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Used lithium batteries are not ordinary waste!

The performance of lithium batteries and storage cells has expanded their areas of technical application (telephony, computers, electric vehicles, rechargeable hybrids and electric bicycles). This development is now resulting in an increase in the number of batteries and storage cells at the end of their service life that must be processed or recycled. But lithium batteries and cells are not harmless objects: the high reactivity of the metal means that their use and processing/recycling, present risks. This is illustrated by recent accidentology.*



Lithium button cell battery (all rights reserved)

Lithium: a concentration of potential hazards

Lithium reacts strongly with water and air and is dangerous for the environment. Potential hazards arise in the event of loss of containment on the battery/storage cell casing, electrolyte leakage (ionized lithium), or when exposed to fire:

- **Hydrolysis in the presence of water** or humid air forms gaseous hydrogen with a risk of explosion in restricted or confined space (ARIA 18298, 15532);
- Inflammation in contact with oxygen, and risk of fire, as the electrolyte is assimilated with flammable liquids (ARIA 18298, 20539, 32208);
- Toxicity for aquatic organisms in the case of a release (ARIA 38858);
- **Toxicity/corrosiveness of smoke** from fire containing lithium hydroxides, metal compounds (Mg oxide...) which could lead to environmental pollution (ARIA 46675, 38858, 20539, 18298);
- Projections and projectile effects (ARIA 38858, 43090, 43482, 44320, 46675).

Increased vulnerability at the end of life

While lithium batteries and storage cells should be handled with caution during their period of use (see recent episodes of laptop battery explosion), their vulnerability and dangerousness are increased during collection, processing or recycling operations, particularly while this waste is being stored. This is due to:

- a diffuse stockpile which is difficult to assess: unknown charge status, diversity in the origin of batteries of different technologies;
- the handling, transport and storage operations could result in unforeseen mechanical impacts (ARIA 18298, 32208);
- used batteries/storage cells are sometimes packaged less carefully than new products (stored in bulk, without dedicated packaging or in non-compliant packaging: ARIA 26812, 26812, 43482, 51459): this increases the risk of short-circuit and self-heating;
- damaged batteries/storage cells are particularly sensitive (movements, infiltration of water or air via wind, rain, dew, etc.);
- the risks of incompatibility are quite high in the case of storage with other waste (ARIA 40306);
- the effects of hazardous phenomena are multiplied during mass storage of batteries/storage cells (heat flow, smoke-generating capacity, projections and projectiles effect) (ARIA 38858).

ARIA 51459 - 25-01-2018 - Jura - France

In a WEEE sorting and dismantling centre, a fire broke out in a metal drum containing used lithium button cell batteries. The stock of batteries concerned had been issued a non-conformity report upon its arrival because they were packed in bulk without plastic blisters, without vermiculite and exposed to moisture (soaked cardboard boxes). In such bulk packaging configuration, no barrier between the batteries increases their risk of short-circuiting.

Following the accident, the operator began reminding customers of the packaging rules when sending back their waste for processing.

The operator also provides all agents with training on the potential fire hazards. The decision was made to prohibit the handling of lithium batteries one hour before the site's scheduled closing time.

ARIA 33986 - 02-07-2007 - United Kingdom

In a hazardous waste management site, a violent fire broke out in an area designated for the storage of drums of used chemicals and solvents. An explosion occurred among the drums, resulting in the projection of hazardous waste. More than 132,000 litres of chemical products were burnt.

The start of the fire was attributed to spontaneous inflammation of lithium batteries. The **batteries in question** had been stored in containers normally used to hold clinical waste, non-watertight and unsuitable for storing used lithium batteries. The batteries were being stored close to various incompatible materials and appropriate segregation rules (flammable liquids, toxic products, corrosive products) were not respected. The company was fined 189 euros.

ARIA 38858 - 26-08-2010 - Moselle - France

In a battery and storage cell recycling centre, a fire broke out in a compartment containing used lithium batteries. The automatic powder-based extinguishing system was unable to contain the fire which spread to other cells used to store other types of batteries (lead, mercury, nickel-cadmium) and miscellaneous sub-products (scrap metal, nickel hydroxide). Employees from nearby companies were evacuated and examined owing to the **toxic fumes** released (sulphuric acid and lithium hydroxide). The 1,000 m² building was destroyed and **batteries were thrown 200 m** from the accident site. The potential projectile effect due to fire in the lithium battery storage area had not been considered in the operator's hazard study. The extinguishing water was pumped and disposed of as hazardous waste (heavy metals, phenols and PCBs were detected).

