymers polytetrafluoroethylene (PTFE) and Polyvinylidene fluoride (PVDF), which are used as liquid binders because of their high-level thermal and electrochemical stability and their effective adhesion between electrode films and collectors. These fluoropolymers have not been classified as hazardous and most concerns related to the use of these compounds in batteries have been associated with their manufacturing process, as this involves nonpolymeric per- and polyfluoroalkyl substances (PFASs), which have bio-accumulative, target organ and reproductive toxic properties. In addition, fluorinated electrolytes based on fluoroethylene carbonate (FEC) are promising electrolytes for high-voltage and high-energy capacity LIBS. Monofluoroethylene carbonate (CAS no. 114435-02-8) has been registered in the EU for use as an electrolyte in batteries (ECHA, 2022c) and has been self-classified in industry as a skin and eye irritant (cat 2), as causing skin sensitisation, and as having fluorine-related effects on the teeth in long-term exposure (STOT RE 1).

Graphite has no harmonised classification. However, according to some notifications provided by companies it may cause serious eye and respiratory irritation.

Carbon nanotubes, including both single-wall carbon nanotubes (SWCNTs) and multi-wall carbon nanotubes (MWCNTs) have also displayed great potential as anode materials for LIBs due to their unique structural, mechanical, and electrical properties. The classification of carcinogenic (cat 1B) has recently been proposed in Europe for Rigid MWCNTs with a diameter >15 nm, which fulfil WHO's definition of fibre (ECHA, 2022d). There are also concerns about the carcinogenicity of <15 nm MWCNTs, but evidence of this is still limited. The same applies to SWCNTs. Overall, the carcinogenicity concern regarding carbon nanotubes depends on the exact type of the nanotube.

Mining involves exposure to air impurities arising from the mining process or caused by ore impurities. Ore impurities may include, for example, quartz, asbestos and many metals such as arsenic, lead, or uranium. Radon radiation may also be an issue in the mining sector. However, as these impurities depend on the specific properties of the ore and the location of the mine, they are not considered any further in this report. We emphasise that the mining process involves several potential hazardous exposures that need to be identified and managed in mines. In addition to ore impurities, diesel engine exhausts from vehicles may be an issue, especially in underground mines.

Table 3. Substances of interest.

SUBSTANCE	**CATEGORISATION ACCORDING TO JRC HAZARD-BASED CRITERIA**	**GROUP DEFINITION**
NICKEL COMPOUNDS	Carcinogenicity Cat.1A	S1 Most harmful substances
NICKEL HYDROXIDE*	Carcinogenicity Cat.1A, Reproductive toxicity 1B	S1 Most harmful substances
COBALT* COMPOUNDS	Reproductive toxicity 1B	S1 Most harmful substances
COBALT DIHYDROXIDE	Carcinogenicity Cat 1A*	S1 Most harmful substances
MANGANESE AND ITS COMPOUNDS	Specific target organ toxicity-repeated exposure, STOT RE2 or RE1*	S2 Chronic effects
LITHIUM HYDROXIDE	Proposed classification as reproductive toxicity cat 1B	S1 Most harmful substances
LITHIUM HEXAFLUOROPHOSPHATE (LIPF6)	Specific target organ toxicity-repeated exposure, STOT RE 1	S1 Most harmful substances
SULPHURIC ACID (H_2SO_4)*	Skin corrosion, Skin Corr. 1A	S3 Other hazard
GRAPHITE	Not classified	
SOLVENTS (ETHYL METHYL CARBONATE EMC, DIETHYL CARBONATE DEC)	Skin irritation, Skin Irrit. 2, Eye Irrit. 2, Specific target organ toxicity- single exposure, STOT SE 3	S3 Other hazard

*Harmonised classification.

2.2 Determining the level of exposure to Ni compounds in an LIB production value chain in a Finnish work environment

In this study, we used biomonitoring data from companies and the FIOH registry of biomonitoring measurements to assess the exposure of cobalt and Ni in the production of LIBs. All the samples from different groups of workers were included in the data as related to a specific life cycle stage. Process operators were the most often measured worker group in almost all the life cycles. Other measured worker groups were maintenance workers, drivers, loaders, drillers, millers, different process operators, field operators, warehouse workers, laboratory workers and white-collar workers. At end of life and during maintenance, these job titles differed: sorter, crusher, and maintenance fitter.

The indicative limit value confirmed by the Finnish Ministry of Social Affairs and Health (2020) for biological exposure to metallic and insoluble Ni compounds is 0.1 µmol Ni/L urine and for soluble compounds, 0.2 µmol Ni/L urine. These indicative biological limit values (BLV) have been set to correspond to air levels of 0.01 mg/m3, as eight hours of TWA exposure. This limit value was exceeded in some of the worker groups measured, especially among operators, drillers, laboratory workers, supervisors and maintenance workers. The BLV in turn was not exceeded at all in some worker groups, such as among white-collar workers, some field operators, and drivers. The BLV was exceeded more often in the refining processes than in mining. If the limit value level is exceeded, measures to reduce exposure are recommended.

