

Lincoln Storm Limited

Hazardous Emissions Calculations and Air Emissions Risk Assessment

Application Reference: EPR/KB3002CW/V004

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1. Introduction

The bespoke recycling and production operation at Lincoln Storm generates products which require containment due to their inherent hazardous properties.

The process of recycling Lithium batteries is a new industry and as yet has no standard guidance, therefore control of the possible environmental impacts necessitates extraction of the salient points and best available techniques from other recycling and chemical engineering sectors. These include Treatment of WEEE materials, Metal Shredding, Chemical Treatment of Hazardous Wastes, DSEAR¹ and HSG71² These sources of guidance are used in this document and incorporated into the Environmental Risk Assessment document and other relevant Lincoln Storm material.

The process at Lincoln Storm has two Process Emission Points which need to be assessed and controlled to minimise the possible release of hazardous material. These are the Battery Discharge/Crushing/Shredding, Drier/Drum Cooler stages and Sieving stage. Power for the operation is provided by electricity from the mains grid, with up to four mobile generators available to provide emergency back-up electricity. These Potential Emission Points, Process and generators, need to be assessed and controlled to minimise the possible release of hazardous material.

This report addresses at each Emission Point:

- the nature of the material at that Emission Point;
- the controls in place at that Emission Point; and
- the likely final emissions which need to be enumerated in respect of that Emission Point.

The types of dust reduction/removal equipment and their efficiencies are examined and the likely residual emissions after such control are also examined theoretically since it is not possible to operate all the machinery and quantify the actual performance.

The plant contains various types of abatement systems for dust and fume control, including activated carbon filters and chemical abatement equipment (including wet scrubbers). These are designed to minimise emissions, and, where possible, more than one type of control element is used to control a single stream of possible emissive discharge. This is because Lithium-ion batteries contain more than one type of contaminant and there is also the potential for chemical reactions taking place during the recycle process.

The recycling of Lithium batteries generates both gaseous and particulate material which require different control measures. These include, for the Process Emission Points, dust extraction, wet scrubbing, VOC adsorption and battery discharge / crushing under water. For any emergency generators covered by the Medium Combustion Plant regulations, we would use an ad-blue exhaust abatement system.

The composition of the products from the full scale plant is known with reasonable confidence (see, for example, the MSDS sheet and REACH analysis for the Storm Black™ black mass product. However, it cannot yet be known with 100% accuracy, and will not be known until the plant has been commissioned and is operational. Notwithstanding this, the estimates of size and composition

¹ The Dangerous Substances and Explosive Atmospheres Regulations 2002

² Chemical warehousing: The storage of packaged dangerous substances

of the dust and other emissions which could be generated both in the absence of control and after designed controls have been applied, can be reasonably evaluated from these results.

2. Abatement Systems

Dust Extractors

The dust extractors operate by using a fan to extract dust and air from the plant. This filters out the dust through a series of filter bags positioned in parallel. To keep the bags clean a bag cleaning system operates via a rapid, high-pressure air jet cleaning, which sends a blast or shock of air through the bag that shatters and discharges the dust cake for disposal. The rapid pulse of air allows for continuous operation with the fan running, and because of it the system is not generally compartmentalised.

Pulse jet models are the most common type of industrial dust collectors, due to their ability to be easily customised, the capability to handle a wide range of temperatures and pressures, and their high collection efficiency. They can be found in most manufacturing environments where bulk solids are processed, including speciality chemical manufacture, mineral production, food processing plants and metal fabrication.

Water/Aqueous Scrubbers

Water / Aqueous scrubbers consist of a fan, water / aqueous hold tank, pump, packed column and a discharge air stack. Water / aqueous and air flows are monitored to ensure that the scrubber is operating and removing particles in accordance with its design, including through monitoring of differential pressure across the packed column. An air emissions monitoring point is located in the stack to facilitate this and any other environmental compliance testing.

Water scrubbers are used widely within the speciality chemical industry as a secondary abatement system to dust extractors / bag houses when handling, or producing powders (eg through processes such as spray drying) in order to ensure particulate emissions are at the lowest level possible. Lincoln Storm have therefore designed the plant to include a wet scrubber as a final abatement for both the front end shredding and drying operations.

Activated Carbon

Activated carbon is widely used for the abatement of gases and liquids to remove contaminant substances. There are numerous types of activated carbon that can be selective in the substances they adsorb. Working with activated carbon suppliers the carbon used will be selected for each process e.g. For VOC around battery discharge and crushing operations and NOx for the power generation.

3. Hazards Associated with Battery Recycling and Black Mass

As the transition from fossil fuels to renewable energy sources gathers momentum, an increasing number of production facilities are being commissioned to meet the demand for millions of tonnes of batteries required for a wide range of applications, including industrial, commercial and residential energy storage systems, and batteries to power electric vehicles.

At the same time, companies are investing in and developing battery recycling technologies to allow them to recover the valuable material and components from within the batteries once they have reached the end of their useful life.

As global recycling capacity ramps up, recycling of batteries will generate tens of thousands of tonnes of battery material, which can be separated into a range of fractions for re-entry into the supply chain. This includes metals used for holding cathode and anode material (aluminium and copper respectively), polymer and highly valuable cathode material. The last of this, a product known as 'black mass' (produced by Lincoln Storm as Storm Black™) is particularly valuable as it is an exact substitute for equivalent material derived from mining ore, and can be used with less environmental and human health impact and requires less energy to produce. The recycling process must be designed in such a way as to minimise the risks posed by the hazardous chemicals within the batteries including from electrolyte solutions held in intact cells and, where the cathode material comprises NMC (rather than, say, LFP) the cathode material itself. Lincoln Storm uses a proven process through which 98% of the input material (typically a whole battery) is recovered.

