"Hazardous Substances potentially generated in "loss of control" accidents in Li-ion Battery Energy Storage systems (BESS): storage capacities implying Hazardous Substances Consent obligations"

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Hazardous Substances potentially generated in “loss of control” accidents in Li-ion Battery Energy Storage Systems (BESS) :
storage capacities implying Hazardous Substances Consent obligations

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Abstract

An outline is given of the primary legislation and the defining Regulations that determine a legal obligation to seek Hazardous Substances Consent (HSC) from the local Planning Authority before installing plant that contains Hazardous Substances (HS) above specified thresholds. The specific provisions and sources relate to installations in England but parallel legislation covers other UK nations and in fact across the EU. A provision found in “Part 3” (Substances Used in Processes) is frequently overlooked. This provides that where it is “reasonable to foresee” Hazardous Substances specified in Parts 1 or 2 being generated “if control of the processes is lost”, then any “Substance(s) S” that are “used in the process” are to be regarded as Hazardous Substances. The Controlled Quantities of such “Substance(s) S” are those amounts which it is believed may generate (in loss of control accidents) quantities exceeding the Controlled Quantities of the Hazardous Substances listed in Parts 1 or 2.

Li-ion BESS are well-known to generate in “loss of control” accidents (popularly if incorrectly known as “battery fires”) several Hazardous Substances listed in Parts 1 or 2. For application of the HSC Regulations to Li-ion BESS one therefore requires a technically sound determination of the Controlled Quantities of the “Substance(s) S” (i.e. battery constituent chemicals) that would oblige the operator to seek HSC.

In the absence of actual closed-container and open fire tests of representative samples of the actual battery cells to be installed, this paper uses literature sources to make estimates of the Controlled Quantities, based on stated energy storage capacity in MWh, since detailed chemical composition is rarely declared.

We analyse the failure behaviour of Lithium Iron Phosphate (LFP) cells versus the qualitatively different “mixed oxide” cell types (NMC, LCO etc), and criteria for HSC obligations based on P2 Flammable Gases and H1 and H2 Acute Toxic Gases, and other considerations such as the explosive failure potential of highly charged cells. We use this to estimate threshold energy storage capacities likely to carry a HSC obligation.

Also explored are: possible classification as Explosive Articles; possible generation of inhalable Nickel Oxides in fire; and possible generation of E1 Environmental Hazard in contaminated firewater.

Table 13 makes clear that most HSC thresholds are well below 50 MWh. Hence Li-ion BESS of capacity 50 MWh, regardless of cell type, will almost inevitably carry a HSC obligation. We also show that if Li-ion BESS cells are regarded as Explosive Articles, the threshold is much lower, about 15 MWh. Many such Li-ion BESS are currently being installed under Planning Consents with rated powers just below 50 MW (and typical storage somewhat above 50 MWh). In such cases, unless HSC has been applied for and granted, it would appear that an offence under S. 23 of the Planning (Hazardous Substances) Act 1990 has occurred.

For those grid-scale BESS with storage of several hundred MWh which are currently planned, the requirement for HSC becomes indisputable.

Version 3.8 11 July 2022

Table of Contents

List of Tables

List of Figures

Executive Summary

1. The Planning (Hazardous Substances) Act 1990 established the District Council (in England) as the Hazardous Substances Authority (HSA). Hazardous Substances (HS, actual, planned or foreseeable) "in, on or over the land" above specified thresholds, require the consent of the HSA. It is an offence to introduce Hazardous Substances (HS) above such thresholds without Hazardous Substances Consent (HSC) being applied for and granted. Persons controlling the land, knowingly introducing Hazardous Substances (HS), or allowing HS to be present, can all be held liable for the offence. The HSA also has the power to issue a Hazardous Substances Contravention Notice.
2. The definition of a Hazardous Substance (HS), and procedural matters, are provided in the Planning (Hazardous Substances) Regulations 2015, referred to here as the HSC Regulations. The related COMAH (Control Of Major Accident Hazards) Regulations are the UK companion to the HSC Regulations from the perspective of operational safety, in compliance with the Seveso III Directive. The COMAH Regulations refer to "Dangerous Substances" but the definitions are identical. Both Regulations use definitions of Hazardous Substances (HS) prescribed by the Seveso III Directive of the EU, and remain in force in the UK implementations.
3. Hazardous Substances HS are defined in the HSC Regulations under Part 1 (Categories of hazard – inflammables, toxics, etc), Part 2 (named substances) and Part 3 ("Substances used in processes") which applies "*where it is reasonable to foresee that a HS falling within Part 1 or Part 2 may be generated during loss of control of the processes*". In such circumstances, any Substance "S" whatever "used in the process" can be held to be a "Hazardous Substance". Part 3 is frequently overlooked, yet it is when "control of the processes is lost" that a Li-ion BESS will generate several Hazardous Substances listed in Parts 1 and 2. A "thermal runaway" or battery "fire" in a BESS represents "loss of control of the processes".
4. Note 6 to the HSC Regulations makes clear that even Hazardous Substances *not* covered by the CLP [Classification Labelling and Packaging] Regulation (which includes waste, and substances contained within "articles") must be assigned to "*the most analogous category falling in the scope of the Regulations*" if they "*possess, or are likely to possess … equivalent properties in terms of major accident potential*".
5. The current position of the Health and Safety Executive (HSE) is that the COMAH and HSC Regulations do not apply to grid-scale BESS because batteries are "articles" under the CLP Regulation. Note 6 makes clear however that being "not covered by the CLP" does not amount to an exemption. Enquiry of HSE has failed to cite any legal provision that provides an exemption for batteries. A companion paper deals with the legal interpretations, but the position of HSE appears to be wrong in law.
6. It is the mere presence of Hazardous Substances beyond the Controlled Quantities (CQs) that leads to the requirement to seek HSC. Note 4 makes clear that it is the *total inventory present* at an "establishment" that must be considered in relation to the Controlled Quantity (CQ). Spatial arrangement of the plant is irrelevant. Nor is the *likelihood* of accidents happening, or of propagating, a relevant consideration. For Part 3 to apply, all that is required is that it must be "*reasonable to foresee*" the generation of HS listed in Parts 1 and 2 "*if control of the processes is lost*", and this is now beyond speculation: it is known fact.

7. Hazardous Substances (HS) listed in Parts 1 and 2 that are known to be generated in Li-ion BESS accidents include: P2 Flammable Gases (Part 1) including methane, ethylene, ethane and carbon monoxide; H1 and H2 Acute Toxic gases (Part 1), including hydrogen cyanide, carbon monoxide, hydrogen fluoride and other unstable toxic fluorides. Explosives hazards explicitly cover "explosive articles" and Li-ion cells can certainly fail explosively and may qualify as Division 1.3 "explosive articles" and thus as a P1a Explosive (Part 1). Hydrogen may also be generated and is a Named Substance under Part 2.
8. The Controlled Quantities (CQs) of substance(s) S under Part 3 (i.e. battery component chemicals) are: *"The amount of S which it is believed may generate (on its own or in combination with other substances used in the relevant process) an amount equal to or exceeding the controlled quantity of the HS in question."* Hence it is necessary to conduct a competent engineering analysis to determine, in failure situations, how much of "S" is needed to generate CQs of the various HS listed in Parts 1 and 2.
9. The only fully reliable way of performing such analysis is by conducting actual closed container tests and open fire tests on representative samples of the actual cells to be installed. The closed container tests are needed to measure quantities of various Flammable Gases; the open fire tests are need to measure quantities of the various Acute Toxic gases such as hydrogen fluoride and carbon monoxide that are generated in various conditions of air supply or fire suppression. Explosive behaviour is determined for regulatory purposes by tests closely specified in the UN Manual of Tests and Criteria (having legal force under the CLP Regulation).
10. In the absence of such explicit tests, this paper takes reports and measurements from the technical and scientific literature to make estimates of quantities of Hazardous Substances listed in Parts 1 and 2 that may credibly be generated, in accidents, from given quantities of "Substances S" (i.e. battery chemicals) that are to be regarded themselves as Hazardous Substances under Part 3.
11. The estimates given are from the known technical literature, and obviously subject to variation depending on actual details. They represent *prima facie* indications of likely behaviour. Uncertainty can only be resolved by actual measurements, per item 9.
12. Because Li-ion battery chemistry is, in detail, a closely guarded trade secret, explicit quantities of multiple chemical components are rarely declared. However most of the literature reports the energy storage capacity of the battery cells, and this will be essentially proportional to chemicals content, by multiplication of identical cells, which may be many thousands in grid-scale BESS. Hence energy storage capacity in MWh is used as the determinant of whether Controlled Quantities (CQs) of Substances S have been exceeded. This approach also avoids needing to list separately Controlled Quantities (CQs) of individual battery component chemicals (Substance(s) "S") under Part 3.
13. "Mixed oxide" cells (e.g. LCO, NMC and other acronyms describing their complex chemistry) behave qualitatively differently from LFP (lithium iron phosphate) cells, which fail less aggressively and generate lower temperatures in accidents. However thermal runaway can still occur and there are documented explosions and fires at LFP BESS installations. LFP cells also generate smaller quantities of Flammables in failures. However they are also documented to generate *larger* quantities of toxic gases. This paper therefore contrasts "mixed oxide" and LFP cells where data is available.