Biomonitoring of Ni used urine samples. Two datasets from 2012–2019 were utilised in the assessment. The total number of Ni samples was 5895, thus, a larger dataset than is typical was available for testing compliance with the available BLVs. Table 4 presents the concentrations of Ni compounds determined from biological urine samples in different LIB life cycles. The average Ni concentration varied from 0.02 to 0.2 µmol/L in all samples (5895 samples). Of the results, 95th percentiles were between 0.03 µmol/L and 0.7 µmol/L. The limit value of Ni compounds (0.1 µmol Ni/L urine) was exceeded at its highest point in every life cycle phase, although not in all workplaces. At the refining stage, the average Ni concentration varied from 0.02 µmol Ni/L to 0.1 µmol Ni/L. Results indicated that exposure is strongly workplace and process dependent. Therefore, general results in certain life cycle stages may mislead exposure estimation. However, some conclusions can still be made on the LIB life cycle. In the refining stage, some biomonitoring results also represent concentrations of soluble Ni compounds. The limit for soluble Ni compounds is higher (0.2 µmol Ni/L) than that for insoluble compounds, and this is taken into account in the results.

The highest average concentrations were achieved at the LIBs end-of-life stage. The refining phase and maintenance phase were also separated from the results. The results of the maintenance phase mainly covered maintenance fitters’ work tasks, but detailed information about the tasks were not available. However, the maintenance work results may have been related to the refining phase. The 95th percentile was 0.4 µmol Ni/L, which was even higher than both levels (insoluble and soluble) of Ni compounds.

The biomonitoring results indicate that the level of exposure has decreased over time, which was evident in the increased number of unexposed workers at Finnish workplaces. For Finns not exposed at work, the Ni concentration in urine is lower than 0.05 µmol Ni/L. Exposure to Ni compounds can also occur e.g., through food and smoking.

Table 4. Concentration of Ni compounds in urine samples.

LIFE CYCLE	TIME	MEAN, µMOL/L	95.PERCENTILE, µMOL/L	BELOW OCCUPATIONALLY UNEXPOSED LIMIT VALUE	OVER BLV
MINING	2012–2015 n=1759	0.04	0.08–0.1	70%–76%	2%–3%
	2016–2019 n=3006	0.02	0.04–0.05	96%–97%	1%
REFINING AND CHEMICALS	2012–2015 n=580	0.02–0.1	0.05–0.4	25%–92%	0%–49%
	2016–2019 n=357	0.02–0.1	0.03–0.3	32%–100%	0%–36%
END-OF-LIFE	2012–2019 n=89	0.05–0.1	0.2–0.7	52%–66%	12%–23%
MAINTENANCE	2012–2015 n=67	0.2	0.4	13%	55%
LABORATORY	2012–2019 n=37	0.03–0.05	0.08–0.09	42%–78%	0%–6%

2.2.1 Nickel compounds in breathing zone samples

To assess workers’ exposure by inhalation, impurities can be measured from the workplace air. Samples from workers’ breathing zones should be measured using personal sampling devices attached to workers’ clothing throughout the workday (SFS EN 689:2018). Breathing zone samples may not directly represent exposure, as they do not consider the control measures used to prevent the exposure. Whether control measures such as respiratory protective equipment (RPE) was used was not clear from the data. Therefore, the data may overestimate ‘true’ exposure.

The RAC’s recommended eight-hour time weighted OEL for inorganic Ni compounds is 0.03 mg/m3 in inhalable dust fractions. This recommendation is based on the carcinogenicity of inorganic Ni compounds. The RAC recommendation is purely health based, meaning that if the exposure remains below this, the health risk is considered low. The EU binding limit values are based on both health risk and socioeconomic considerations. Therefore, the EU commission proposal for the OEL for Ni compounds is higher, at 0.05 mg/m3 for inhalable dust fraction (Directive 2004/37/EC).

The average Ni concentrations varied from 0.01 mg/m3 to 0.14 mg/m3 in the inhalable breathing zone samples. The number of samples was 185. The measurement data were collected in 2012–2019. Most of the samples were related to the life cycle phase of mining, but some samples (11%) were also related to refining. There was no clear difference between the concentrations of these two life cycles. The 95th percentile point estimate varied between 0.04 mg/m3 and 0.6 mg/m3. The Ni OEL value was exceeded in many of the breathing zone samples. For example, a statistical review of the results indicated that with the highest certainty permitted by the available data, 3%–26% of the results were over the OEL value (0.05 mg/m3). Compared to the more health-based value (0.03 mg/m3) suggested by the RAC, 6%–34% of the results exceeded the recommendation.

The RAC recommendation for Ni compounds in respirable fraction is 0.005 mg/m3 (ECHA, 2018). The EU commission proposal is 0.01 mg/m3 for respirable Ni. The average respirable Ni concentration was 0.004 mg/m3. The 95th percentile point estimate was 0.02 mg/m3. Ni compounds from respirable fraction were clearly measured less than inhalable nickel compounds. Only eight results were available relating to the LIB value chain. The proportion of the exposure profile exceeding the OEL was 10%, whereas that exceeding the RAC recommendation was 25%.