Many companies are either entering the recycling sector for the first time or moving into the production and handling of hazardous chemicals for the first time. Such companies may not necessarily comprehend the severity of the risks associated with battery chemicals. Information pertaining to the hazards is widely available but scattered throughout the published literature which may not be accessible to some companies.

There is no existing document that links the hazards specifically found on a battery recycling plant and describe how a normal situation found on a plant could lead to elevated risk levels. It is intended to use the existing government guidance on the treatment of WEEE waste, DSEAR, shredding of metal and chemical treatment.

It is also important to consider the hazards and risks of storage, handling and processing batteries prior to recycling and any chemicals used during the process. These hazards include electrical and fire hazards associated with the handling and storage of the batteries. The storage of process chemicals and received batteries will be stored following HSG71 guidance.

There are also several hazards associated with the recycling process itself such as the risk of fires and explosions. This document focuses on the risks and hazards associated with material handling throughout the recycling process as these risks are new to the recycling industry and are not yet well defined nor fully understood.

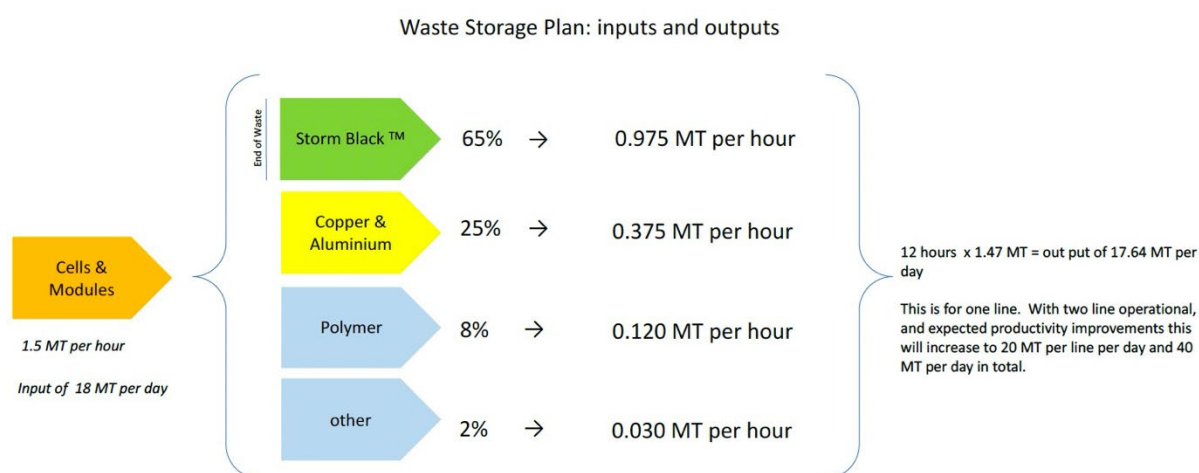
The document should not be used as a comprehensive list of hazards associated with battery recycling but rather as a starting point to understanding some of the known and unknown hazards that a recycler is likely to face. It is the legal responsibility of all recyclers, including Lincoln Storm, to carry out and maintain a comprehensive Hazard and Operability study (HAZOP), Hazard

Identification study (HAZID) and DSEAR risk assessment for their processes once the design has been established.

4. Typical Lithium Battery components

A generic lithium-ion cell contains several different components. Once shredded, these components must be separated from each other before they can individually be refined and recycled. **Table 1** shows a typical composition of the materials found in an 18650 lithium-ion cell.

As can be seen, the majority of the mass is accounted for by the cathode and the anode active material powders. The cathode active powder may contain valuable metals such as nickel, cobalt, manganese alongside lithium. Together with the copper current collector, these five metals make up around 90% of the value in an end-of-life cell. Other constituents present being Aluminium, plastic, and polymer. The diagram below (taken from Lincoln Storm’s Waste Storage Plan) shows the proportions of material produced by Lincoln Storm’s recycling process:



Generally, recycling processes are set up to recover the cathode and anode powders to form what is known as black mass. **There is no strict definition of what constitutes black mass**, but it is a ubiquitous term used throughout the battery recycling industry to refer to shredded battery components which appear as a black powder due to the presence of graphite. Lincoln Storm’s black mass product, Storm Black™ is a high purity form of black mass. The MSDS for Storm Black™, and its REACH analysis describe its composition and characteristics.

In an ideal process, the cathode and anode powders will be further separated out to produce two high purity streams. This is typically carried out by next stage refiners, in parallel with the mined ore derived equivalent when producing the compounds of the individual constituent metals, such as lithium carbonate.

Component	Material	Typical Mass %
Cathode active powder	Lithium-transition metal-oxide	30-40%
Anode active powder	Graphite mostly	15-25%
Separator	Plastic (such poly ethylene, poly propylene etc)	3%
Binder	Polyvinylidene fluoride (PVDF)	0.6-1.5%
Electrolyte salt	Lithium hexafluorophosphate	1.5-2%
Negative current collector	Copper	15%
Positive current collector	Aluminium	10%
Casing	Aluminium, steel	5-15%
Organic carbonates	Various including (but not limited to) <ul style="list-style-type: none"> • Ethylene carbonate • Diethyl carbonate • Dimethyl carbonate • Ethyl methyl carbonate • Propylene carbonate 	12-15%

Table 1 Typical composition of materials found in a Lithium-ion cell.