14. Physical Hazards include generation of Flammable Gases under anoxic conditions which have, when mixed with air, led to several well-documented explosions. From the estimates in this paper, the Controlled Quantities (CQs) are exceeded for an installation of 23.5 MWh for the “mixed oxide” cell types. The same cell type exceeds the Controlled Quantity for carbon monoxide alone at a capacity of 45.7 MWh. For cells qualifying as P1a Explosives, the Controlled Quantities are exceeded for installations of around 15.5 MWh capacity.
15. Health Hazards include the generation of highly toxic hydrogen fluoride and other toxic gases (including carbon monoxide, which has a dual classification). From the estimates in this paper, the Controlled Quantities (CQs) are exceeded for the LFP cell types at a capacity of 16.7 – 22.1 MWh, depending on assumptions regarding carbon monoxide. The Controlled Quantity of hydrogen fluoride alone is exceeded at 25 MWh capacity, given LFP cells.
16. Environmental Hazards could include the generation of CQs of contaminated fire water if used. The Controlled Quantity is readily exceeded by the volumes of water conceivable. A contaminant potentially applicable to all cell types is copper oxide generated by burning copper foil used in the cells. Copper oxide is listed as Acute Toxic to the aquatic environment at low concentrations. Other highly toxic contaminants such a cobalt compounds may be generated from some of the “mixed oxide” cell types. Data on generation of contaminants generated in fires is however lacking, so the environmental hazard requires further investigation, but important because complete oxidation of the copper foil in fire could imply a particularly low threshold for HSC, as low as 1 MWh, for any Li-ion cell type.
17. For Nickel-based cathodes (e.g. NMC), the generation of inhalable nickel oxides in the form of smoke is reported in fire tests and supported by experts. The very low Controlled Quantity for such inhalable dusts would require HSC at a threshold around 2.75 MWh storage.
18. The various thresholds estimated in this paper below 50 MWh of energy storage capacity are summarised in Table 13, for various stated cell types and conditions. Any one of these being satisfied would imply, *prima facie*, a need to seek HSC. Per item 9, the only fully reliable way to determine a requirement would be actual fire tests on representative samples of the cells. It appears to be the responsibility of the operator to determine, and notify, the requirements; this responsibility is explicit under the related COMAH Regulations.
19. Referring to Table 13, a BESS of 50 MWh capacity based on LFP cells would exceed the Controlled Quantity CQ for the highly toxic hydrogen fluoride gas more than two-fold, without making any assumptions regarding the amount of carbon monoxide generated in fires. From the literature sources cited, it is unlikely that such installations would escape an HSC obligation, unless actual fire tests show objectively that Toxic Gas generation is below the cited estimates. If the cells behave explosively under the specified tests for explosives, then the obligations would commence at around 15.5 MWh.
20. A BESS of 50 MWh based on mixed oxide cathodes (e.g. NMC, LCO etc) would exceed the Controlled quantity of “P2 Flammable gases” at 28.3 MWh. It would exceed the CQ of carbon monoxide alone (as a Flammable Gas) at 45.7 MWh. As for LFP cells, from the literature sources cited, it is unlikely that such installations would escape HSC obligations. Mixed Oxide BESS are less likely to exceed CQs of Toxics, but more likely to exceed CQs of Flammables.
21. Operation of Li-ion BESS at 50 MWh storage, of any electrode type, without HSC, is thus likely to constitute an offence under S. 23 of the Planning (Hazardous Substances) Act 1990.

1.0 The Planning (Hazardous Substances) Act 1990

The designation (in England) of the District Council as the Hazardous Substances Authority (HSA) for installations sited in their area derives from the Planning (Hazardous Substances) Act 1990[1] (P(HS)A 1990) s.1. Various special cases are given, but the default HSA is the District Council.

The Act controls the presence (actual, planned, or foreseeable) of "hazardous substances" (HS) at industrial sites ("in, over or under the land"[2] s.4(1)) as part of the Planning process. Where involved in any site at or above "controlled quantities" (s. 4(2)) the applicant must make application for Hazardous Substances Consent (HSC) to the HSA which may grant or refuse the application, or grant subject to conditions.

It is an offence under s.23 of the Act[3] for hazardous substances present on any site without HSC being applied for and granted. The persons liable for that offence include:

s. 23(3)(b)	the person in control of the land i.e. the operator;
s. 23(3)(a)(i)	any person knowingly causing HS be present;
s. 23(3)(a)(ii)	any person allowing HS to be so present.

Fines imposed by the Court may be scaled according the financial benefit derived from the offence, s. 23(4A).

The HSA has the power under s. 24(1)[4] to serve a "hazardous substances contravention notice" which may specify such steps as appear to be required to remedy the contravention.

The meaning of "any person allowing HS to be present" in s. 23(3)(a)(ii) is not clear, but both Councillors and officers may need to consider if they are unlawfully "allowing HS to be present" by failing to require applications for HSC in respect of BESS above a certain size.

What constitutes a "hazardous substance" or the "controlled quantity" is not specified in the Act. These are determined by Regulations made by the Secretary of State under s. 5(1)(a)[5].

The present Regulations are the Planning (Hazardous Substances) Regulations 2015, (S.I. 627 of 2015)[6] which provide detailed definitions of hazardous substances, controlled quantities and procedures to be followed. These are commonly referred to as "the HSC Regulations" although that is not their formal title, and the legislation requiring HSC is the P(HS)A 1990, not the Regulations themselves.

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[1] https://www.legislation.gov.uk/ukpga/1990/10/section/1

[2] https://www.legislation.gov.uk/ukpga/1990/10/section/4

[3] https://www.legislation.gov.uk/ukpga/1990/10/section/23

[4] https://www.legislation.gov.uk/ukpga/1990/10/section/24

[5] https://www.legislation.gov.uk/ukpga/1990/10/section/5

[6] https://www.legislation.gov.uk/uksi/2015/627/introduction/made

1.1 The Planning (Hazardous Substances) Regulations 2015 (“the HSC Regulations”)

The current Regulations were made in 2015, under the authority of the P(HS)A 1990 and also of the European Communities Act 1972. In their detailed form they derive from the requirements of the “Seveso III Directive” 2012/18/EU[7] and implement the land use planning aspects of the Seveso Directive.

The HSC Regulations specify procedural matters, such as the requirement to publish notices of applications under Reg. 6(1)[8], the forms to be supplied, the notification of applications to the “COMAH competent authority” under Reg. 9(1)(b)[9] etc. However the most important aspect is that they define “for the purpose of the Act” (Reg. 3)[10] what are “hazardous substances” (HS) (Reg. 3(a)) and what are the “controlled quantities” (CQ) (Reg. 3(b)).

It is noteworthy that Reg. 3 describes “hazardous substances” as being “substances, mixtures or preparations, present as raw materials, products, by-products, residues or intermediates” – which covers a very wide range of forms in which “substances” may be present, to be covered by the Act (P(HS)A 1990).

The hazardous substances HS and their controlled quantities CQ (always listed by weight, in tonnes) are itemised in Schedule 1 to the Regulations[11], which has three Parts, each in two Columns. Column 1 lists the hazardous substances HS (Reg. 3(a)) and Column 2 lists the controlled quantities CQ in tonnes (Reg. 3(b)).

Part 1 (“Categories of Substances”) lists hazardous substances according to the “hazard categories” contained in the CLP (Classification Labelling and Packaging) Regulations. These include Health Hazards (Section H), Physical Hazards (Section P), Environmental Hazards (section E) and “Other” Hazards (Section O). To decide if a particular substance falls within any of these hazard categories require consulting the CLP Regulations and the very many listings of chemicals contained therein, and their defined hazard categories. Reg. 3(a)(i) specifies that any substance falling into one of these categories in Part 1 is a “hazardous substance” for the purposes of the Act.

Part 2 (“Named Hazardous Substances”) lists named hazardous substances which may or may not have a CAS[12] number [“only for indication”], and specifies particular substances with well-known associated hazards and specific controlled quantities which may be different from the CQ in Part 1 determined on the basis of the Hazard Category of the substance. Reg 3(a)(ii) specifies that any substance specified in Part 2 is a hazardous substance for the purposes of the Act.

Definition for this paper: For clarity in what follows, in this paper we will refer to a “*listed* hazardous substance” or “*listed* HS” to be any HS specified in either Part 1 or Part 2. This is to distinguish these HS clearly from the hazardous substances description given in Part 3.

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[7] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32012L0018

[8] https://www.legislation.gov.uk/uksi/2015/627/regulation/6/made

[9] https://www.legislation.gov.uk/uksi/2015/627/regulation/9/made

[10] https://www.legislation.gov.uk/uksi/2015/627/regulation/3/made

[11] https://www.legislation.gov.uk/uksi/2015/627/schedule/1/made

[12] CAS=Chemical Abstracts Service, a division of the American Chemical Society, a US-based chemicals database. A CAS Registry Number or “CAS number” is a unique serial number identifying a particular chemical compound.

Part 3 ("Substances used in Processes") defines a hazardous substance as:

> Where it is reasonable to foresee that a substance falling within Part 1 or Part 2 ("HS") may be generated during loss of control of the processes, including storage activities in any installation within an establishment, any substance which is used in that process ("S").