2.2.2 Nickel compounds in process area samples

The average inhalable Ni concentration varied from 0.01 mg/m3 to 0.1 mg/m3 in stationary measuring points in 2012–2019, when the crude Ni ore and chemicals were processed in relation to the LIB value chain. Most, that is, 52% of the results were over the OEL of Ni compounds (0.05 mg/m3). The 95th percentile point estimate was between 0.02 mg/m3 and 0.7 mg/m3. The data consisted of 366 Ni samples.

The respirable Ni fraction was also assayed (72 samples). The average concentration of Ni compounds varied from 0.02 mg/m3 to 0.06 mg/m3. The OEL for respirable Ni is 0.01 mg/m3. The 95th percentile point estimate was between 0.02 mg/m3 and 0.06 mg/m3, which also exceeded the OEL. It is important to remember that the samples represent the concentrations in the process area. Workers typically move around the workplace and therefore stationary measuring points may poorly represent exposure.

2.2.3 Exposure assessment of nickel

Biological monitoring or biomonitoring is the measurement of the body burden of toxic chemical compounds, elements, or their metabolites, in biological fluids, typically from the urine or the blood. Biomonitoring measures overall exposure and takes into account all routes of exposure: air, skin and the digestive tract. The information on the overall chemical concentration is particularly important when substances can accumulate in the body during continuous and repeated exposure or when exposure via several routes is expected. Biomonitoring is the only way to quantitatively assess the exposure caused by dermal absorption. Although metals do not generally pass through the skin, hand contamination may contribute significantly to total exposure due to hand-to-mouth behaviour, resulting in gastrointestinal exposure. Exceedances of the BLV of Ni compounds (0.1 µmol Ni/L urine) was observed in all the studied life cycle steps. The OEL value (0.05 mg/m3) set for Ni compounds in the air was also occasionally exceeded.

To assess the hazard Ni may cause in the value chain, we used the criteria presented in Tables 1 in Methods. According to the hazard categorisation proposed by JRC (2020), Ni compounds are categorised as most harmful chemicals (S1 group) due to their carcinogenicity and reproductive toxicity (Table 3). Table 2 shows the magnitude of exposure that was created for to ease the comparison of the results.

In mining, the 95th percentile of the biomonitoring samples varied between 0.04 µmol/l and 0.1 µmol/l. BLV was exceeded in less than 5% of the results. The results indicated that the level of exposure has decreased over time. This is most likely related to the advanced occupational and safety practices used in Finland. However, the 95th percentile point estimate varied between 0.04 mg/m3 to 0.6 mg/m3 in breathing zone samples. Ni concentrations in the breathing samples exceeded the OEL value, indicating high potential exposure risk. In the refining of LIB chemicals, the exposure differed in different workplaces, resulting in different risk levels. BLV was exceeded in up 49% of the samples at specific workplaces. The 95th percentile varied between 0.03 mg/m3 and 0.4 mg/m3. In some workplaces, the limit value was not exceeded at all, and all the results represented the level of the unexposed. The 95th percentile was 0.4 mg/m3 in breathing zone samples. Of the breathing zone results, 25% of the samples exceeded the OEL value. Concentrations indicated a high exposure in refining of nickel chemicals -related work, but we observed differences also between workplaces.

The BLV was exceeded in over 5% of samples, indicating a high risk in battery chemicals production. Air concentrations were not available for this life cycle phase. At the end of LIBs life cycle stage, the BLV was exceeded in 12%–23% of biomonitoring samples and indicated high risk exposure. The 95th percentile varied from 0.2 mg/m3 to 0.7 mg/m3 at this point of the value chain. Some air concentrations measured at this stage in stationary measuring points were clearly less than 10% of the OEL. However, the number of samples was too limited to draw conclusions, as the data consisted of only two samples.

More than 55% of biomonitoring samples exceeded the BLV in maintenance work, meaning that the risk is high at these activities. The 95th percentile was 0.4 mg/m3, as the BLVs are 0,1 for insoluble and 0.2 µmol/l for soluble Ni compounds. No data on air concentrations were available for these activities. Several knowledge gaps were also found regarding Ni concentrations in the production phases of precursor materials (pCAM) and lithium-ion cathode active battery materials (CAM) production and cell/battery production. On the other hand, although no measurement data were available, exposure to Ni compounds was evaluated as irrelevant in battery integration and end users, and in transport.

2.3 Determining the level of exposure to Co compounds in an LIB production value chain in the Finnish work environment

The current indicative limit value for biological exposure confirmed by the Finnish Ministry of for Social Affairs and Health (2020) for Co concentration in urine is 0.13 µmol Co/L. The reference limit for occupationally non-exposed population for urinary Co (U-Co) is 0.025 µmol Co/L urine. According to recent ECHA's RAC opinion (ECHA 2020), which gives a limit value of 0.5 µg/m3 for respirable Co and 1 µg /m3 for inhalable Co in the air, has recently recommended that in order to protect against the carcinogenic and non-carcinogenic lung effects of Co, the U-Co levels of workers should remain below these general population levels. Thus, it is recommended that this limit be used as a target level to below which exposure to Co should be minimised at workplaces.