5. Battery Recycling Process: A Brief Description

Lincoln Storm's battery recycling process is based on shredding, drying and material separation and will be configured along the lines of the diagram shown in **Figure 1**.

Where necessary, the dismantled cells or modules are first discharged. Discharging achieves two aims which are critical for safe battery recycling. When the cell is charged, lithium is stored at the negative electrode (anode), resulting in a highly volatile and unstable compound called graphite-lithium (C_6Li). The lithium is in an elemental form and therefore highly reactive towards other chemicals such as oxygen and water providing there is a pathway for it to do so. It must be noted that the normal charge/discharge band for a lithium ion cell is 20-80%, therefore, even when discharged, the anode will still contain some elemental lithium.

Lincoln Storm operate a commercially confidential process which allows a charged battery to be crushed (to remove encasing steel) and shredded in an aqueous solution, thereby removing the requirement for a separate electrical or salt water based discharging stage pre-shredding.

This lithium will still be present when the battery is shredded and its material separated out. Discharging the cell forces most of the elemental lithium in the anode to go to the cathode where it forms a stable compound. During the aqueous crushing and shredding process, the cells are cut open and the separator is damaged, allowing internal short circuits to occur through a direct pathway between the cathode and anode. This allows an uncontrolled flow of high-energy electrons to flow from the anode to the cathode, generating large quantities of heat, leading to sparks and possibly a thermal runaway.

Thermal runaway is an uncontrollable battery failure which occurs when the cathode material becomes unstable, generating oxygen and allowing the organic carbonates within the electrolyte to combust which further increases the temperature, releasing more oxygen until the cell bursts open from the high internal pressure, exposing the flammable material to atmosphere and allowing complete combustion of the flammables.

Discharging the cells decreases the quantity and the intensity of internal short circuits that will inevitably occur during the shredding process, preventing the temperature of the shred from reaching a point where sparking and combustion can occur. As referenced above, **the batteries are discharged and shredded through mechanical means with the batteries immersed under water at all times**. Being immersed under water there is no available oxygen and therefore no fires or explosions can occur. The additional advantages of discharging and shredding under water are:

- Dust prevention, dust and particulate emissions are greatly reduced / eliminated when shredding or grinding is undertaken under water.
- Water will remove any soluble organics, this, depending on the organics within the cell, can reduce the organic content of the cell by up to 90% during this process stage. This greatly reduces the potential for VOC emission and creation of odours further down the process.
- The chemical reactions i.e. Potential of forming HF is managed at the start of the process and any HF formed can then be chemically removed at point of formation. The risk of HF emissions further down the process is therefore significantly reduced. This also reduces the risk of operator exposure to HF.
- Commercially, active powders released into the aqueous solution can also be recovered.

The shredded battery cells are then separated from the aqueous solution. The flash point of the recovered aqueous material is routinely tested to ensure that the flash point is above 60C at all times. Once the plant is commissioned the quantity of water used per ton of batteries can be determined. Once the water is spent it will be disposed of via road tanker to a suitably licensed Waste Water Treatment Facility.

The shredded battery cells are then dried and then cooled before the material is milled to exfoliate the remaining cathode and anode active powders from the foils, this is then followed by another screening step to collect the black mass and finally some more separation steps to separate the copper from the aluminium

This is followed by separation steps where air current density separation and eddy current separation are used to remove the lighter components such as the plastics and the non-ferrous metals respectively.

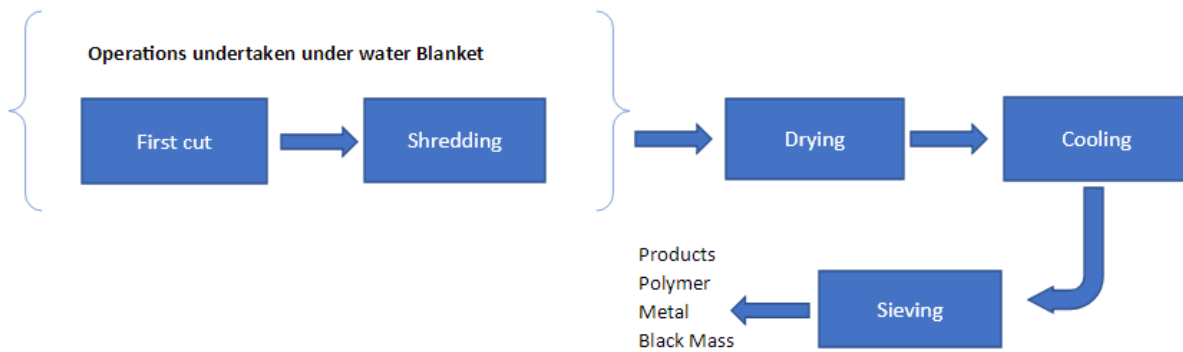


Figure 1 Schematic of a typical battery recycling process.

5. Types of Hazards Associated with Lithium-ion Battery Recycling





A typical lithium-ion battery recycling process will have the following hazards associated with it:

- Gaseous/Vapour
- Dust
- Fire
- Explosion
- Chemical
- Toxic

Table 2 summarises all the components that could be present within recycled battery material. These include: cathode and anode active powders, electrolyte components including organic carbonates such as diethyl carbonate ($C_5H_{10}O_3$) and ethyl methyl carbonate ($C_4H_8O_3$), lithium hexafluorophosphate ($LiPF_6$) and its decomposition products such as hydrofluoric acid (HF), which are chemically removed through the presence of calcium hydroxide ('lime') in the aqueous solution (HF reacts with lime to produce calcium fluoride). Copper and aluminium foils as well as plastics and rubber make up the balance. There are a variety of hazards related to each of these compounds, some are flammable, others are toxic and some are carcinogenic, hence Lincoln Storm must consider these risks when dealing with the material to avoid serious injury or potential loss of life.