Reg. 3(a)(iii) defines a HS as one "meeting the description in Column 1 of Part 3 of that Schedule" i.e. Schedule 1 to the Regulations. "The description in Column 1" is quoted above.

In other words, *any substance "S" whatever* is to be considered a hazardous substance (HS) for the purposes of the Act, under Reg 3(a)(iii) and Schedule 1 Part 3 Column 1 — provided only that it is "*reasonable to foresee*" the *listed* HS (in Parts 1 or 2) being "*generated* [from S] *during loss of control of the processes*".

The Controlled Quantity (CQ) of the substance(s) "S" (e.g. the chemical components of battery cells) is defined in Column 2 of Part 3, and reads:

> The amount of S which it is believed may generate (on its own or in combination with other substances used in the relevant process) an amount equal to or exceeding the controlled quantity of the HS in question.

In other words, the CQ of substances "S" (e.g. battery chemical components) are those amounts which may generate quantities of *listed* HS (i.e. Hazardous Substances listed in Parts 1 or 2) above the CQs for those *listed* HS, "during loss of control of the processes".

The provisions of Part 3 are frequently overlooked, consistently so in Planning Applications for BESS installations across the UK, although the point has been raised in respect of individual Planning Applications, and one example will be cited below. Yet the Regulations are the UK implementation of the Seveso III Directive, and have their origin in the Seveso disaster of 1976, which was itself a "loss of control" accident. The entire history of the Seveso directive shows that it was always intended to cover not only hazardous substances present by design, but also hazardous substances generated in accidents, where "control of the processes is lost".

Moreover, "loss of control" accidents in Li-ion BESS are the principal safety hazard that these systems present to the public and to the environment. In normal operation, they will be innocuous, and the chemicals on which the battery technology is based are either not "*listed* HS" at all, or else are typically present below the CQs. In other words, Parts 1 and 2 are unlikely to compel the operator of a Li-ion BESS to seek HSC.

Part 3 is an entirely different matter. The well-known phenomenon of "thermal runaway" is a known failure mode of Li-ion batteries, and is equally well-known to generate HS in the hazard classes H1 and P2 of Part 1 and at least one "Named HS" in Part 2 when such accidents occur. The substances "S" are then all the chemicals integral to the Li-ion cells, which under Part 3 and Reg. 3(a)(iii) are to be considered as "hazardous substances" (HS) for the purposes of the Act, even though not listed in Parts 1 or 2, because they have the potential to generate "*listed* HS" during "loss of control of the processes" i.e. if thermal runaway or a "battery fire" occurs.

1.2 Hazardous Substances and Controlled Quantities under Part 3:

Part 4 of Schedule 1[13] contains various Notes to Parts 1 to 3. Note 4 in Schedule 1 says:

> The controlled quantities set out in Parts 1 to 3 of this Schedule relate to each establishment.
>
> The quantities to be considered for the application of these Regulations are the maximum quantities which are present or are likely to be present at any one time.

The first sentence shows that the Controlled Quantities are the aggregate quantities contained in each "establishment" i.e. land under the control of a single operator. **It is the mere presence of the HS above the CQ which requires HSC; spatial arrangement of plant or containers is irrelevant, and is mentioned nowhere in the Act or in the HSC Regulations.**

In the second sentence, with regard to Part 3, it must be remembered that the regulated "hazardous substances" under Part 3 are any and all of those substances "S" that may generate *listed* HS in loss of control accidents. It is those "substances "S" that are the regulated "hazardous substances" under Part 3, *not* the "*listed* HS" that may be generated in loss of control. Therefore, the "maximum quantities which are present or likely to be present at any one time" can only refer to the maximum quantities of such substances "S". In the case of BESS, this is the maximum aggregate chemical components of all the battery cells present in the "establishment".

It would be inconsistent to read Note 4 as referring to the "maximum quantities of *listed* HS that are likely to be *generated* during particular loss of control accidents." This is simply *not* what this Note to the Regulations says. To interpret Note 4 in this way would be wholly inconsistent with the application of the HSC Regulations to a substance listed in Parts 1 or 2.

It should also be noted that nothing in the Regulations requires consideration of the likely *extent* of a "loss of control" situation, or the likelihood of a major accident relative to a localised incident. The Regulations require only that it be "reasonable to foresee" that a *listed* HS may be generated in loss of control accidents.

The controlled quantities of substances "S" under Part 3 are then clearly defined: the CQ(s) are those quantities of substance(s) "S" required to generate an amount exceeding the CQ of any *listed* HS in Parts 1 or 2, taking account of the Aggregation Rule given in the following Note 5.

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[13] https://www.legislation.gov.uk/uksi/2015/627/schedule/1/made

1.3 The "Aggregation Rule" of Note 5:

It is critical also to consider Note 5, sometimes called[14] the "Aggregation Rule", which specifies how multiple HS in the same hazard class are to be aggregated to determine if the CQ has been exceeded. If no single substance is present (or "foreseeably generated") above its CQ, then the Regulations still apply if quantities of multiple HS are aggregated according to the Rule given in Note 5:

> The following rule governing the addition of hazardous substances, or categories of hazardous substances, applies where appropriate.
>
> In the case of an establishment where no individual hazardous substance is present in a quantity above or equal to the relevant controlled quantity, the following rule must be applied to determine whether the establishment is covered by the relevant requirements of these Regulations.
>
> These Regulations apply to establishments if the sum
>
> $q_1/Q_{L1} + q_2/Q_{L2} + q_3/Q_{L3} + q_4/Q_{L4} + q_5/Q_{L5} + \ldots$ is greater than or equal to 1,
>
> where
>
> q_x = the quantity of hazardous substance x (or category of hazardous substances) falling within Part 1 or Part 2 of this Schedule; and
>
> Q_{LX} = the relevant controlled quantity for hazardous substance x (or category of hazardous substances x) from Column 2 of Part 1 or from Column 2 of Part 2 of this Schedule (except for those substances for which column 2 contains a quantity Q*, in which case, for Hydrogen, Q is equal to 5, and for Natural Gas (including liquefied natural gas), Q is equal to 50).[15]
>
> This rule must be used to assess the health hazards, physical hazards and environmental hazards. **It must therefore be applied three times—**
>
> (a) for the addition of hazardous substances listed in Part 2 that fall within acute toxicity category 1, 2 or 3 (inhalation route) or STOT SE category 1, together with hazardous substances falling within section H, entries H1 to H3 of Part 1;
>
> (b) for the addition of hazardous substances listed in Part 2 that are explosives, flammable gases, flammable aerosols, oxidising gases, flammable liquids, self-reactive substances and mixtures, organic peroxides, pyrophoric liquids and solids, oxidising liquids and solids, together with hazardous substances falling within section P, entries P1 to P8 of Part 1;
>
> (c) for the addition of hazardous substances listed in Part 2 that fall within hazardous to the aquatic environment acute category 1, chronic category 1 or chronic category 2, together with hazardous substances falling within section E, entries E1 and E2 of Part 1.
>
> **The relevant provisions of these Regulations apply where any of the sums obtained by (a), (b) or (c) is greater than or equal to 1.**

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[14] The COMAH Regulations 2015: Guidance on Regulations L111 (3rd edition) ISBN 978 0 7176 6605 8 https://www.hse.gov.uk/pubns/priced/l111.pdf See page 92 of 132 Guidance Note 384.

[15] The majority of named hazardous substance in Part 2 have the same controlled quantities as for "lower tier" establishments under the COMAH Regulations. However the CQs for Hydrogen (entry 15) and for Natural Gas (entry 18) are lower, being 2 tonnes and 15 tonnes respectively under the HSC Regulations, and are marked with an asterisk, i.e. "Column 2 contains a quantity Q* ". Where the establishment does not exceed these quantities for Hydrogen or for Natural Gas alone, this qualification under the Aggregation Rule in Note 5 reverts the applicable quantities for aggregating Hydrogen or Natural Gas to those listed for the same Rule under the COMAH Regulations, viz. 5 tonnes and 50 tonnes respectively.

1.4 Other relevant Notes in Part 4:

Note 1: Substances and mixtures are classified in accordance with the CLP Regulation.

This refers primarily to the hazard categories used in Part 1. However it has been argued that batteries are classified as "articles" under the CLP Regulation, and hence not "substances" at all as regards application of the law. Under this argument, there can be no "substance S" to consider within Part 3, so Part 3 would not apply.

However this is not the case. Batteries are classified under the REACH Regulation as "articles with integral substance(s)"; hence the "substance(s) S" referred to in Part 3 are simply those "substances integral to the article" in the meaning of the CLP Regulation i.e. the chemical components of the battery cells. This point is examined in more detail elsewhere.

Note 2: Mixtures shall be treated in the same way as pure substances provided they remain within concentration limits set according to their properties under the CLP Regulation, or its latest adaptation to technical progress, unless a percentage composition or other description is specifically given.

This Note confirms in respect of mixtures the language of Reg. 3(a):

> hazardous substances are substances, mixtures or preparations— [*in Parts 1 2 or 3*]
> … and present as raw materials, products, by-products, residues or intermediates;

Note 6: In the case of hazardous substances which are not covered by the CLP Regulation, 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 must be provisionally assigned to the most analogous category or named hazardous substance falling within the scope of these Regulations.