Biomonitoring of Co used urine samples. Two datasets from 2012–2019 were utilised. The total number of Co samples was 1318, which was smaller than that of Ni. Table 5 presents the concentrations of Co compounds in the urine samples in different LIB life cycles. Average Co concentrations varied from 0.004 µmol/L to 0.3 µmol/L. The 95th percentile was between 0.01 µmol/L to 2.1 µmol/L in all the results. The limit value (0.13 µmol Co/L) was exceeded particularly at the refining of LIB chemicals stage and at the end of LIB life. In mining it was not exceeded at all. The limit value was also not exceeded in some maintenance tasks. However, the nature of maintenance tasks remained unclear.

The results indicate a decrease in Co concentration over time. For example, up to 43% of the Co results were over the BLV in 2012–2015, whereas up to 21% of the results exceeded the limit value in 2016–2019. The number of workers whose U-Co remained below the occupationally non-exposed U-Co level increased after 2015.

Table 5. Concentration of Co compounds in urine samples.

LIFE CYCLE	TIME	MEAN, µMOL/L	95.PERCENTILE, µMOL/L	BELOW OCCUPA-TIONALLY UNEXPOSED LIMIT VALUE	OVER BLV
MINING	2012–2015 n=233	0.007	0.02	97%	0%
	2016–2019 n=97	0.004	0.007–0.009	100%	0%
REFINING AND CHEMICALS	2012–2015 n=260	0.01–0.3	0.04–2.1	10%–92%	0%–43%
	2016–2019 n=625	0.01–0.1	0.05–0.3	22%–100%	0%–21%
END-OF-LIFE	2012–2019 n=88	0.10–0.15	0.35–1.2	15%–23%	17%–23%
MAINTENANCE	2012–2019 n=15	0.01	0.03	93%	0%

2.3.1 Cobalt compounds in breathing zone samples

As discussed earlier (Chapter 3.2. Ni compounds in breathing zone samples), breathing zone samples may not directly represent exposure. The average Co concentration varied from below 0.0003 mg/m3 to 0.007 mg/m3 in the inhalable breathing zone samples. The number of samples was 164. The 95th percentile point estimate was between 0.002 mg/m3 and 0.03 mg/m3. Current OEL for cobalt compounds in inhalable fraction is 0.02 mg/m3 (Ministry of Social Affairs and Health, 2020) in Finland. RAC health-based recommendation for inhalable fraction is 0.001 mg/m3(ECHA 2020).

The data consisted of measurements from 2012–2019. Most of the samples were related to the life cycle stage of mining, although some samples (4%) also related to the refining and chemicals stage. At workplaces where the highest Co concentrations were measured in relation to LIBs, the proportion of the exposure profile exceeding the OEL was 8%. The proportion exceeding the RAC recommendation was 60%. OEL value was exceeded in the mining stage, but not in the refining or in quality control operations.

2.3.2 Cobalt concentrations in process area samples

The average concentrations of Co varied from 0.0001 mg/m3 to 0.005 mg/m3. The number of samples was 163. The 95th percentile point estimate was between 0.002 mg/m3 and 0.03 mg/m3, which was the same level as that in the worker's breathing zone samples. Most of the samples related to the refining of LIB chemicals, but also two at the end-of-life stage.

2.3.3 Exposure assessment of cobalt

Exposure to Co was assessed in the same way as the exposure to Ni compounds. JRC's hazard categorisation (2020) proposes that Co compounds are categorised in the S1 group of the most harmful chemicals due to reproductive toxicity and carcinogenicity.

The Finnish BLV of (0.13 µmol Co/L urine) and the OEL value (0.02 mg/m3) of Co compounds were both exceeded occasionally in battery chemical refining phases. BLV was not exceeded in mining. The 95th percentile of biomonitoring measurements was 0.02 µmol/l. The result is clearly below the current BLV and also below the reference limit for the occupationally non-exposed population indicating low exposure. However, some air concentration samples exceeded the OEL of Co. This indicates potential for high exposures in some tasks related to mining life cycle stage.

In the refining of LIB chemicals, up to 31% of the biomonitoring samples exceeded the BLV. The 95th percentile varied from 0.04 µmol/l to 2.1 µmol/l. We found differences between workplaces and the number of unexposed was high and no BLV exceeding in some workplaces. The OEL was not exceeded in most of the workers’ breathing zone samples at this stage. However, the 95th percentile was at the level OEL in air concentration samples in stationary measuring points indicating moderate exposure risk. In battery chemicals production, 95th percentile varied from 0.3 µmol/l to 1.01 µmol/l and was above the OEL. Clearly over 5% of the results exceeded the BLV, indicating high exposure. However, air concentration data indicated moderate concentrations. At the end-of-life stage, the 95th percentile was above the BLV. BLV was exceeded in 17%–23% of the biomonitoring samples, indicating the high risk of exposure, whereas the air concentrations (two samples) indicated low risk. Surprisingly, the BLV was not exceeded in the maintenance phase at all. The number of unexposed was also relatively high in this phase, making the risk low. There was no air concentration data for the maintenance activities.