Table 2 Summary of hazards for different components in Lithium-ion batteries

Component	Chemical Formula	CAS Number	Hazard Statements	Hazard Labelling
Lithium cobalt oxide (LCO)	LiCoO_2	12190-79-3	H351: suspected of causing cancer H360Fd: May damage fertility. Suspected of damaging the unborn child H400: very toxic to aquatic life H410: very toxic to aquatic life with long-lasting effects	
Lithium nickel manganese cobalt oxide (NMC)	Various; $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$	346417-97-8	H317 May cause an allergic skin reaction. H351 is Suspected of causing cancer.	
Lithium iron phosphate (LFP)	FeLiO_4P	15365-14-7	Not a hazardous substance	
Lithium Nickel Cobalt Aluminium Oxide (LCA)	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	193214-24-3	H317 May cause an allergic skin reaction. H351 is Suspected of causing cancer.	
Lithium Manganese Oxide (LMO)	LiMn_2O_4	12057-17-9	H302 Harmful if swallowed H332 Harmful if inhaled H413 May cause long-lasting harmful effects on aquatic life	
Lithium Nickel Titanate (LTO)	Li_2TiO_3	12031-82-2	H302 Harmful if swallowed H315 Causes skin irritation H319 Causes serious eye irritation	
Lithium Nickel Cobalt Aluminium Oxide (NCA)	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ $\text{LiNi}_{0.84}\text{Co}_{0.12}\text{Al}_{0.04}\text{O}_2$	193214-24-3	H317 May cause an allergic skin reaction. H351 is Suspected of causing cancer.	
Carbon Black	C	133-86-4	H251 Self-heating; may catch fire H351 Suspected of causing cancer H372 Causes damage to organs through prolonged or repeated exposure (lung)	
Graphite	C	7782-42-5	H319 Causes serious eye irritation. H335 May cause respiratory irritation.	

Lithium hexafluorophosphate	LiPF_6	21324-40-3	H302 Harmful if swallowed. H314 Causes severe skin burns and eye damage. H318 Causes serious eye damage. H335 May cause respiratory irritation. H372 Causes damage to organs (Bone, Teeth) through prolonged or repeated exposure if inhaled.	
Ethyl Methyl Carbonate*	$\text{C}_4\text{H}_8\text{O}_3$	623-53-0	H225 Highly flammable liquid and vapour	
Ethylene Carbonate*	$\text{C}_3\text{H}_4\text{O}_3$	96-49-1	H302 Harmful if swallowed H319 Causes serious eye irritation H373 May cause damage to organs (Kidney) through prolonged or repeated exposure if swallowed	
Copper foil	Cu	7440-50-8	Not a hazardous substance	
Aluminium foil	Al	7429-90-5	H228 Flammable solid H261 In contact with water releases flammable gas	

* Ethyl methyl carbonate and Diethyl carbonate are just two examples. Many other organic carbonates are used see table 3

Other products that may be present in the black mass

Component	Chemical Formula	CAS Number	Hazard Statements	Hazard Labelling
Lithium	Li	7439-93-2	H260 In contact with water releases flammable gases which may ignite spontaneously H314 Causes severe skin burns and eye damage	
Lithium Hydroxide	LiOH	1310-65-2	H301 Toxic if swallowed H314 Causes severe skin burns and eye damage	
Hydrofluoric Acid	HF	7664-39-3	H300 + H310 + H330 Fatal if swallowed, in contact with skin or if inhaled H314 Causes severe skin burns and eye damage	

6.1 Workplace Exposure Limits (WEL)

The first category to be aware of is the Workplace Exposure Limits (WEL). In the UK, WELs are occupational exposure limits set to ensure the health and safety of workers who may be exposed to hazardous materials at work. WEL limits are given as a maximum concentration of a hazardous substance in the air, averaged over a specified time average, known as time weighted averages (TWA). These limits are set over two time periods; long-term exposure (8 hours) and short-term exposure (15 minutes).

Substance	CAS number	Workplace exposure limit			
		Long-term exposure limit (8 hour TWA)		Short-term exposure limit (15 minute TWA)	
		ppm	mg/m ³	ppm	mg/m ³
Lithium cobalt oxide (LCO) *	12190-79-3	-	0.1	-	-
Lithium nickel manganese cobalt oxide (NMC) *	346417-97-8	-	0.1	-	-
Lithium iron phosphate (LFP) *	15365-14-7	-	5	-	-
Lithium Nickel Cobalt Aluminium Oxide (LCA) *	193214-24-3	-	0.1	-	-
Lithium Manganese Oxide (LMO) *	12057-17-9	-	0.5	-	-
Lithium Nickel Titanate (LTO) *	12031-82-2	-	0.1	-	-
Lithium Nickel Cobalt Aluminium Oxide (NCA) *	193214-24-3	-	0.1	-	-
Carbon Black	133-86-4	-	3.5	-	7
Graphite Inhalable dust Respirable dust	7782-42-5	-	10 4	-	-
Copper dust	7440-50-8	-	1	-	2
Aluminium foil Inhalable dust Respirable dust	7429 -90 -5	-	10 4	-	-
Lithium Hydroxide	1310-65-2	-	-	-	1
Hydrofluoric Acid	7664-39-3	1.8	1.5	3	2.5
Lithium hexafluorophosphate	21324-40-3	None established			

Table 3 WELs for common substances encountered when shredding LIBs

*No formal WELs have been established for most of the cathode powders used in lithium ion batteries. The UK health and safety executive HSE advises the use of TWA levels of the primary compound within the material e.g Co, Mn and Ni and it is these that are provided in the table.