This Note shows that "unlisted" substances outside the scope of the CLP Regulation must nevertheless be assigned provisionally to the most analogous category within the scope of the HSC Regulations. Only a fraction of the registered chemicals in the ECHA database have Harmonised Classifications; that is an ongoing "work in progress". Whether a chemical has a Harmonised Classification or not, it still falls under the CLP Regulation once it has any of the hazardous properties defined by the UN GHS classification methodology. An example would be the toxic (and unstable) gas Phosphoryl Fluoride POF_3 known to be evolved from BESS "fires" but which lacks a Harmonised Classification under the CLP Regulation.

This Note also shows that "waste" (which is not covered by the CLP Regulation) is nevertheless covered by the HSC Regulations. "Waste" will always be ill-defined as to chemical composition and likely to be mixed with many chemical substances, parts, objects, and could well include hazardous substances contained within "articles".

It is clear that the drafters did not intend there to be "loopholes" for hazardous substances, even if such are *not* covered by the CLP Regulation. This Note effectively refutes the HSE position that BESS are "articles" (not covered by CLP) and therefore exempt.

Note 7: In the case of hazardous substances with properties giving rise to more than one classification, for the purposes of these Regulations the lowest controlled quantities apply. However, for the application of the rule in note 5, the lowest controlled quantity for each group of categories in notes 5(a), 5(b) and 5(c) corresponding to the classification concerned must be used.

This Note resolves potential ambiguities in dual classifications in Part 1, and with application of the Aggregation Rule Note 5. For example, Carbon Monoxide is both toxic (section H) and inflammable (section P) and therefore has a dual classification under the sections of Part 1.

Note 9: The hazard class Explosives includes explosive articles (see Section 2.1 of Annex I to the CLP Regulation). If the quantity of the explosive substance or mixture contained in the article is known, that quantity must be considered for the purposes of these Regulations. If the quantity of the explosive substance or mixture contained in the article is not known, then, for the purposes of these Regulations, the whole article must be treated as explosive.

Note 10: Testing for explosive properties of substances and mixtures is only necessary if the screening procedure according to Appendix 6, Part 3 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria (UN Manual of Tests and Criteria)(**1**) identifies the substance or mixture as potentially having explosive properties.

Notes 9 and 10 raise the possibility that BESS cells should be considered as "explosive articles". BESS cells can certainly fail explosively, but this behaviour depends of the cell's State of Charge (SoC). The point will be examined further below.

Note 23: Where a hazardous substance falls within both Parts 1 and 2 of this Schedule, the controlled quantity in Part 2 applies.

This Note resolves ambiguities between substances classified in both Parts 1 and 2.

Note 24: In relation to Part 3—
(a) where S also falls within Part 1 or Part 2, the classification with the lowest controlled quantity applies; and
(b) where S also falls within Part 1 and Part 2, the controlled quantity which is lowest when the controlled quantities under Part 2 and Part 3 are compared applies.

This Note resolves ambiguities between substances S controlled under both Part 3, and Parts 1 or 2.

2.0 Applicability of the HSC Regulations to BESS

In relation to Li-ion BESS, not only is it "reasonable to foresee" that *listed* HS may generated "if control of the processes is lost", it is certain, and well-documented in the technical literature. Moreover, the failure mode of "thermal runaway" is well-known and an increasing list of BESS "fires" in many parts of the world shows that such accidents are now matters of record, not speculation. It is now impossible to argue that generation of *listed* HS in loss of control accidents would not be "reasonable to foresee": such generation, and the occurrence of loss of control accidents in BESS, are documented facts.

Therefore, under Part 3, any substance "S" used in the BESS cells should be considered a Hazardous Substance, and it is those cell component chemicals "S" that are controlled, and have the controlled quantities CQ applied to them.

The CQs are *not* the quantities of *listed* HS predicted to be generated in any particular accident. Nothing in the Regulations depends on likelihood of occurrence, or predicted extent of accidents; the Regulations simply regulate the total inventory of hazardous substances.

Under the loss of control considerations of Part3, any substances "S" "foreseeably generating" *listed* HS are to be considered hazardous substances themselves, and the CQ is that amount of "S" which may generate a CQ of a *listed* HS in loss of control.

It is hard to see how grid-scale BESS can escape the "loss of control" provisions of Reg 3(a)(iii) and Part 3 of Schedule 1.

It is equally hard to see how the quantity determining the requirement for HSC under P(HS)A s.4(2)[16] can be other than the total inventory of battery chemical components "S", regulated as hazardous under Part 3, that are present in the "establishment" (P(HS)A s.4(2)(aa)).

The technical question requiring consideration is therefore to determine the CQ of those substances "S", being integral components of the battery cells, which would generate controlled quantities of *listed* HS "if control of the process is lost", aggregated over the whole establishment. Some estimates are made in subsequent sections.

2.1 Determination of CQ of integral substance(s) S considered hazardous under Part 3

From the foregoing considerations, the determination of a CQ under Part 3, for BESS integral substances "S", requires consideration of:

i. The *listed* hazardous substances foreseeably generated in loss of control of the processes;
ii. the quantity of all *listed* HS generated from given quantities of battery components "S";
iii. the application of the Aggregation Rule to determine if the CQs are exceeded;
iv. the separate application of the Aggregation Rule for Toxics (H), Flammables (P) and potentially Environmental (E) hazards.

The requirement for HSC commences at the lowest BESS inventory which first results in either an individual substance exceeding its CQ, or one particular hazard class (H, P or E) exceeding unity when calculating the sum given in the Aggregation Rule.

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[16] https://www.legislation.gov.uk/ukpga/1990/10/section/4

2.2 Relationship of the HSC Regulations to the COMAH Regulations

Operational health and safety aspects of the Seveso Directive were implemented in the form of the Control of Major Accident Hazards (COMAH) Regulations 2015[17] under the provisions of other parent legislation (in particular the Health and Safety at Work etc Act 1974[18]). The COMAH Regulations are not the concern of the local Planning Authority, however the same list of dangerous substances together with controlled quantities appears in the COMAH Regulations, and the HSC Regulation 9(1)(b)[19] requires the HSA to notify the "COMAH competent authority" on receipt of a HSC application. In England, the "COMAH competent authority" is the Health and Safety Executive (HSE) plus the Environment Agency (EA) acting jointly (Reg. 4)[20].

Apart from the change of language from "hazardous substances" (HSC Regulations e.g. Reg. 3[21]) to "dangerous substances" (COMAH Regulations e.g. Reg. 2[22]), inspection of the Schedules to both sets of Regulations show that the substances in question are essentially identical, being based on the same hazard classes in the CLP (Classification Labelling and Packaging) Regulation[23]. It was necessary for both sets of regulations to be aligned in this way in order for the UK to be compliant with the Seveso III Directive[24] 2012/18/EU; that is the reason that the Schedules prescribe essentially the same substances.

The Controlled Quantities in the HSC Regulations correspond to the Controlled Quantities in the "lower tier" of the COMAH Regulations. "Upper tier" in the COMAH Regulations prescribes more stringent controls in accident prevention but those higher thresholds do not affect the operation of the HSC Regulations.

Two named substances, viz. Hydrogen and Natural Gas, have lower Controlled Quantities for the purposes of the HSC Regulations than they do for the purposes of the COMAH Regulations, but these are specific exceptions.

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[17] https://www.legislation.gov.uk/uksi/2015/483/introduction

[18] https://www.legislation.gov.uk/ukpga/1974/37/contents

[19] https://www.legislation.gov.uk/uksi/2015/627/regulation/9/made

[20] https://www.legislation.gov.uk/uksi/2015/483/regulation/4

[21] https://www.legislation.gov.uk/uksi/2015/627/regulation/3/made

[22] https://www.legislation.gov.uk/uksi/2015/483/regulation/2

[23] https://www.legislation.gov.uk/eur/2008/1272/contents ; also https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32008R1272 and "Guidance in the application of the CLP criteria" Regulation EC 1272/2008 on classification labelling and packaging of substances and mixtures" ECHA version 5.0 July 2017 https://echa.europa.eu/documents/10162/23036412/clp_en.pdf/58b5dc6d-ac2a-4910-9702-e9e1f5051cc5

[24] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32012L0018

3.0 Hazardous Substances under Parts 1 or 2 generated in loss of control accidents in BESS

The principal failure mode ("loss of control of the processes") that has to be considered is that of "thermal runaway" described in a previous report[25]. Popularly called a "battery fire" this need not involve flames at all, but generation of a toxic and inflammable "vapour cloud" that if mixed with air and ignited may cause a rapid deflagration or "vapour cloud explosion". The 2019 accident at McMicken, Arizona[26], was of this nature, and did not involve flames except in the explosion itself[27]. It derived just one rack out of 27 in a relatively small BESS, but resulted in a dramatic explosion that caused life-limiting injuries to three out of four first-responders.

Actual fires are also possible and have occurred in the increasing catalogue of major BESS fires, and even in a fully discharged BESS would probably involve combustion of the organic components of the cells, producing gases "typical of a plastics fire".