We found several gaps in the knowledge on Co concentrations in the production phase of pCAM and CAM production, and cell/battery production. However, although no measurement data were available, exposure to Co compounds was evaluated as irrelevant in battery integration, among end users, and in transport.

2.4 Other concentrations determined in an LIB production value chain in the Finnish work environment

Two TVOC samples were measured in the workplace air at stationary measuring points related to the end of LIB life. The highly flammable diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) were detected in the workplace air during crushing. The measured concentration of volatile organic compounds, TVOCs, was about 9–12 mg/m3. Since about 44% and 53% of TVOCs were representing DEC and EMC, the DNEL values given for diethyl carbonate and ethyl methyl carbonate (10 mg/m3 and 70 mg/m3, respectively, (ECHA, 2022e,f)) were not exceeded. However, the determined concentration was only indicative, as the analysis method used was not quantitative.

As many as 195 samples contained indicative sulphuric acid data. The results showed that the average concentrations varied between 0.2 mg/m3 and 0.4 mg/m3. The 95th percentile point estimate was between 0.5 mg/m3 and 0.8 mg/m3 and was above both OEL values of sulphuric acid (<0.05 mg/m3 and 0.1 mg/m3). The risk of sulphuric acid was estimated to cause a high potential risk in the refining phase of LIB chemicals. Due to the lack of more precise information on the sampling situation and analysis method, the result is considered relatively inaccurate, despite the large dataset.

A lithium concentration of about 0.001 mg/m3 was also measured (two samples). Cathode materials for LIBs include lithium cobalt oxide (or lithium manganese oxide or lithium nickel oxide) and lithium iron phosphate, which are typically manufactured from lithium hydroxide. No OELs are available for lithium compounds, but the REACH Registration Dossiers for lithium hydroxide and lithium sulphate give DNELs of 10 mg/m3 for these substances. This value does not, however, consider the possible reprotoxic properties of the lithium ion. Lithium salts have been used as medication for manic-depressive disorders. The measured levels were low in comparison to the doses that have been suspected of causing reproductive effects in humans (ECHA 2020). As discussed above, the potential reproductive toxicity of the lithium ion depends on its solubility and bioavailability, and this varies among different lithium compounds. If the lithium is in the form of a poorly soluble lithium compound, the reproductive risk is even lower. It should, however, be noted that the measurement data are very limited and there is very little information on the solubility of lithium in the different phases of the process. Therefore, further studies on lithium exposure in the LIB value chain are needed. This also includes biomonitoring, which would provide information on internal exposure to bioavailable lithium.

2.5 Exposure in an LIB production value chain in abnormal situations

Large quantities of highly toxic carbon monoxide (CO), phosphoric and fluorine compounds, cyanides and chlorides, and flammable gases such as hydrogen, ethylene, methane and propane are formed in LIB fires. Irritant and corrosive gases such as hydrogen chloride (HCl), sulphur dioxide (SO2) and hydrogen fluoride (HF) are also released in LIB fires. The composition of the gas released is highly dependent on the individual battery. In addition, the solvents used in batteries such as EMC and DEC are classified as flammable liquids (Flam. Liq. 2 or 3, ECHA, 2022e,f). The risk related to battery fires may be divided into four categories related to the size of the battery and the environment in which the battery fire takes place. Level 1 includes PCs and mobile phones; Level 2 electric cars, hybrid cars, buses or similar vehicles, all outdoors; Level 3 is similar to Level 2 but indoors; and Level 4 covers large system battery fires in fully electric or hybrid vessels, larger buildings or in industry. Small Level 1 fires can be by civilians in control of fire services. Larger fires require large amounts of water and the appropriate expertise. The release of hazardous fire smoke is common to all levels.

Level 3 carries the risk of gas explosions, as gases may accumulate in a closed area. (DSP 2021)

The chemicals in LIBs are bound in the battery and therefore no exposure is expected in typical use of the battery. In the case of e.g., an accident or short circuit that may result to an uncontrollable thermal runway (TR), the risk of exposure increase. Risks associated with firefighters’ exposure have recently been studied in relation to the formation of HF smoke from burning LIBs (Veen & Koppen 2020). The results suggest that HF penetration into fire hoods and short-term exposure to HF-containing smoke after LIB fires may lead to local effects on the skin such as irritation and pain. However, HF is formed in most car and plastic fires (DSP 2021). Exposure to fire gases may occur by inhalation or through skin if not prevented with appropriate control measures such as fire safety clothing and respiratory equipment. Contamination of firefighters’ clothing may also cause exposure (Szmytke, Brzezińska, Machnowski & Kokot, 2022). This concerns all personnel who maintain extinguishing or protective equipment after fires, and it should be also take into account in the risk assessment.