* In this document, we do not focus on the manufacturing and use phases, which are also rich in accidentology (e.g.: ARIA 7437, 17235, 17385, 33658, 34581, 34599, 35175, 38031, 38194, 45383, 48365, 44998, 45807, 50033, 49708, 50643 / 36215, 46017, 46083, 48170, 48187, 49516, 50925) but **only on the waste processing sector**.

Definitions

- Batteries and storage cells are elementary electrical systems used to store the energy generated by electrochemical reactions. A storage cell is rechargeable, as opposed to a battery, which is not rechargeable.
- Lithium batteries come in button or stick format. The anode consists of a metallic lithium, the electrolyte is a lithium salt dissolved in an organic solvent and the cathode is a metallic compound.
- A wide variety of storage cells exists (Liion, Li-polymer, Li-metal, etc.).

A growing sector (ADEME 2017)

In 2016, in France:

- 2% increase in number / 8% in tonnage for portable lithium batteries and storage cells (use for mobile electronic devices).
- 16% increase in tonnage for industrial batteries and storage cells (use in electrical and rechargeable hybrid vehicles and electric vehicles).

Organisation of the collection and processing sector in France

Collection/grouping

- Private individuals must bring their used batteries (including removing the battery or storage cell from the device) to the nearest collection point (60,000 throughout France: battery or cell sales points, ecocentres, etc.)
- Professionals must have their portable batteries and storage cells collected via approved channels.
- For the management of portable battery waste, two eco-organisations are approved by the public authorities for the period 2016-2021: COREPILE and SCRELEC. From the collection points, these organisations manage the transport of waste batteries and storage cells to grouping centres. They are then shipped to sorting and processing sites.

Processing/recycling

The batteries and storage cells are classified as hazardous wastes. They must be processed by an authorised operator who must implement the best techniques available. Material recovery should be preferred to other processing methods whenever technical and cost conditions allow.

ARIA 32208 - 14-05-2006 - Haute Garonne - France

In a factory manufacturing electrical equipment for vehicles, a fire broke out in a container used to store an unsorted mixture of discarded lithium and alkaline batteries. The failure to partition the waste storage cells caused the fire to spread. The flammable (solvents) and combustible materials (pallets) located nearby were ignited by the flames

The lithium battery storage area was designated as the source of the overheating, leading to thermal runaway. The plant's discarded lithium button cells were equipped with metal tabs soldered on their positive and negative poles. A very light impact is sufficient to deform these tabs and put them into contact with one another, resulting in a short circuit. A spark may have occurred, sufficient to ignite a micro-atmosphere composed of hydrogen from the oxidation of the various cells or leakage from batteries stored just a few centimetres from the cells.

The operator issued internal emergency instructions concerning the sorting and storage of used batteries. Measures have been taken to ensure that safety distances are respected, the storage areas are isolated from the batteries in a closed construction with a fire wall and manual and automatic fire detection, and extinguishing devices were installed

ARIA 46675 - IC - 23-05-2015 - Gironde - France

Nine drums of lithium batteries caused an explosion in a company specialising in the recovery of electrical and electronic equipment. Owing to the reaction produced, some lithium batteries were projected several meters away and ignited plastic "dry cell fence batteries" stored nearby on pallets

Due to a misunderstanding between the operator and the fire brigade, the firefighting system's containment valve was closed late. Extinguishing water contaminated by the lithium batteries was discharged into the industrial estate's wastewater network.

The site specialises in the manual sorting of various types of batteries (alkaline, saline and lithium) received from green organisations. Alkaline and saline batteries are ground up on site although primary lithium batteries are stored in drums with vermiculite pending their shipment to processing installations. Lithium batteries are normally stored under shelter in 2 bunkers. On the day of the accident, the bunkers were full and drums had been placed in front of the access doors. The operator had, unsuccessfully, made repeated requests to the green organisations to take the battery stocks to the approved outlets. It was the drums stored outside that reacted, due to unknown reasons (no change in temperature or other specific meteorological factors).

The operator took several measures following the accident:

- implementation of a procedure to guickly remove drums from bunkers as soon as the stock reaches 80% of the maximum authorised guantity;
- installation of an explosion-proof system to limit the effects of an explosion in the bunkers
- gathering of feedback on the storage methods used for primary lithium in France and Europe, and analysis of the possibility of an alternative storage medium on its own site.

