

Flammability of Lithium-Ion Batteries and the Possibility of a Major Accident

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By replacing one technology with another, people try to enhance the current solution or they try to meet new legal requirements by imposing restrictions on current solutions. This happens more and more often in an attempt to reduce threats to both the natural and the working environment.

Lithium-ion batteries, or energy banks, are among the solutions that have generated considerable controversy due to their flammability and fire hazards. It is worth noting that neither rechargeable batteries nor energy banks are hazardous substances under EU regulations, i.e. Regulation (EC) No. 1272/2008 of the European Parliament and of the Council (so-called CLP Regulation). Therefore, they are not directly covered by the requirements of the directive 2012/18/EU of the European Parliament and of the Council (so-called Seveso III Directive) as dangerous substances.

The chemicals used in lithium-ion batteries, however, have hazardous properties. These include substances with acute toxic effects (e.g., lithium chloride, thionyl dichloride, cobalt oxide). Some substances can also form flammable gases when in contact with water (Water-react. 1, H260). The composition of batteries is manufacturer-specific. The properties of the substances present in them mean that in the event of improper handling/use, failures can occur, leading to fire, explosion or release of hazardous substances. In a major accident situation, substances present in lithium-ion batteries can contribute to the formation of flammable gases that can spontaneously combust or gases with toxic effects from inhalation, including hydrogen fluoride (Acute Tox. 2; H330 - Acute Toxicity Category 2; inhalation is fatal), hydrogen chloride, etc. Obviously, the kind of substances formed as a result of a major accident depends on the composition of the lithium-ion batteries.

The article attempts to determine the correlation between the substances present in a product (a battery) and the hazardous substances that may be generated by a fire in the product, with reference to the definition of the presence of a dangerous substances set forth in no 12 of Article 4 of the Seveso III Directive.

1. Introduction

As an example of a major accident involving lithium-ion batteries, a fire and series of explosions involving 184,000 pounds of lithium-ion batteries (the estimate of U.S. Environmental Protection Agency EPA) stored at the Federal Paper Board facility in Morris, (about 70 miles southwest of Chicago) in the US on June 29, 2021. Morris Mayor Chris Brown said that both officials and those involved in the rescue operation were unaware that the building, which had likely not been used since the plant closed nearly 35 years ago, contained about 100 tons of lithium-ion batteries. Chief Steffes pointed out that firefighters initially tried to suppress the fire with water, unaware of the presence of lithium-ion batteries, so firefighters' early attempts to extinguish the fire caused it to escalate and led to a series of explosions. Heavy rains overnight also contributed to the uncontrollable situation. By Wednesday morning, local officials had ordered the evacuation of some 1,000 homes and businesses in the area, evacuating 3,000 to 5,000 nearby residents for more than three days (EPA 1309187).

Another example is the fire on 16 January 2023 at the Bollore Logistic plant warehouse in the town of Grand Couronne, near Rouen in France. The fire from a few thousand lithium-ion batteries (12 000 according to Fire Protection Association FPA (2023)) spread to the nearby Districash plant warehouse, where around 70 000 tyres were stored. Smoke and flames were visible from the south coast of the UK. The warehouses were not in an area classified as 'Seveso'. No evacuation was announced, but residents of the town of Orival, which is located a few kilometres south of Grand-Couronne, were asked to stay indoors. Prefect Pierre-André Durand assured that "there is no danger to the population" and promised to reveal the results of the air measurements. Analyses obtained from 28 measuring points set up by firefighters on and around the site, "showed that hydrogen fluoride levels remained at zero", the prefecture said in a press release. Firefighters also checked for the presence of nitrogen oxide, hydrogen chloride and hydrogen cyanide in the air in particular. Atmospheric samples "showed no danger to the population", the statement added. According to Colonel Reme Weclawiak, deputy director of the SDS76 department, it was a matter of weather conditions ("the smoke was rising very high and there was good dispersion") (Prefet de la Seine-Maritime, 2023).