3 Discussion

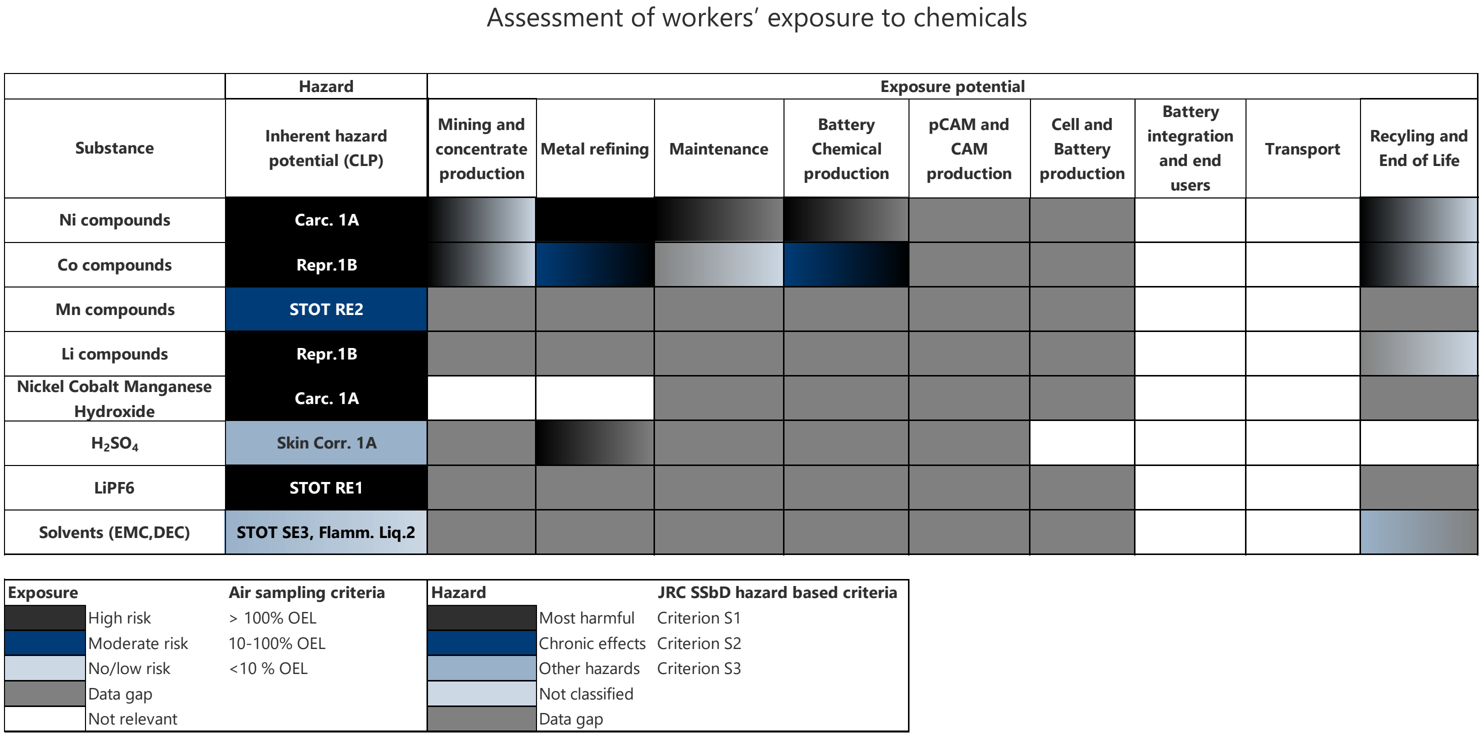
Several compounds are involved in the production chain of LIBs, that may pose health risks during the LIB life cycle. We used biomonitoring and air concentration data to assess exposure, which was compared to the available limit values given for biological and air samples. Ni and Co compounds were revealed as substances that could be examined in the value chain due to extensive measurement data from FIOH registers. The data covered various worker groups. Nearly 30 different worker groups were related to mining, about 20 to the refining stage, nearly 30 to chemicals in refining and battery chemical production, and about 10 to the end-of-life cycle. Some of the work titles described work activity poorly and the sample information did not specify the details of the process. Limit values were exceeded in almost all the life cycles and worker groups, apart from white-collar workers.

High potential exposure concentrations related almost to all life cycle stages. However, the measured U-Ni and U-Co results indicated low exposures in mining and concentrate production phase in Finland. U-Co results also indicated low exposures in maintenance stage. In Finland, advanced occupational and safety practices are in place with established occupational exposure limit values, therefore exposures may remain rather controlled. Therefore, this does not necessary apply to countries outside Europe. Work environment conditions vary in specific workplaces, and generalising exposure results may lead to wrong conclusions. This applies especially mining of raw materials. It is well known that a large proportion of Co worldwide comes from Congo (Dias, Blagoeva, Pavel & Arvanitidis, 2018), and there are huge exposures to Co among the working force and general population living next the cobalt mines (Banza et al. 2009, Cheyns et al. 2014). Similarly, Wang et al. (2017) suggested that the heavy metal risk of employees in some in secondary battery production sites was low, but the risk was higher in another site in China (Wang et al. 2017).