Lithium batteries and storage cells mixed with other waste: the new "needle in a haystack"

Beyond accidents in facilities dedicated to the processing of lithium batteries and storage cells, many events are related to such elements that pass through the "wrong system" and end up where they should not be.

Theoretically, batteries and storage cells should be removed from equipment that is no longer operational before being deposited at a collection point. However, the batteries are not always removed. Such batteries and storage cells are thus collected via the WEEE sector and not by the eco-organisations of the battery/storage cell sector. In addition, many lithium batteries (particularly smartphone batteries) are found in non-hazardous waste sorting/transit centres, often because private individuals dispose of them in household waste. These batteries and storage cells are a real challenge for sorting/transit centre operators because they are almost impossible to find in a waste heap. However, accidents can easily arise from contact of batteries and storage cells with flammable waste such as paper/cardboard and plastic.

ARIA 50605 - IC - 27-10-2017 - Sarthe - France

A fire broke out in a waste sorting and composting centre. The building, the bio-filter and deodorisation fans were destroyed. The mechanical-biological sorting system was rendered unusable. The fire started from a scrap metal sorting container under the refining conveyor. Based on the masses of molten metals found there, the temperature may have risen to above 1,200 °C. The expert analysis suggested that the lithium batteries had heated up.

ARIA 49889 - 06-05-2017 - Pas-de-Calais - France

At around 2:20 am, a fire broke out on a pile of freshly crushed electronic cards in a waste electrical and electronic equipment (WEEE) treatment centre. A technician at the unit noted the outbreak of fire. Employees used the site's fire hose to put out the fire. The fire brigade was notified but the fire had already been extinguished when they arrived.

The fire was started by the presence of both flammable material (fine particles of plastic and resins contained in the shredded material), air and a source of heat. The heat may have come from a hot spot produced by the shredding of a lithium battery which may not have been removed from the electronic waste by the supplier.

Some points of vigilance and safety instructions

Transport:

- Precondition the lithium batteries and storage cells upstream from the collection circuit by neutralising them (immersion in saline water) or by protecting their terminals (ARIA 44320);
- Implement a protocol suitable for the transport of damaged lithium batteries and storage cells (ARIA 50152: handling at -20 °C to freeze the liquids inside).

Storage/Sorting/Processing:

- Train all parties in the specific risks (ARIA 44320);
- Raise awareness among players upstream (do not discard batteries and storage cells with general household waste, remove batteries and storage cells before they are brought to the collection point (ARIA 51459, 52020);
- Implement operating instructions to limit the risk of accidents during periods of reduced activity: manage the receiving times for better monitoring (ARIA 51459);
- Be particularly vigilant during handling to avoid drops, impacts (ARIA 18298, 32208);
- Take preventive measures and feedback into account for appropriate organisation of storage facilities: safety distances from flammable materials (consider the risk of projectile effect), firewalls, isolation rules, sorting of batteries by type, consideration of the risk of incompatibility with other waste/products, vigilance on the nature of the containers used (avoid the introduction of water) (ARIA 40306, 26812, 32208, 33986, 38858). These preventive measures are all the more important when storage takes place in locations where the public is present (rubbish dumps);
- Provide the appropriate extinguishing agents (powder or sand for metal fires), adding water to a lithium fire can rekindle the flame and cause the release of flammable hydrogen (water remains necessary for cooling and to avoid the dispersion of toxic fumes) (ARIA 40306);
- Prevent the occurrence of degraded operating situations: do not delay processing (ARIA 40306), evacuate stocks of batteries, and storage cells awaiting shipment to their processing site before reaching the maximum available capacity (ARIA 46675).

Despite their undeniable advantages, lithium batteries and storage cells are dangerous owing to the high reactivity of this metal. Moreover, lithium remains expensive though it is abundant on Earth. Research is currently underway to develop cheaper and less reactive alternatives. Zinc-based batteries, a low-response and less expensive metal, are emerging as a promising alternative to lithium in portable electrical and electronic equipment and electric vehicles.

> For all comments / suggestions or to report an accident or incident: barpi@developpement-durable.gouv.fr The accident summaries recorded in the ARIA database are available at www.aria.developpement-durable.gouv.fr

Fire in drums containing lithium batteries

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