Any substance that has an assigned WEL must be handled according to COSHH requirements to prevent or control human exposure.

Some substances may not have an allocated WEL, this does not mean that the substance is not hazardous but rather it has not been established yet whether or not it has hazardous characteristics. Table 3 below provides the WELs for substances that will be present in lithium-ion battery shred.

6.2 Acute Hazards to Human Health

To avoid physical exposure to the battery shred, the battery recycling plant must have an adequate extraction system and the process must be designed such that the shredded components are processed internally, keeping the material within the process machinery and not exposed to the environment. This is true of the Lincoln Storm system where all the process steps are enclosed to prevent unintentional dust emissions.

Workers must have adequate personal protective equipment (PPE) such as chemical and cut-resistant gloves and overalls that protect their skin from exposure as well as safety specs and adequate masks.

6.2.1 Cuts

Post shredding, the battery material can have very sharp edges created when the shredder blades cut through the various metal parts of the cells or modules. These sharp edges can easily damage and penetrate the skin. The shred may also be contaminated with electrolyte components which can enter the body through the cut.

6.2.2 Sensitising Powders

Many of the cathode active powders contain metal oxide powders such as nickel and cobalt oxides. These are known skin sensitisers and can cause allergic reactions if body parts are exposed to them.

Lincoln Storm is mindful that production of such material could eventually fall under Registration, Evaluation, Authorisation and Restriction of Chemicals Regulations (REACH) protocols and The Control of Major Accident Hazards (COMAH) Regulations and the turnkey providers have designed their processes to comply with such regulations to avoid unwanted stoppages and redesigns. Lincoln Storm has commissioned its own independent REACH analysis for Storm Black™ which accompanies this document.

6.2.3 Inhalation of Electrolyte Vapours

Lithium-ion batteries generate large quantities of electrolytes, consisting mainly of the organic carbonates that are used in the electrolyte. These vapours produce a strong *ethereal* odour and can be irritating to the eyes and respiratory tract, with prolonged exposure causing severe injury to vital organs such as the kidneys.

The vapour from the electrolyte is reduced to the minimum as the majority of the electrolytes are removed at the aqueous shredding stage and before any material residue is removed during the drying process.

6.2.4 Cancerous Dust

Many of the cathode materials contain metal oxides such as cobalt and nickel oxide. These oxides are classified as having the potential to cause cancer if inhaled. The enclosed aqueous shredding process captures these particles, with any other dust is captured through active carbon filters and wet scrubbers.

From **Table 3**, it can be seen that the exposure limits for cathode dust is as low as $0.1\text{mg}/\text{m}^3$ for some of the cathode materials.

6.3 Lithium Hexafluorophosphate (LiPF₆) Hazards

LiPF₆ is the most toxic chemical present in lithium-ion batteries. Not only is it toxic itself, but it can also generate further toxic and poisonous by-products on decomposition. The LiPF₆ can be present in two forms; wet or dry. The wet form is how it is found inside the battery where it is dissolved into the organic carbonates. This is the form most likely to be encountered during the recycle process

Wet Shred LiPF₆ Hazards

Battery electrolyte solution normally contains 1 Molar LiPF₆ (152g LiPF₆ per kg of electrolyte mixture) meaning that a tonne of lithium-ion batteries can contain between 15-20kg (1.5% to 2% wt/wt) of LiPF₆.

Hydrogen Fluoride gas as well as a variety of other flammable and toxic chemicals can be generated during the shredding process, particularly if the shredding is carried out when the cells still contain charge as shown in **Figure 2**.

As mentioned above, the gases from the shredder are routed through a bag filter, an active carbon filter and a wet scrubber before being released into the environment.

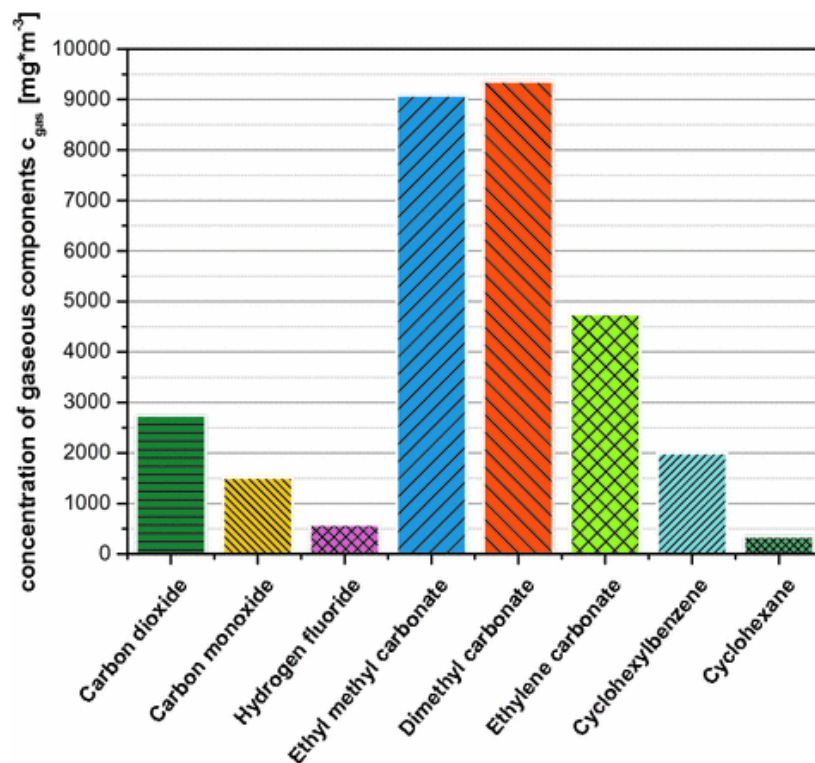
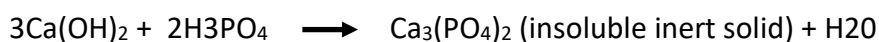
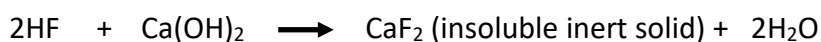