The highest exposure risks were related to the production of LIBs and the end-of-life. The assessment of exposure is difficult or even impossible if the concentrations at the workplaces are not known. Not enough data exist to examine the whole LIB value chain comprehensively. We found several gaps in the knowledge about the concentrations of work impurities in manufacturing phases such as pCAM, CAM, and cell/ battery production. Although no measurement data are available, in some parts of the value chain exposure cannot be ruled out. In the battery integration and end user phases, as well as in the transport phase, exposure to all identified chemicals is considered irrelevant. As the chemicals are inside the battery housing, no exposure is expected.

Finland has a long tradition of extractive industries and safety work. The results also indicated decreasing exposure over time. Therefore, the result may differ elsewhere, and the representativeness of these results in other countries cannot to be assured. Exposure is always dependent on workplace conditions such as work processes, work activity, and existing control measures such as ventilation or protective equipment. In some cases, the results indicated high concentrations in the breathing zone samples, but the biomonitoring results showed the opposite, suggesting that the role of RPE in the prevention of exposure is significant. However, this cannot be verified from the results due to the lack of knowledge about the work environment conditions. It must, however, be noted that the results were not totally completely comparable, as the samples may not have been collected from exactly the same work tasks. Due to the high potential exposure, effective risk management measures are necessary for to prevent exposure in all stages of production.

Figure 1 provides a summary of the risk assessment in the Finnish work environments studied. It is important to understand that the current risk assessments do not represent exposure in individual workplaces or of individual workers. Concentrations vary greatly between individual workplaces and processes, making an overall assessment challenging. For some phases of the process and for some substances, only limited information on exposure was available. The main phases of limited information include pCAM and CAM as well as cell and battery production and recycling phases. The potential substances with limited information included lithium (especially exposure to the soluble lithium ion which can be absorbed to the human body) and manganese. For example, a high concentration of manganese (Mn) has been reported in South African mine workers (Dlamini, Nelson, Nielsen & Racette et al. 2020). There are concerns about fluoropolymer manufacture in particular, which may cause exposure to nonpolymeric PFASs. We did not explore this aspect in detail in this analysis. Their end-of-life phases may also be cause for concern, as this is still largely an unexplored area (Lohmann et al., 2020). Overall, further studies are needed on the exposures in the LIB value chain in different environments.



Assessment of workers' exposure to chemicals

	Hazard	Exposure potential								
Substance	Inherent hazard potential (CLP)	Mining and concentrate production	Metal refining	Maintenance	Battery Chemical production	pCAM and CAM production	Cell and Battery production	Battery integration and end users	Transport	Recyling and End of Life
Ni compounds	Carc. 1A									
Co compounds	Repr.1B									
Mn compounds	STOT RE2									
Li compounds	Repr.1B									
Nickel Cobalt Manganese Hydroxide	Carc. 1A									
H_2SO_4	Skin Corr. 1A									
LiPF6	STOT RE1									
Solvents (EMC,DEC)	STOT SE3, Flamm. Liq.2									

Exposure		Air sampling criteria	Hazard		JRC SSbD hazard based criteria
	High risk	> 100% OEL		Most harmful	Criterion S1
	Moderate risk	10-100% OEL		Chronic effects	Criterion S2
	No/low risk	<10 % OEL		Other hazards	Criterion S3
	Data gap			Not classified	
	Not relevant			Data gap	

Figure 1. Visualisation of exposures in the LIB chain in Finland.

References

AIHA (2022) IHSTAT+:v.235, 2013. IHSTAT macro-free version | AIHA.

Banza, C. L., Nawrot, T. S., Haufroid, V., Decrée, S., De Putter, T., Smolders, E., Kabyla, B. I., Luboya, O. N., Ilunga, A. N., Mutombo, A. M., & Nemery, B. (2009). High human exposure to cobalt and other metals in Katanga, a mining area of the Democratic Republic of Congo. Environmental research, 109(6), 745–752.