The only fully reliable method of determining a complete list of hazardous substances that might be generated in loss of control situations would be to perform actual "fire tests" with comprehensive chemical analysis, including fire-fighting situations involving water cooling, and contaminated "fire water". Such tests should ideally be done on representative samples of the actual battery cells proposed to be installed, whose exact composition is usually a strongly protected trade secret. Such comprehensive tests have rarely if ever been performed, but a list of leading contenders may be derived from reports in the technical literature, both from laboratory reports and published scientific papers, and engineering failure analyses of major BESS "fires" that have received *post hoc* investigation.

Flammable and Toxic Gases: From the technical literature, the gases listed in Table 1 are potentially generated in loss of control accidents.

Some of these, such as Hydrogen Cyanide (HCN) and Hydrogen Chloride (HCl), are probably generated from incidental packaging or insulation polymers such as polyurethane (PU) or poly(vinyl chloride) (PVC); Li-ion BESS chemicals are dominated by fluorine-containing polymers, and are predominantly not nitrogen-containing nor chlorine-containing. Nevertheless, HCN in particular is a well-known hazard to fire-fighters, a common cause of death in fires, and was an explicit cause of concern to professional fire-fighters in the 2019 McMicken incident. Also, expert reports indicate that "a common signature of a suspected thermal runaway event is the presence of HCN, HCl, or HF", so HCN and HCl toxic gases require consideration from an operational and fire-fighting perspective even if they may be minor components.

The remaining gases fall into two groups. Hydrogen, Ethylene, Methane and Carbon Monoxide are all known to be evolved in thermal runaway and are classified as "P2 Flammable Gases" under the HSC Regulations. Hydrogen Fluoride and Phosphoryl Fluoride are evolved in thermal runaway, and in subsequent air-dependent fires Carbon Monoxide will continue to be produced where

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[25] Fordham E J, Allison W & Melville D (2021) "Safety of Grid-scale Li-ion Battery Energy Storage Systems", 5 June 2021 On *Research Gate* preprint server DOI: 10.13140/RG.2.2.11566.79687

[26] Hill D (2020). McMicken BESS event: Technical Analysis and Recommendations, Arizona Public Service.
Technical support for APS related to McMicken thermal runaway and explosion." Report by DNV-GL to Arizona Public Service, 18 July 2020. Document 10209302-HOU-R-01

[27] McKinnon M B, DeCrane S, Kerber S (2020). Four fire-fighters injured in Lithium-ion Battery Energy Storage System explosion – Arizona. *Underwriters Laboratories* report July 28, 2020. UL Firefighter Safety Research Institute, Columbia, MD 20145

combustion of organic materials or graphite from battery anodes is incomplete. These gases are classified as “H1 or H2 Acute Toxic” health hazards (CO is both combustible and toxic).

Environmental hazards (substances Toxic to the aquatic environment): Finally, the possibility of substances Toxic to the Aquatic Environment must be considered. The most serious source of aquatic toxic substances in a loss of control event at a BESS arises when water is used in fire-fighting. Although the Controlled Quantity of substances E1 “Hazardous to the Aquatic Environment in Category Acute 1 or Chronic 1” is 100 tonnes, this tonnage of contaminated fire water easily arises if a cumulative amount of water exceeding 100 m^3 is deployed in firefighting.

Moreover, the CQ of E1 Environmentally hazardous substances need not refer to a tonnage of pure substance; generally speaking they do not. The tonnage refers to the contaminated fire water (or other similar mixture). The concentrations of toxic materials which may be regarded as “toxic to the aquatic environment” may be quite low, and are specified by means “M-factors” (short for “multiplying factor”)[28] which are assigned for substances classified as toxic to the aquatic environment on the basis of LC_{50} or EC_{50} or NOEC concentrations in tests against fish, crustacea or plants. Details are explained in Annexes to the CLP Regulation.

In the practical application of M-factors, what matters for the purposes of this paper is the concentration at which contaminated fire water would be considered as “E1 Toxic to the aquatic environment”. This is itself likely to be a complex mixture in fire situations, and toxic substance concentrations must be summed according to the “Summation Method”[29]. This is a technical part of the CLP Regulation and a different summation from that required in the Aggregation Rule of Note 5 to the HSC Regulations; the Summation Method is a method for classifying *mixtures* of environmentally toxic substances according to the environmental toxicity assessed for the substances.

For substances classified as “Acute 1”, the Summation method is a simple addition (more complicated sums are defined for mixtures of substances with lower Categories of toxicity). Then[30] a mixture is classified as “Acute 1” if the sum of concentrations of toxic components multiplied by their M-factors is $\geq$ 25%. Similar considerations[31] apply for mixtures to be classified as “Chronic 1”.

This means for example that a 2.5% concentration (by weight) of a substance classified as Acute Toxic 1 with a M-factor of 10 is to be classified as Acute Toxic (to the aquatic environment) Category 1, and similarly for Chronic Toxicity. Both Category 1 classifications are classified as E1 under the HSC Regulations. Chronic Category 2 mixtures are classified E2 under the HSC Regulations.

Cobalt (II) oxide is an oxide conceivably generated in oxidising fires from cells with cobalt-containing cathodes. An M-factor of 10 is listed; if present at 2.5% by weight in water, this would be classified as an E1 environmental hazard. If additional toxic metal oxides or other compounds with M-factor 10 were present, the contaminated fire water becomes a E1 Environmental hazard if the summation of all toxic compounds exceeds 2.5% by weight in water.

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[28] See appropriate sections of the CLP Regulation for the use of M-factors

[29] Annex I to the CLP Regulation, section 4.1.3.5.5. See Guidance document https://echa.europa.eu/documents/10162/23036412/clp_en.pdf/58b5dc6d-ac2a-4910-9702-e9e1f5051cc5

[30] Rule defined in Table 4.1.1 of Annex I to the CLP Regulation, also in the above Guidance document.

[31] Table 4.1.2 of Annex I to the CLP Regulation.

Some potentially relevant environmentally toxic substances are listed in Table 2 with M-factors where available. One (cobalt lithium nickel oxide) is an actual Li-ion battery cathode material. The others are toxic substances conceivably generated during BESS "fires" or thermal runaway events. Some of these oxides will occur only for certain electrode chemistries, for example the popular "NMC" (nickel manganese cobalt" cathode chemistry. The "LFP" (Lithium iron phosphate) cathode chemistry does not contain cobalt or nickel so the cobalt compounds would not be present.

However all classes of Li-ion battery have the same anode concept, which is finely divided graphite (carbon) supported on a thin copper foil. Large tonnages of copper foil will be present in grid-scale BESS which are likely to oxidise in fires to form copper oxides; both copper (I) oxide and copper (II) oxide are Acute and Chronic Toxic to the aquatic environment in Category 1. Moreover both these oxides of copper have a large M-factor (100) for acute toxicity in the aquatic environment, meaning that solutions or dispersions (mixtures) of these oxides in water as low as 0.25% by weight are classified as Acute Toxic, Category 1, and E1 environmental hazards under the HSC Regulations.

Therefore, fire water contaminated with copper oxides at only 0.25% is classified as an E1 environmental hazard under the HSC Regulations. A fire-fighting operation using 100 m^3 of fire water then exceeds the Controlled Quantity of E1 Environmental Hazard, provided only that the fire water is contaminated with 0.25% by weight (i.e. 0.25 tonnes or 250 kg) of copper oxides generated in a large fire.

Other copper compounds potentially generated are copper fluoride CuF_2, which forms in oxidising conditions from Cu metal, oxygen and HF at temperatures above 400 °C, with water (steam) as the other reaction product[32]. This is a conceivable reaction in a fire also generating HF gas; the CuF_2 is slightly soluble in water and decomposes in hot water forming copper hydroxide[33], another listed compound with a harmonised Classification as Acute and Chronic Toxic, Category 1.

Transition (Group III) metals such as Cobalt, Nickel, Manganese and Copper are well-known to form compounds which are persistent and toxic to living systems except in trace quantities. It is no surprise therefore that listed compounds already have Aquatic Toxicity classifications and assigned M-factors for application to the CLP Regulation and hence to the HSC Regulations. Whilst some of the problems associated with the NMC electrode chemistry could be avoided by using the LFP chemistry, because *all* designs of Li-ion battery to date use copper foil as a support for graphite in the anodes, the environmental toxicity problems associated with copper compounds cannot be avoided.

The variety of cathode chemistries in Li-ion battery cells, the ubiquitous presence of copper foil as an anode structure and the toxic compounds that may be generated in BESS fires all warrant further investigation for the application of the Environmental Hazard section of the HSC Regulations (and of course for environmental protection in general).