Figure 2 - Gas emissions from the electrolyte during and after the shredding of lithium-ion batteries at an 80% state of charge³

Stoichiometrically, 1kg of LiPF₆ requires just 118ml of water to hydrolyse, producing 271g of HF and generating 683g or 160L of phosphoric fluoride, POF₃, gas. The POF₃ gas is a highly corrosive and toxic gas that rapidly hydrolyses in water, if sufficient water is not present, it has the potential to become airborne and escape. It is the design intent of Lincoln Storm's battery recycling process to use a large excess of water during the first stage of the process with the intent to hydrolyse any LiPF₆ present within the cell. The potential for toxic gas generation is therefore removed.



The reactions can continue until phosphoric acid is formed. The HF and any phosphoric acid are then reacted out of solution using lime.



Should elemental lithium be present in the battery shred, it can prevent the formation of hydrofluoric acid by first reacting with the water to form LiOH and then ultimately react with any phosphoric acid to form Li₃PO₄

A perceived downside to shredding under water is that the organics can't be recycled. With the large number of battery cells and from various suppliers the organics' will be a mix. In order to recover the each individually would require a specialist solvent recycler. The potential presence of these organics in the aqueous solution means that in the current process the spent solution will be handled on the basis that it is a hazardous waste (EWC 161001*), although we believe testing will confirm that it will be EWC 161002 (i.e. non-hazardous).

6.4 Hydrogen Fluoride Gas

Hydrogen fluoride gas is generated when HF molecules evaporate from a bulk hydrofluoric acid solution and enter the gas phase. This process can occur readily as hydrofluoric acid has a relatively high vapour pressure, allowing it to evaporate easily. Lincoln Storm remove the HF during the initial stage of the process by neutralisation and hence the potential for HF gas generation during the drying stage has been removed.

6.5 Inhalation of Carbon Black, Graphite and Metal Oxide Dust

Carbon Black

Carbon black is used as an additive in the electrodes to improve electrical conductivity. Carbon black is much lighter than both graphite and cathode powders and hence it is much more likely to become airborne and come into contact with workers. Long-term exposure can cause serious harm such as damage to organs or cancer as seen in **Table 2**.

Graphite

Graphite is more dense than carbon black but it is still able to be entrained in air and generate dust. Though less hazardous than carbon black, the quantity available is much greater and therefore presents a bigger risk. Graphite dust can irritate the eyes and respiratory lining. Graphite dust containing elemental lithium is more hazardous for human health as the lithium will react with any moisture in the body to form lithium hydroxide solution (in a highly exothermic reaction) which is a highly corrosive caustic solution that can damage the eyes, nose and respiratory lining. However by shredding under water the potential for this is remote.

Metal Oxide Dust

Dust from cathode materials such as LCO or NMC etc, can be very dangerous to human health since not only are they sensitising but they are also potentially carcinogenic. Cathode powders tend to have high densities so do not travel very far but the nature of the separation processes mean highly energetic movements could propel the material farther than would be the case naturally, generating cathode dust, particularly when the material has been dried of the organic carbonates.

6.6 Flammable and Explosive Hazards

Flammable carbonate vapours

The biggest fire hazard associated with lithium-ion batteries comes from the organic carbonates that make up the electrolyte. Some of the organic carbonates readily vaporise to form a flammable and potentially explosive atmosphere.

Lithium-ion battery electrolytes mainly consist of two organic carbonates (50/50% by mass) and lithium hexafluorophosphate (LiPF₆) with small quantities of additives to help improve performance. Unfortunately, manufacturers do not specify what these additives are, hence it is not possible to discern what hazards they can create in a recycling plant.

Table 3 below shows some organic carbonates used in lithium-ion batteries as well as their properties. Of these, dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC) and ethylene carbonate (EC) are by far the most common. As can be seen, some of these carbonates have low boiling and flash points, making them very hazardous if not stored and handled correctly.

Figure 3 shows the flash points and self extinguishing time for the various organic carbonates present in LIB electrolytes. As can be seen, many of the common electrolytes have flash points below 40°C.

Table 4 Properties of organic carbonates used in Lithium-ion battery electrolytes.