2. Legislation - definitions

The term lithium-ion battery is a collective name for a whole group of batteries containing different cell geometries and different combinations of materials such as cathode, anode, electrolyte and separator. According to EU Regulation (Regulation 2023/1542):

'battery' means any device delivering electrical energy generated by direct conversion of chemical energy, having internal or external storage, and consisting of one or more non-rechargeable or rechargeable battery cells, modules or of packs of them, and includes a battery that has been subject to preparation for re-use, preparation for repurposing, repurposing or remanufacturing;

The regulation also defines different types of batteries, e.g. industrial battery, electric vehicle battery, stationary battery energy storage system and others. Each time, however, a battery refers to an appliance designed for a specific use (battery that is specifically designed for industrial uses). It is worth emphasizing, however, that under the above EU regulation, a battery is an appliance and not a product.

There are at least two possible ways to link lithium-ion batteries (especially large ones with >100 Wh per battery and/or >12 kg gross per battery using the breakdown used in (VdS 3103) to the prevention and mitigation of major industrial accidents. The first is related to the possibility of hydrogen fluoride formation as a result of a battery fire. Thus, according to the Seveso III Directive:

'dangerous substance' means a substance or mixture covered by Part 1 or listed in Part 2 of Annex I, including in the form of a raw material, product, by-product, residue or intermediate;

Hydrogen fluoride HF is a dangerous substance within the meaning of the Seveso III Directive as a substance with acute toxic effects by all routes of exposure (Acute Tox. 2; H330, Acute Tox. 1; H310, Acute Tox. 2; H300). However,

'presence of dangerous substances' means the actual or anticipated presence of dangerous substances in the establishment, or of dangerous substances which it is reasonable to foresee may be generated during loss of control of the processes, including storage activities, in any installation within the establishment, in quantities equal to or exceeding the qualifying quantities set out in Part 1 or Part 2 of Annex I;

This means that in the case of hydrogen fluoride, for example, it is not only the creation itself that is important, but also the amount that will be created. For category 1 acute toxic substances, the threshold value for a lower-tier plant is 5 tonnes. Such a quantity correlates with the definition:

'major accident' means an occurrence such as a major emission, fire, or explosion resulting from uncontrolled developments in the course of the operation of any establishment covered by this Directive, and leading to serious danger to human health or the environment, immediate or delayed,

By that approach a fire in a single lithium-ion battery that creates a small amount of hydrogen fluoride cannot be classified as a major accident due to the small amounts of HF generated. And a plant using a single battery, even with a large capacity, will not be a plant subject to the requirements of the Seveso III Directive.

The second possibility, relates to the fire-explosive potential of lithium-ion batteries and the possibility of thermal runaway. In Europe, it is accepted to classify batteries as 'articles' within the meaning of Regulation 1272/2008 (CLP Regulation). However, according to this EU regulation, which is directly applicable in all EU countries:

'article' means an object which during production is given a special shape, surface or design which determines its function to a greater degree than does its chemical composition;

In the case of lithium-ion batteries, it is not so much the shape, surface or external appearance that determines their function as an energy carrier, but their construction and operating principle. There is a whole range of batteries available in different shapes, surfaces and external appearances, which create a certain problem in accepting without question the definition of 'product' as applied to batteries. On the other hand, the chemical composition of batteries can be different. However, the substances used must have certain properties and must perform certain functions in order for the whole battery to fulfil its function as an energy carrier. This means that the CLP Regulation's definition of an article does not fit precisely with lithium-ion batteries and, as such, may be called into question, even more so in light of the definition in EU Regulation 2023/1542.

Products as such are not subject to the requirements of the CLP Regulation, nor is waste. In this situation, note 5 of Annex 1 of the Seveso III Directive is worth noting:

In the case of dangerous substances which are not covered by Regulation (EC) No 1272/2008, including waste, but which nevertheless are present, or are likely to be present, in an establishment and which possess or are likely to possess, under the conditions found at the establishment, equivalent properties in terms of major-accident potential, these shall be provisionally assigned to the most analogous category or named dangerous substance falling within the scope of this Directive.

When analysing whether products could, even in theory, be treated as dangerous substances, it is worth noting the position of Explosives in the qualification criteria of the Seveso III Directive (categories P1a and P1b, Annex 1, Table 1), because a dangerous substance is not only a substance understood in strictly chemical terms. Thus, according to point 2.1.1.1 of the CLP Regulation, the class of explosives comprises:

b) explosive articles, except devices containing explosive substances or mixtures in such quantity or of such a character that their inadvertent or accidental ignition or initiation shall not cause any effect external to the device either by projection, fire, smoke, heat or loud noise;

The classification criteria for explosives (2.1.2.1, 2.1.2.2.) of the CLP Regulation refer to substances, mixtures and articles. This means that the Seveso III Directive allows for the qualification of an establishment on the basis of articles present or likely to occur on its premises.