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[32] Subramanian, M.A. and Manzer, L.E. (2002) *Science* **297** 1665 DOI: 10.1126/science.1076397

[33] *Wikipedia* entry for Copper (II) fluoride

Name of Gas	Chemical formula	HSC ("Seveso") hazard category	GHS[34] Hazard Codes, Classes and Categories as listed in the C&L Inventory of ECHA or GB Mandatory Classification and Labelling List	Controlled Quantity (tonnes)	Source of data
Hydrogen	H_2	P2 Flammable Gas (Part 1) Named substance (Part 2)	H220 Flammable Gas, Cat. 1A	2 (named, HSC) 5 (COMAH) & for Aggregation Rule	HSC Regs C&L Inventory[35]
Ethylene	C_2H_4	P2 Flammable Gas	H220 Flammable Gas, Cat. 1A H336 STOT SE, Cat. 3	10 (P2)	HSC Regs C&L Inventory
Methane	CH_4	P2 Flammable Gas	H220 Flammable Gas, Cat. 1A	10 (P2)	HSC Regs C&L Inventory
Carbon Monoxide	CO	P2 Flammable Gas H2 Acute Toxic, Cat. 3, inhalation	H220 Flammable Gas, Cat 1A. H331 Acute Toxicity, inhalation, Cat. 3 H372 STOT RE 1 H360D Reproductive Toxicity, Cat. 1	10 (P2) 50 (H2)	HSC Regs C&L Inventory
Hydrogen Chloride	HCl	H2 Acute Toxic, Cat. 3, inhalation Named substance (Part 2) if liquefied	H331 Acute Toxicity, inhalation, Cat. 3 H314 Skin corrosion, Cat. 1A,B,C	50 (H2) 25 (named)	HSC Regs C&L Inventory
Hydrogen Cyanide	HCN	H1 Acute Toxic (as mixture) H2 Acute Toxic (as pure substance) E1 Aquatic Hazard Acute, Cat. 1 E1 Aquatic Hazard Chronic, Cat. 1	H300 Acute Toxic, oral, Cat. 2 H330 Acute Toxic, inhalation, Cat. 2 H310 Acute Toxic, dermal, Cat. 1 H400 Aquatic Hazard, Acute, Cat. 1 H410 Aquatic hazard, Chronic, Cat 1	5 (H1) 50 (H2) 100 (E1)	GB Mandatory Classification and Labelling List, HSE[36]
Hydrogen Fluoride	HF	H1 Acute Toxic (dermal) H2 Acute Toxic (oral, inhalation)	H300 Acute Toxic, oral, Cat. 2 H310 Acute Toxic, dermal, Cat. 1 H330 Acute Toxic, inhalation, Cat. 2 H314 Skin Corrosion, Cat. 1A	5 (H1) 50 (H2)	HSC Regs C&L Inventory
Phosphoryl Fluoride	POF_3	Not determined but precursor of HF so likely to be H1 Acute Toxic per Note 6	Not listed in C&L Inventory or GB MCL List but "provisionally assigned" H310 per Note 6	5 (H1)	HSC Regs

Table 1: Gaseous Hazardous Substances generated in BESS loss of control accidents

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[34] GHS= Global Harmonised System is a UN-sponsored classification to which the EU and UK voluntarily adhere for the purposes of the CLP Regulation. Hazard codes are defined and explained in multiple chemicals databases and in UNECE documents e.g. https://unece.org/DAM/trans/danger/publi/ghs/ghs_rev07/English/06e_annex3.pdf

[35] The C&L Inventory is a database of the European Chemicals Agency ECHA containing many Harmonised Classifications for the purposes of the CLP Regulation https://echa.europa.eu/information-on-chemicals/cl-inventory-database?p_p_id=dissclinventory_WAR_dissclinventoryportlet&p_p_lifecycle=0&p_p_state=normal&p_p_mode=view

[36] Harmonised Classification is only H2 for the pure substance though the great majority of Notified Classifications reckon HCN as Acute Toxic Category 1 hence H1. The HSE GB MCL list is authoritative for GB (though not for NI) after Brexit and was therefore consulted here. "All existing EU harmonised classification and labelling in force on 31 December 2020 are retained in GB as the GB Mandatory Classification and Labelling List" https://www.hse.gov.uk/chemical-classification/legal/clp-regulation.htm

Name of Substance	Chemical formula	HSC (“Seveso”) hazard category	GHS Hazard Codes, Classes and Categories as listed in the C&L Inventory of ECHA	M-factors	Controlled Quantity (tonnes)	Source of data
Cobalt (II) Oxide	CoO	E1 Hazard to Aquatic Environment, Acute 1 or Chronic 1	H400 Aquatic Acute Cat. 1 H410 Aquatic Chronic Cat. 1 H370 STOT SE 1 is Notified to CLP but not Harmonised	10	100 (E1)	EC List number 215-154-6
Cobalt (II,III) Oxide	Co_3O_4	Provisionally E1 Aquatic hazard, per Note 6	No harmonised classification found but likely to be H400 and H410 for same reasons as for CoO	Not found	100 (E1)	EC List number 215-157-2
Cobalt Lithium Nickel Oxide	Complex. IUPAC name: cobalt dihydrate lithium hydride nickel	E1 Hazard to Aquatic Environment, Acute 1 or Chronic 1 H3 STOT SE Cat. 1	H400 Aquatic Acute Cat. 1 H410 Aquatic Chronic Cat. 1 H372 STOT RE 1	Not found	100 (E1) 50 (H3)	EC List number 442-750-5
Copper (I) oxide	Cu_2O	E1 Hazard to Aquatic Environment, Acute 1 or Chronic 1	H400 Aquatic Acute Cat. 1 H410 Aquatic Chronic Cat. 1 Harmonised classification	100 (acute) 10 (chronic)	100 (E1)	EC List number 215-270-7
Copper (II) oxide	CuO	E1 Hazard to Aquatic Environment, Acute 1 or Chronic 1	H400 Aquatic Acute Cat. 1 H410 Aquatic Chronic Cat. 1 Harmonised classification	100 (acute) 10 (chronic)	100 (E1)	EC List number 215-269-1
Copper (II) hydroxide	$Cu(OH)_2$	E1 Hazard to Aquatic Environment, Acute 1 or Chronic 1	H400 Aquatic Acute Cat. 1 H410 Aquatic Chronic Cat. 1 Harmonised classification	10 10 (chronic)	100 (E1)	EC List number 243-815-9
Copper (II) Fluoride	CuF_2	Provisional E1 – see text	Not found in C&L Inventory	Use value for $Cu(OH)_2$	100 (E1)	Listing in Wikipedia
Dicopper chloride trihydroxide	$Cu_2Cl(OH)_3$	E1 Hazard to Aquatic Environment, Acute 1 or Chronic 1	H400 Aquatic Acute Cat. 1 H410 Aquatic Chronic Cat. 1 (Harmonised Classification)	10 10 (chronic)	100 (E1)	EC List number 215-572-9
Copper (I) chloride	$CuCl$	E1 Hazard to Aquatic Environment, Acute 1 or Chronic 1	H400 Aquatic Acute Cat. 1 H410 Aquatic Chronic Cat. 1 (Harmonised Classification)	Not found	100 (E1)	EC List number 231-842-9

Table 2: Environmentally Hazardous Substances potentially generated from electrode materials in BESS loss of control accidents (indicative only: not exhaustive)

3.1 Routes to generation of Part 1,2 Hazardous Substances in loss of control accidents in BESS: (I) Generation of P2 Flammable gases in Anoxic conditions

An early consequence of “thermal runaway” events in BESS is known to be the generation of inflammable gases. These are necessarily generated in anoxic conditions within the cell or the gases would immediately burn. A cloud of combustible vapour and organic electrolyte droplets may form, which subsequently mixes with air and may then ignite in a so-called “vapour cloud explosion” or they may burn in other modes. The details of subsequent fire or explosion are immaterial to the application of the HSC Regulations which are concerned solely with the quantities of the flammable gases (or other “Physical” hazards) which may be generated in loss of control events.

One literature source, by Golubkov *et al.*[37], gives quantities of gases evolved from typical Li-ion battery cells and is widely relied upon by industry experts analysing BESS accidents. The gases detected include the hydrocarbons in Table 1, hydrogen, and carbon monoxide and dioxide. A limitation of the measurement system was that the known reaction product hydrogen fluoride (HF) was not detected; this highly toxic gas can however be estimated from other sources (below).

Proportions and total quantities are given for various cell types, including the widely used “NMC” and “LFP” electrode chemistries. A hybrid cathode, LCO-NMC, is included. Typical compositions of whole cells (by mass) are also given, together with temperatures reached at and in thermal runaway. The LCO-NMC and LFP types describe the range of behaviour in thermal breakdown. An abstract of relevant parameters[38] taken from this paper is given in Table 3, including the total amount of gases evolved. The same source provides measurements of proportions of the different gases evolved during thermal runaway (in anoxic conditions). For application to commercial BESS, where cell details are unlikely to be disclosed for reasons of commercial sensitivity, but overall energy storage capacities in MWh will generally be disclosed, or required by regulatory authorities, we need estimates of the masses of different gases evolved, per unit energy storage in Wh (or on the large scale, in MWh). These are given in Table 4, calculated using standard molecular weights, and the energy storage estimates in Table 3.

For application of the HSC Regulations we require quantities as masses (over the whole site, in tonnes). For the “P2 Flammable Gases” only, the same masses are given in Table 5 scaled to a nominal 50 MWh of energy storage, and their contributions to the summation in the Aggregation Rule are shown in the right-most columns, for the two cell types. The energy storage at which the Aggregation Rule sums exceed unity is also given, in MWh.

We may conclude from the data given in this published source, that BESS based on LCO-NMC cathodes should trigger a HSC assessment at a storage capacity of 28.3 MWh, based on the Aggregation Rule. For BESS based on LFP cells, the assessment threshold is higher, at 126 MWh. A HSC assessment would be required for the LCO-NMC electrode type, on the basis of Carbon Monoxide alone (CQ = 10 tonnes[39]) at 45.7 MWh.