Organic Carbonate	Acronym	Boiling point (°C)	Vapour Pressure at 25°C (kPa)	Self Extinguishing Time, SET, (s/g)	Flash Point, FP, (°C) at 1 atm
Dimethoxy ethane	DME	84.5		122	-2
Ethyl Acetate	EA	77.1	14.3	98	0.5
Dimethyl carbonate	DMC	90.5	8.0	122	16
Ethyl methyl carbonate	EMC	107	3.9	143	23.5
Diethyl Carbonate	DEC	126	2.4	158	33
Cyclohexanol	cHexOH	160		190	68
Propylene carbonate	PC	242		-	135.5
Ethylene carbonate	EC	248		-	145.5

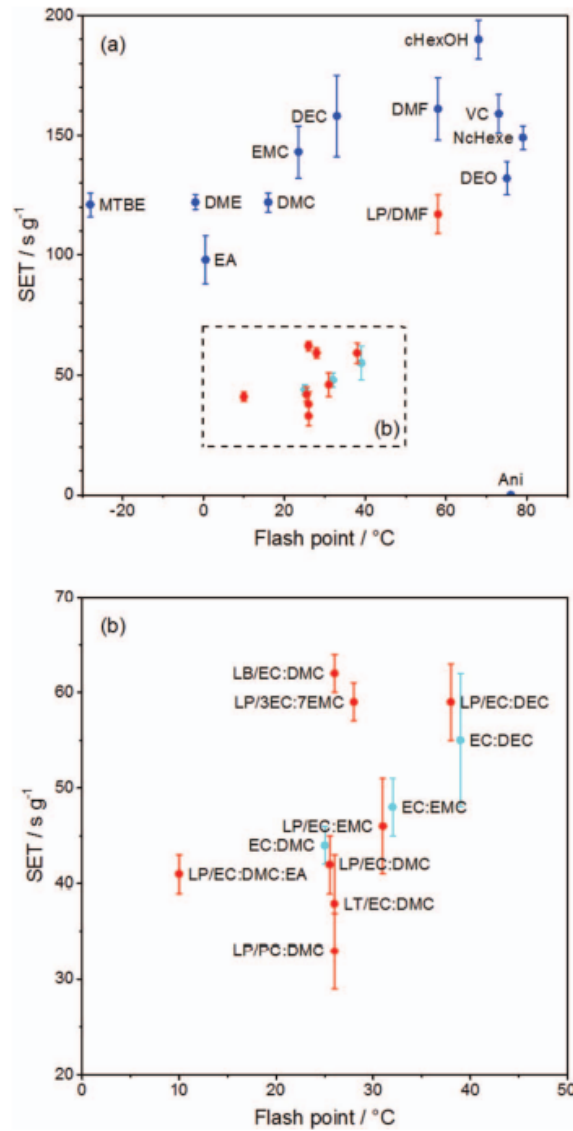


Figure 3 Flash points of common electrolyte mixes.

Shredding under water removes at least 90% of these organic carbonates therefore the flammability risk during drying is significantly reduced as is the potential for VOC release.

6.9 Explosion from Graphite Dust

Graphite can readily become airborne and suspended in the air forming a dust cloud. In recycling plants, this can be a particularly acute problem since many of the machinery used for separation and material conveyance involves highly energetic movements such as granulation and vibration which tends to eject the material into the air.

In unconfined areas, the graphite dust can irritate the eyes and respiratory lining if workers are exposed to it.

In confined areas, the graphite dust can generate an explosive atmosphere if there is sufficient mass in the air and a source of ignition is found. Physical and chemical reactions are undertaken within the cells throughout the cells operational lifespan and these can alter the degree of explosivity associated with graphite. This is the case when processing spent pot linings from the aluminium industry. Cathode carbon on testing has no detectable explosivity, Lincoln Storm therefore are testing the explosivity of the Black Mass at each processing stage.

If all the dust generated by the plant is considered as Carbon Black/Graphite (which is not the case) then the total theoretical release was measured (see Section 7), being 0.33 g/m³ from the main emission stack of the separation plant.

The usual value for the Lower Explosive Limit for Carbon Black is 60 mg/m³, therefore even if the explosivity testing determines potential explosivity, if the controls are operational, the maximum theoretical level of dust in the atmosphere will be approximately a factor of 200 below the LEL.

Any failure in any of the abatement systems requires an instant shut down of the process to avoid the hazards mentioned.

7. Dust Emission Levels and Control based on Experimental Analysis and according to UK Govt Guidance - Air Emissions Risk Assessment for your environmental permit

Having examined all the possible hazards associated with breaking of Lithium Batteries, Lincoln Storm have independently analysed by Third Party (SOCOTEC) the dust emissions from the Separation plant and its Sieving process - See Appendix 1, Lincoln Storm Main Stack Emission Report. Lincoln Storm have also measured the particle size distribution, 90% of the particle size are under 20 micron. The bag filter and carbon filtration system servicing the sieving plant are super efficient.

Measured amount of Black Mass which could escape into the scrubber stack = 0.33mg/m³

Equivalent to 3.39g/h

Whilst the plant is operation, the main stack will require a continuous monitoring system to provide data for the on-going development of the process after commissioning. It is intended to use the monitoring standard in accordance with the web guide 'Monitoring Stack Emissions: low risk MCPs and Specified Generators'.

7.1 Air emissions risk assessment for your environmental permit

Guidance: Steps to complete this risk assessment

To complete an air emissions risk assessment you need to follow these steps.

1. Calculate the environmental concentration of each substance you release into the air – known as the process contribution (PC).
2. Identify PCs with insignificant environmental impact so that they can be ‘screened out’ – this means that you do not have to assess them any further.
3. For substances not screened out in step 2, calculate the predicted environmental concentration (PEC) for each substance you release to air – the PEC is the PC plus the concentration of the substance already present in the environment.
4. Identify emissions that have insignificant environmental impact – these can be screened out.
5. Get ‘detailed modelling’ (also known as detailed assessment or computer modelling) done for the emissions you cannot screen out.
6. For each substance you’ve released to air, compare the PC and PEC with the relevant environmental standard and summarise your results.
7. Check if you need to take further action.
8. Check if you need to do any other risk assessments.