Caldeira, C., Farcal, R., Moretti, C., Mancini, L., Rauscher, H., Rasmussen, K., Riego Sintes, J., Sala, S. (2022) Safe and Sustainable by Design chemicals and materials. Review of safety and sustainability dimensions, aspects, methods, indicators, and tools. JRC Technical Report. ISBN 978-92-76-47560-6

Cheyns, K., Banza Lubaba Nkulu, C., Ngombe, L. K., Asosa, J. N., Haufroid, V., De Putter, T., Nawrot, T., Kimpanga, C. M., Numbi, O. L., Ilunga, B. K., Nemery, B., & Smolders, E. (2014). Pathways of human exposure to cobalt in Katanga, a mining area of the D.R. Congo. The Science of the total environment, 490, 313–321. https://doi.org/10.1016/j.scitotenv.2014.05.014

Dias, A. P., Blagoeva, D., Pavel, C., Arvanitidis, N. (2018). Cobalt: demand-supply balances in the transition to electric mobility. JRC Science for Policy Report. ISBN 978-92-79-94311-9. https://ec.europa.eu/jrc

Directive 2004/37/EC - carcinogens, mutagens or reprotoxic substances at work | Safety and health at work EU-OSHA (europa.eu)

Dlamini, W. W., G. Nelson, S. S. Nielsen and B. A. Racette (2020). "Manganese exposure, parkinsonian signs, and quality of life in South African mine workers." American Journal of Industrial Medicine 63(1): 36-43.

ECHA. 2018. Committee for Risk Assessment RAC. Opinion on scientific evaluation of occupational exposure limits for Nickel and its compound. ECHA/RAC/ A77-O-0000001412-86-189/F, Adopted 9 March 2018. 9e050da5-b45c-c8e5-9e5e-a1a2ce908335 (europa.eu)

ECHA. 2020. Committee for Risk Assessment RAC. Committee for Socio-economic Analysis (SEAC) Opinion on an Annex XV dossier proposing restrictions on: Cobalt sulphate, Cobalt dichloride, Cobalt dinitrate, Cobalt carbonate and Cobalt di(acetate) ECHA/RAC/RES-O-0000006741-74-01/F, Adopted 17 February 2020. 9e050da5-b45c-c8e5-9e5e-a1a2ce908335 (europa.eu)

ECHA. 2020. CLH report Proposal for Harmonised Classification and Labelling Based on Regulation (EC) No 1272/2008 (CLP Regulation), Annex VI, Part 2 International Chemical Identification: [1]

ECHA. 2022a. Substance inforcard: Nickel compounds Substance Information - ECHA (europa.eu) [accessed Nov 2022]

ECHA. 2022b. Registration dossier for cobalt, Registration Dossier - ECHA (europa.eu) [accessed Nov 2022]

ECHA. 2022c. Substance inforcard: 1,3-Dioxolan-2-one, 4-fluoro-. Substance Information - ECHA (europa.eu) [accessed Nov 2022]

ECHA. 2022d. Committee for Risk Assessment RAC Opinion proposing harmonised classification and labelling at EU level of Multi-Walled Carbon Tubes (synthetic graphite in tubular shape) with a geometric tube diameter range ≥ 30 nm to < 3 μm and a length ≥ 5 μm and aspect ratio ≥ 3:1, including Multi-Walled Carbon Nanotubes, MWC(N)T. [04.01-ML-014.03] (europa.eu)

ECHA. 2022e. Registration dossier for diethyl carbonate, Registration Dossier - ECHA (europa.eu), accessed 1.11.2022

ECHA. 2022f. Registration dossier for ethyl methyl carbonate, Registration Dossier - ECHA (europa.eu). accessed 1.11.2022

ECHA. 2022g. Registration dossier for lithium hydroxide, Registration Dossier - ECHA (europa.eu). accessed 1.11.2022

ECHA. 2022h. Registration dossier for lithium sulphate, Registration Dossier - ECHA (europa.eu). accessed 1.11.2022

The Finnish Ministry of Social Affairs and Health. HTP Values 2020. Concentrations Known to be Harmful., Helsinki, 2020.

Lohmann, R. Cousins, I.T., DeWitt, J.C, Glüge, J., Goldenman, G., Herzke, D., Lindstrom, A.B., Miller M.F., Ng, C.A., Patton, S., Scheringer, M., Trier,X. & Wang, Z. (2020). Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? Environmental Science & Technology 54 (20), 12820-12828. DOI: 10.1021/acs.est.0c03244

van Veen, N., Koppen, A. (2020). Emergency responses in smoke from Li-ion batteries FIVE2020. National Institute for Public Health and the Environment & University Medical Center Utrecht, National Poisons Information Center Utrecht. FIVE-2020

Emergency responses in smoke from Li-ion batteries V1.1 def - Emergency responses in smoke from Li-ion batteries.pdf

SCOEL, 2011. Recommendation from the Scientific Committee on Occupational Exposure Limits for manganese and inorganic manganese compounds. SCOEL/SUM/127 June 2011

Szmytke E., Brzezińska D., Machnowski W., Kokot S. (2022) Firefighters' Clothing Contamination in Fires of Electric Vehicle Batteries and Photovoltaic Modules-Literature Review and Pilot Tests Results. Int J Environ Res Public Health. 2022;19(19):12442. doi:10.3390/ijerph191912442.

Wang,Y., Yu,Y., Huang,K., Gong, Y., Yao, Y., Wu, F. (2017) Does heavy metal hurt in the secondary battery production sites? The case study of occupational risk from Yangtze River Delta, China, Human and Ecological Risk Assessment: An International Journal, 23:6, 1285-1299, DOI: 10.1080/10807039.2017.1294975