These estimates are derived from a single source. Further accuracy could only be obtained from actual closed container tests on representative samples of the actual cells to be installed, with detection of hydrogen fluoride and other toxic fluorides added to the measurement system.

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[37] Golubkov A W, Fuchs D, Wagner J *et al.* (2014). Thermal runaway experiments on consumer Li-ion batteries with metal-oxide and olivin-type cathodes. *RSC Advances* **4**, 3633-3642 doi: 10.1039/c3ra45748f

[38] The data for the plain “NMC” cathode type is omitted for clarity in this discussion. The results are intermediate between the LOC-NMC and LFP types and qualitatively similar to the LCO-NMC.

[39] As a Physical Hazard rather than a Health Hazard.

Cathode type:	LCO-NMC	LFP
Energy storage capacity[40], Wh	9.4	3.3
Energy density[41], Wh/kg	211	85
Temperature at onset of thermal runaway, °C	149 ± 2	195 ± 8
Maximum temperature reached, °C	853 ± 24	404 ± 23
Quantity of gas evolved, mmol	265 ± 44	50 ± 4

Table 3: Energy densities, thermal runaway temperatures, and total gas generation in anoxic conditions, from two contrasting cell types in thermal runaway

		Proportions[42] of gases (mole %):		Masses (mg / Wh):	
	MW / g mol^{-1}	LCO-NMC	LFP	LCO-NMC	LFP
H_2	2	30.0	30.9	17.0	9.4
CO_2	44	24.9	53.0	310.2	353.3
CO	28	27.6	4.8	218.8	20.4
CH_4	16	8.6	4.1	39.0	9.9
C_2H_4	28	7.7	6.8	61.0	28.8
C_2H_6	30	undetected	0.3	n/a	1.36

Table 4: Published gas mole fractions, and implied masses per unit energy storage, from two contrasting cell types in thermal runaway

	Controlled Quantity (tonnes)	Masses (mg / Wh) (equivalent to kg/ MWh)		Masses (tonne / 50 MWh)		Contribution to Aggregation Rule	
		LCO-NMC	LFP	LCO-NMC	LFP	LCO-NMC	LFP
H_2	5 [43]	17.0	9.4	0.85	0.47	0.170	0.094
CO	10 [44]	218.8	20.4	10.94	1.02	1.094	0.102
CH_4	10	39.0	9.9	1.95	0.50	0.195	0.050
C_2H_4	10	61.0	28.8	3.05	1.44	0.305	0.144
C_2H_6	10	n/a	1.36	n/a	0.068	n/a	0.0068
Aggregation Rule sums for 50 MWh Reference Case:						1.764	0.396
Storage (MWh) at which Aggregation Rule for **Physical** Hazards > 1 :						28.3 MWh	126 MWh

Table 5: Calculated gas masses[45] from Table 4; the same data in tonnes/50 MWh; and contributions to the sum required in the Aggregation Rule (for a 50 MWh BESS).

Table 5 represents an application of the Aggregation Rule for the "Physical Hazards" category only. As Note 5 makes clear, the Aggregation Rule must be applied *3 times*, for the Physical, Health and Environmental hazard classes. A subsequent section considers Health hazards.

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[40] Not listed directly in paper. Estimated from charge capacity in Ah and mid-range terminal voltages given in V

[41] Calculated from estimated energy capacity and all-up cell weight given in paper. Typical values cited elsewhere for these technologies c. 2014 are 200 and 90 Wh/kg respectively, so the values correspond to literature elsewhere.

[42] The paper is not explicit that these are mole fractions rather than mass fractions. However they are measured by gas chromatography which would normally be calibrated to deliver a mole fraction or mole % in the gas.

[43] For the purposes of the Aggregation Rule. The CQ of H_2 alone in the HSC Regulations is, exceptionally, 2 tonnes.

[44] As a P2 Flammable Gas, not as a H2 Health Hazard, where a CQ of 50 tonne applies.

[45] CO_2 omitted because non-flammable.

3.2 Other Physical Hazards: P1a and P1b Explosives.

The hazard class P1a Explosives includes those substances, mixture or articles that have Explosive properties in Divisions 1.1, 1.2, 1.3, 1.5 or 1.6 of the CLP Regulation[46] for which ECHA Guidance Notes are available[47].

Annex I Reg. 2.1.2.2(b) defines a Division 1.2 substance, mixture or article as:
Division 1.2: Substances, mixtures and articles which have a projection hazard but not a mass explosion hazard;

Annex I Reg. 2.1.2.2(c) defines a Division 1.3 Explosive as:
Division 1.3: Substances, mixtures and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard:
(i) combustion of which gives rise to considerable radiant heat; or
(ii) which burn one after another, producing minor blast or projection effects or both;

Annex I Reg. 2.1.2.2(d) defines a Division 1.4 Explosive as:
Division 1.4: Substances, mixtures and articles which present no significant hazard:
substances, mixtures and articles which present only a small hazard in the event of ignition or initiation. The effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire shall not cause virtually instantaneous explosion of almost the entire contents of the package;

Division 1.4 Explosives do not qualify as Explosives in Hazard Class P1a but they are included in Hazard class P1b. Hence any Explosive in Divisions 1.1 to 1.6 inclusive is a Hazardous Substance in Part 1 of Schedule 1[48]. The CQ for P1a Explosives (Divisions other than 1.4) is 10 tonnes; the CQ for P1b Explosives (Division 1.4 Explosives) is 50 tonne.

It is clear from Note 9 in Part 4 of the HSC Regulations that the Hazard class of Explosives includes explosive **articles**. In this classification there is no question of "articles" being exempt: it is openly explicit.

The question is thus whether Li-ion battery cells should be considered as Explosives, and if so in which Division 1.1 through 1.6 they should be placed. The practical matter for the application of the HSC Regulations is whether they qualify as Division 1.4 or otherwise; the CQ is 50 tonne for Division 1.4 Explosive articles (P1b Explosives) but 10 tonne for the other Divisions (P1a Explosives).

Li-ion battery cells are certainly capable of failing explosively, although this is well-known to depend on their State of Charge (SoC). They can fail explosively either by heating (which is the central failure risk of Li-ion cells undergoing thermal runaway) or by electrical overcharging, or by internal failure when in a high SoC (both of the latter being typical initiating events of thermal runaway accidents). Examples are openly available in the form of internet videos (i) for small cylindrical consumer cells of 2.6 Ah (about 9 – 10 Wh); [49] and also (ii) what appears from the rectangular form to be a stack of pouch cells, in a deliberate fire test initiated by overcharging. [50]

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[46] https://www.legislation.gov.uk/eur/2008/1272/annex/I/division/2/division/2.1/division/2.1.2/division/2.1.2.2

[47] "Guidance in the application of the CLP criteria" Regulation EC 1272/2008 on classification labelling and packaging of substances and mixtures" ECHA version 5.0 July 2017 https://echa.europa.eu/documents/10162/23036412/clp_en.pdf/58b5dc6d-ac2a-4910-9702-e9e1f5051cc5

[48] https://www.legislation.gov.uk/uksi/2015/627/schedule/1

[49] Li-ion batteries video: 2.6 Ah consumer cells. [redacted]

[50] Li-ion batteries video: stack of pouch cells [redacted]

Frames from the first video are abstracted in **Figure 1**, illustrating the damage done to a non-faulty cell, simply by overheating externally. The failure is certainly explosive, with an obvious projectile hazard in addition to considerable heat release. The cell is fully charged.

Other examples of explosive failure with projectile hazard are shown initiated by mechanical abuse. The same video makes the point that discharged cells do not fail explosively and are not dangerous unless abused to the point of destruction.

Figure 1: (a) A charged 2.6 Ah cell being deliberately overheated. (b) at the point of rupture (c) the cell takes off as a rocket (d) seconds later the discharge is complete, and the cell is red hot. 5:56 mins to 6:24 mins.

Frames from the second video are abstracted in **Figure 2**, showing what appears to be a stack of rectangular format pouch cells being tested behind a reasonably secure fire bunker. The initiating event is deliberate overcharging; the first cell then explodes with a conspicuous fireball and sideways dual jets of flame; later in the sequence other cells go sequentially into thermal runaway with similar fireball behaviour as they fail.

Figure 2. (a) Stack of fully-charged pouch cells in fire bunker for thermal runaway tests. (b) The first cell fails explosively in a white-hot fireball at 0:09/2:13 minutes. (c) subsequent jets of flame last another 8 seconds (d) (over page) a second cell goes into thermal runaway (0:33/2:13 minutes) with a similar fireball, lasting about 5 seconds (e) (over page) the last of 5 or 6 such fireballs (1:55/2:13 mins).

(b): 0:09 minutes. This fireball emerges in less than 0.5 s from first precursors.

(c): The same event at 0:12 minutes, 3 seconds later

(d): Second cell fails at 0:33 minutes

(e): the last of 5 or 6 similar fireballs at 1:55 minutes

3.2.1 Field tests by Paul Christensen, Professor of Pure and Applied Electrochemistry, School of Engineering, Newcastle University.

Figure 3 shows a sequence from a video[51] by Christensen showing the effect if mechanical damage on a single Electric Vehicle module of stored energy 1.7 kWh, and in a 100% State of Charge. The energy of 1.7 kWh is substantially larger than either of the previous videos, but still much smaller than the stored energy of a grid-scale BESS, where even small storage cabins can accommodate around 2 MWh, i.e. over 1000 times larger than the energy in the EV module shown in these videos.