In contrast, in the US, lithium-ion batteries are not treated as articles according to the official position of the EPA and OSHA (Occupational Safety and Health Administration):

„OSHA has determined that lithium-ion batteries are not considered to be “articles” and are subject to the OSHA HCS regulations. Lithium-ion batteries are not considered to be articles because although they are sealed, they have the potential to leak, spill, or break during normal conditions of use and in foreseeable emergencies causing exposure to chemicals.” (EPA LIB)

And just as the first link to hydrogen fluoride arising from a fire seems to be uncontroversial, the second quandary can provoke extreme reactions. This situation only demonstrates the need for clear and uniform regulations in this area and globally harmonised requirements.

3. Run-away reactions

The treatment of batteries as “products” in Europe means that relevant safety data sheets are not required. However, safety data sheets [SDS] or information sheets are often available (Example of SDS). Information sheets are publicly available, usually with a note that they are voluntary. It is not uncommon for them to state that they are prepared as “an expression of responsibility and care towards the user”. In such charters, in the section on dealing with fire and in the section on dealing with unintentional releases into the environment, manufacturers explicitly mention the possibility of toxic substances being formed in a fire, while also emphasising the flammability of batteries. There is also information about the possibility of explosion if the battery is heated above a certain temperature, e.g. 125 °C. In many cases it is stated that batteries should not be stored in temperatures above 60 degrees (140°F) or below -20°C (-4°F).

The temperature conditions of battery storage are related to the hazards associated with their construction and the possibility of thermal runaway. Thermal runaway of Li-ion batteries is the phenomenon of exothermic chain reactions within the battery. These reactions usually cause a sharp increase in the internal battery temperature causing the inner structures of the battery to destabilize and degrade, which can lead to the total failure of the battery. Thermal runaway can occur from various forms of mechanical, electrical, and thermal abuse. All of these lead to an internal short-circuit of the battery as the separator between the anode and the cathode either collapses, tears down, or is pierced. This generates a high amount of heat, which in turn intensifies the degree of electrochemical reactions causing excessive heat generation. This cycle continues, which increases the temperature of the battery sharply and releases large amounts of flammable gases. The release of gases causes an increase in the internal pressure of the battery resulting in the expansion of the outer casing, causing potential explosion and fire to the battery (Shahid and Agelin-Chaab, 2022).

In addition, thermal runaway propagation depends on many factors, e.g., cell spacing, intermediate materials, the entire cell stack setup and the degree of charge. Furthermore, the choice of cell chemistry plays a decisive role in the safety design of a battery system.

Depending on the application, there are lithium cobalt (LiCoO₂) - so-called LCO batteries with high energy density and low thermal stability (risk of thermal runaway) used in mobile phones and laptops, lithium manganese (LiMn₂O₄) - so-called LMO batteries, which have a high charge and discharge current, and the absence of cobalt results in greater thermal stability, used to power tools, medical instruments and electric and hybrid cars, lithium nickel manganese cobalt (LiNiMnCoO₂ - so-called NMC) batteries configurable to have high energy density but low power, or conversely, low energy density but high power. The ability to achieve high energy density (generally at the expense of durability), makes NMC cells popular for powering tools, electric bicycles, electric cars or home energy storage for photovoltaics. The last of the batteries analysed are lithium iron phosphate (LiFePO₄) batteries - so-called LFP batteries. Their main features are lower energy density than NMC batteries, long life, high current, and better thermal stability. LFP batteries are most commonly used in home energy storage for photovoltaics, electric cars and electric bicycles and as replacements for lead-acid batteries.

However, such materials with higher energy densities have low thermal stabilities, which can lead to safety issues such as thermal runaway. (Noh, 2013, Shahid and Agelin-Chaab 2022).

The variety of batteries, including the substances contained in them, results in different experimental outcomes. However, it is uncontroversial to conclude that, in broad terms, exceeding the permissible temperature (e.g. about 60°C) causes the electrolyte to begin to evaporate, shut down (separator softened/impermeable to lithium ions), separator melting/internal short-circuiting occurs and an exothermic reaction and thermal runaway occurs. Some cross-cutting publications e.g. Shahid and Agelin-Chaab (2022) present various stages of thermal runaway during accelerating rate calorimetry (ARC) testing, as thermal runaway mechanisms include mechanical abuse, electrical abuse and thermal abuse based on published experimental work.