Lincoln Storm Black Mass has been analysed by third party accredited MCERTS accredited laboratory using ICP OES. The release rates calculated using Third Party Analysis of emissions from the stack. The following elements were analysed for but the results were under the limit of detection for ICP OES

Lanthium, Godolinium, Germanium and Antimony

The full results are detailed in Appendix 2, Lincoln Storm Black Mass Analysis and for the emission data in Appendix 1, Lincoln Storm Main Stack Report.

Worst case results were used for each element in the calculations.

Measured dust released from stack 3.39g/h			
Element	Analysis	Mass	Release Rate
	%	g/h	g/s
Fe	2	0.0678	0.000018833
Li	4.79	0.162381	0.000045106
P	4.41	0.149499	0.000041528
Ni	27.58	0.934962	0.000259712
Co	7.81	0.264759	0.000073544
Cu	33.71	1.142769	0.000317436
Al	9.05	0.306795	0.000085221
Mn	9.18	0.311202	8.6445E-05
Ca	0.24	0.008136	0.00000226
Mg	0.31	0.010509	0.000002919
Pb	0.077	0.0026103	7.25083E-07
Zn	0.082	0.0027798	0.000000772
As	0.002	0.0000678	0.000000019
Cr	0.013	0.0004407	0.000000122
Sn	0.028	0.0009492	0.000000264
Ga	22	0.7458	0.000207167
K	0.28	0.009492	0.000002637
Na	0.97	0.032883	0.000009134
C	42.6	1.44414	0.00040115

7.2 Assumptions

- The maximum feed rate of the plant is 2000 kg/hr
- The release into the atmosphere is 3.39g/h
- The actual amount of black mass is measured therefore
 - Correction Factor (**CF a**) = 1
- The analysis demonstrates that heavy elements are very low with carbon being >96% of the Black Mass therefore
 - Correction Factor (**CF b**) = 0.04
- The theoretical time of operation is 365 days at 24 hrs a day = 8760 hours
- The actual time of proposed operation is 250 days at 12 hrs a day = 3000 hours
 - Correction Factor (**CF c**) = $3000/8760 = 0.342$
- The efficiency of the abatement system is 99.9% which therefore allows 0.1% passing
 - Correction Factor (**CF d**) = 0.001
- The Total correction Factor
 - Correction Factors = 0.00001368
- Emissions are discharged at 6 metres
- Long Term Dispersion Factor = 148
- Short Term Dispersion Factor = 3900
- Long Term standard is reported on an annual basis
- Short Term standard is reported on an hourly basis

PC to Air = release rate x dispersion factor x (correction factors)
= RR x DF x (CF a) x (CF b) x (CF c) x (CF d)

Element	Release Rate	Short Term	Long Term
	g/s	148	3900
Fe	0.000018833	0.002787333	0.07345
Li	0.000045106	0.006675663	0.17591275
P	0.000041528	0.00614607	0.16195725
Ni	0.000259712	0.038437327	1.0128755
Co	0.000073544	0.010884537	0.28682225
Cu	0.000317436	0.046980503	1.23799975
Al	0.000085221	0.012612683	0.33236125
Mn	8.6445E-05	0.01279386	0.3371355
Ca	0.00000226	0.00033448	0.008814
Mg	0.000002919	0.000432037	0.01138475
Pb	7.25083E-07	0.000107312	0.002827825
Zn	0.000000772	0.000114281	0.00301145
As	0.000000019	0.000002787	0.00007345
Cr	0.000000122	0.000018118	0.000477425
Sn	0.000000264	0.000039023	0.0010283
Ga	0.000207167	0.030660667	0.80795
K	0.000002637	0.000390227	0.010283
Na	0.000009134	0.001351857	0.03562325
C	0.00040115	0.0593702	1.564485

PC to Ground = **long term** PC to Air × release rate × 0.01 × 3 × 86,400

Element	Release Rate	PC to Ground
	g/s	
Fe	0.002787333	0.53065921
Li	0.006675663	3.043874493
P	0.00614607	2.580078344
Ni	0.038437327	100.912331
Co	0.010884537	8.092035554
Cu	0.046980503	150.7555188
Al	0.012612683	10.86557898
Mn	0.01279386	11.17998129
Ca	0.00033448	0.007641493
Mg	0.000432037	0.012749088
Pb	0.000107312	0.00078657
Zn	0.000114281	0.000892038
As	0.000002787	0.000000531
Cr	0.000018118	0.00002242
Sn	0.000039023	0.000104009
Ga	0.030660667	64.20976436
K	0.000390227	0.010400921
Na	0.001351857	0.124824313
C	0.0593702	240.7547768

VOC

- Initial Electrolyte (VOC) content of the batteries is a maximum of 15% of feed mass of batteries
- Aqueous cut and shredding removes 90% of the VOC into the aqueous phase
- Carbon Filter system removes 99% of VOC in vacuum exhaust gas
- Water / aqueous scrubbing removes 99% of VOC

Mobile Combustion Plants

- On start up Lincoln Storm will use 4 MCP units all sub 1MW to deliver the power to the plant
- These will be located off site
- Each MCP is fitted with AdBlue abatement system
- The emissions from these MCP will be monitored
- Lincoln Storm are currently investigating the possibility of moving to mains power supply. It is therefore envisaged that the use of MCP's will be short term solution to the power requirement.

Appendix I - Lincoln Storm Main Stack Emission Report

Appendix II - Lincoln Storm Material Analysis

Appendix III - Lincoln Storm Particle size distribution