4. Hazardous substances generated

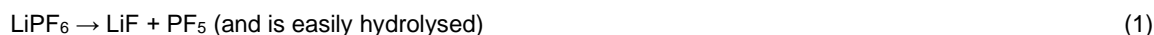
Rappsilber et al. (2023) conducted a meta-analysis of heat release and smoke gas emission during thermal runaway of lithium-ion batteries. Their analysis comprises 76 experimental research papers from 2000 to 2021. It allowed them to realize that two very important aspects for the characterization of the thermal runaway effects are the heat and the gases released. Corresponding experimental data published in the literature show a large fluctuation range.

Of all the toxic gases produced by a fire involving lithium-ion batteries, hydrogen fluoride is the most hazardous. For this reason, it can be a reference point in analyses related to the prevention of major industrial accidents.

Rappsilber et al. (2023) notice that in most cases fully charged LFP pouch cells release a smaller amount of HF during thermal runaway than discharged LFP cells. They concluded that one possible explanation is that higher state of charge is associated with higher reaction temperatures during thermal runaway, which causes the generated HF to decompose and/or react to other fluorine-containing compounds, making the HF gas undetectable. This regularity was not observed in all publications. In the test series by Lecocq et al. (2016), there is a tendency for HF production to decrease with increasing state of charge. In contrast, in the test series of Andersson et al. (2013), the decreasing HF release with increasing state of charge is interrupted by a peak at a state of charge of 50 %.

Additionally to the turbulent gas emission, which poses a challenge for reproducible detection of the gases, various reasons for deviating HF curves are given in the test results. For example, it was found that HF components from the sample gas are adsorbed in the FTIR filter and thus do not enter the measurement cell (Rappsilber et al., 2023). Larsson et al. (2017) also note that HF was temporarily clogged in the sampling system during their measurements. However, the test method is not the only reason for different measured values. (Rappsilber et al., 2023).

The problem with the possible amount of fluorine-containing compounds in the battery is that it is not only the electrolyte that can contain fluorine. According to Rappsilber et al. (2023), polyvinylidene fluoride (PVDF) is used as a binder for chemically active substances in electrodes and fluorophosphates in flame retardants in the electrolyte and separator. However, compared to the quantities, these are not as large as the electrolyte itself. Unfortunately, LiPF_6 is already thermally unstable above about 70°C . It also always contains at least traces of hydrogen fluoride due to natural decomposition according to the reaction (Lu et al., 2006, Yang et al., 2006):



The most commonly used salt in lithium-ion cell electrolytes is LiPF_6 . This salt is thermally unstable and decomposes to form LiF and PF_5 . These products react with trace amounts of water to form HF according to reactions (1-2) and (3). In contrast, the reaction environment causes the cathode to dissolve and its components to pass into the electrolyte.



Assuming hypothetically that hydrogen fluoride can only be formed from the LiPF_6 electrolyte according to reactions 1-3, it can be concluded that no more hydrogen fluoride will be formed than correlates (stoichiometrically) quantitatively with the electrolyte. Of course, this will be influenced by the percentage of battery charge, but it can be assumed that a maximum of 2HF will be formed per 1LiPF_6 . This is not a revealing thought, but such a simple correlation can be the basis for a very rough estimate of the maximum possible amount of hydrogen fluoride formed.

This will certainly be a highly overestimated result, but perhaps such a trivially simple relationship can be the basis for starting a discussion on developing relationships that can be easily understood and applied by control and supervisory bodies or representatives of authorities responsible for land-use planning. Not so much on academic grounds, but on a practical level.

5. Conclusions

Lithium-ion batteries are worth considering not only as a potential source of toxic hazardous substances, which under adverse conditions may pose a threat to human life and health, but also as a potential source of domino effects, due to their potential for fire and explosion should a fire occur. As major accidents are always based not only on the type, but also on the quantity of the hazardous substance, the determination of the quantities of the resulting substances in a fire (mainly hydrogen fluoride) will also fulfil the legal requirements. When relating the calculated quantities to the threshold values, it is worth bearing in mind that if only slightly smaller quantities of dangerous substances are generated than the threshold values, the establishment will not be an upper-tier establishment, but a non-Seveso establishment.

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