Figure 3 (a). A 23 kg hammer and nail begins to fall on the EV Li-ion module:

Australia 2021 | Part 1

If the gasses ignite immediately, long flare-like flames can result.

Hammer + nail weighs ~ 23kg!!!

Single EV module 1.7 kWh at 100% SOC, nail penetration.

Figure 3 (b). The hammer at the instant of penetration:

Australia 2021 | Part 1

If the gasses ignite immediately, long flare-like flames can result.

Hammer + nail weighs ~ 23kg!!!

Single EV module 1.7 kWh at 100% SOC, nail penetration.

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[51] PV Magazine “Insight”, online conference 14 October 2021, Presentation 6 “Rundown on thermal runaway” by Prof Paul Christensen (Professor of Pure and Applied Electrochemistry, University of Newcastle)

[redacted]

Figure 3 (c). The hammer of 23 kg weight is thrown back into the air as the cells in the EV battery module disrupt explosively:

Australia 2021 | Part 1

If the gasses ignite immediately, long flare-like flames can result.

Hammer + nail weighs ~ 23kg!!!

Single EV module 1.7 kWh at 100% SOC, nail penetration.

Figure 3(d). A fraction of a second later, a black cloud of what is said by Prof Christensen to be "cathode material" emerges.

Australia 2021 | Part 1

If the gasses ignite immediately, long flare-like flames can result.

Hammer + nail weighs ~ 23kg!!!

Single EV module 1.7 kWh at 100% SOC, nail penetration.

It should noted that this black cloud potentially contains inhalable Nickel Oxides, a "Named Dangerous/Hazardous substance" under Part 2 (Item 11)[52] with particularly low CQ or QQ in Column 3 of the Schedule to the COMAH Regulations. Potential generation of just 1 tonne would classify such installations as "higher-tier" COMAH if the chemical content is verified. See Tables 12 and 13.

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[52] https://www.legislation.gov.uk/uksi/2015/483/schedule/1

Figure 3 (e). Ignition of flammable gases follows in a fraction of a second later, with a large fireball emitting considerable radiant heat:

Australia 2021 | Part 1

If the gasses ignite immediately, long flare-like flames can result.

Hammer + nail weighs ~ 23kg!!!

Single EV module 1.7 kWh at 100% SOC, nail penetration.

Figure 3 (f). The “long, flare-like flames” last for several minutes as the fire progresses after the initial explosion and ignition

Australia 2021 | Part 1

If the gasses ignite immediately, long flare-like flames can result.

Hammer + nail weighs ~ 23kg!!!

Single EV module 1.7 kWh at 100% SOC, nail penetration.

3.2.2 Charged cells as Explosive Articles:

The video evidence certainly suggests, *prima facie*, that charged Li-ion cells should be regarded as Explosive Articles in Division 1.2 (for the cylindrical cells with a projectile hazard) or Division 1.3 (for the stack of pouch cells) which certainly seems to correspond qualitatively, in the test abstracted in Figure 2, to the description in Annex I Reg. 2.1.2.2(c) of the CLP Regulation[53]:

> Division 1.3: Substances, mixtures and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard:
> (i) combustion of which gives rise to considerable radiant heat; or
> (ii) which burn one after another, producing minor blast or projection effects or both;

The subsequent behaviour in the Christensen field tests likewise corresponds qualitatively to a Division 1.3 Explosive Article. These tests use mechanical penetration to initiate failure (as is done elsewhere in the video[54] of the cylindrical consumer cells) but the other evidence makes clear that either overheating, or overcharging[55], are capable of initiating cell failure.

There are test procedures mandated in the CLP Regulation for assignment of substances, mixtures or articles to the various Divisions of the Explosives class. These are referenced to the United Nations Recommendations on the Transport of Dangerous Goods (UN RTDG) Manual of Tests and Criteria[56] (MTC) published by the UN Economic Commission for Europe (UNECE) which sets out clear standards of testing for assignment of articles or substances to the various Divisions of Explosives. It is explicitly mandated by the CLP Regulation, as seen in many places, but explicitly in Annex I Reg. 2.1.4.1[57]:

> 2.1.4.1.The classification of substances, mixtures and articles in the explosives hazard class and further allocation to a division is a very complex, three step procedure. Reference to Part I of the UN RTDG Manual of Tests and Criteria is necessary.

Section 16 of the MTC defines “Test Series 6” which is the critical set of tests for assignment of explosives, as in the decision flowchart required by the CLP Regulation Annex I, Figure 2.1.3[58], distinguishing the various Divisions. It is not known whether tests according to this specification have ever been explicitly carried out for BESS cells (as opposed to consumer product batteries) but they are the tests mandated by the CLP Regulation.

For example Test 6 (c) is an “External fire (bonfire) test” with the stated objective “to determine whether there is a mass explosion or a hazard from dangerous projections, radiant heat and/or violent burning when involved in a fire”. The test package is to be not less than 0.15 m^3 (150 litres) which is significantly larger than the stack of cells shown in the test of Figure 2. The test package is placed on a support grid above a wood, kerosene or gas fire which achieves a temperature of 800 °C, and there are witness screens (2mm thick aluminium sheets) in four quadrants at 4 m from the edge of the test packages.

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[53] https://www.legislation.gov.uk/eur/2008/1272/annex/I/division/2/division/2.1/division/2.1.2/division/2.1.2.2

[54] Li-ion batteries video: 2.6 Ah consumer cells. [redacted]

[55] Li-ion batteries video: stack of pouch cells [redacted]

[56] United Nations (2019). Manual of Tests and Criteria, 7th revised edition, ST/SG/AC.10/11/Rev.7 UN Publication Sales No. E.20.VIII.1 ISBN 978-92-1-130394-0 https://unece.org/fileadmin/DAM/trans/danger/publi/manual/Rev7/Manual_Rev7_E.pdf

[57] https://www.legislation.gov.uk/eur/2008/1272/annex/I/division/2/division/2.1/division/2.1.4/division/2.1.4.1

[58] See e.g. Guidance on application of CLP criteria, version 5.0 July 2017, page 99

Allocation criteria on the basis of this bonfire test are given in section 16.6.1.4 of the MTC[59]. Because the available evidence from Figure 2 is in a much smaller test packaged than specified in the MTC, it is not possible to decide definitively how a specified test package (150 litres) would behave in such a fire test. However the behaviour in Figure 2 already corresponds to the 1 m fireball criterion of paragraph 16.6.1.4.5 (a) which would assign a 150 litre test package to Division 1.4. A standard size test package of 150 litres would be significantly larger and very plausibly would exhibit a larger fireball passing criterion 16.6.1.4.4 (a) (fireball greater than 4 m distance) which would assign the article to Division 1.3. The burning time or irradiance criteria of paragraph 16.6.1.4.4 (c) would also assign the article to Division 1.3 and from the behaviour in Figure 2 the burning time is much shorter than the criterion's 35 seconds, albeit for a smaller package than the 100 kg reference.

Without more detail on the cell types, sizes, energy stored for the cell stack shown in Figure 2, it is not possible to say definitely how a test standard cell-stack (150 litres) would behave in the Series 6 Type (c) "bonfire" test of the MTC, and certainly not possible to decide quantitatively on the criteria listed in section 16.6.1.4 which would discriminate between Division 1.3 and 1.4 Explosives.

Such determinations would require actual tests according to the specifications laid out in the UN MTC. Because the behaviour is known to depend on the cell's SoC, such tests should be performed at several different SoCs, including 100% charged.

Although cells may be shipped and installed at lower SoCs than 100% (30% is the recognised standard SoC for shipping consumer product Li-ion batteries) the cells in a BESS are designed to be taken to high SoCs several times a day: that is the normal design operation of a BESS functioning for grid-scale energy storage.

Hence such cells are likely to pass through states qualifying as Explosives in the Series 6(c) tests of the MTC, several times daily.

In the absence of actual tests, the available evidence suggests that Li-ion cells should be regarded as Explosive articles in Hazard class P1a (for Division 1.3 Explosive articles). Qualitatively, the video evidence corresponds to the description in Annex I Reg. 2.1.2.2(c) for a Division 1.3 Explosive, presenting "a fire hazard and either a minor blast hazard …" and "considerable radiant heat". It does *not* correspond to the description of a Division 1.4 Explosive with "effects largely confined to the package" and an external fire *not* causing "virtually instantaneous explosion of almost the entire contents" .

A typical BESS composition (from an actual Planning Application document) is given later in Table 7, with an inventory of active substances in the cells of 6.46 tonne per MWh of energy storage. This will vary according to cell type and manufacturer, but may be taken as representative.

The 10 tonne CQ for the P1a Explosive category is exceeded for an energy storage of 15.5 MWh.

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[59] Page 171 of the MTC, 7th edition.

3.3 Routes to generation of Part 1,2 Hazardous Substances in loss of control accidents in BESS: (II) Generation of H1 and H2 Acute Toxic gases in oxidising conditions

Toxic gases in Table 1 include not only the incidental hydrogen chloride HCl and hydrogen cyanide HCN "typical of plastics fires" but also the notoriously corrosive hydrogen fluoride HF and the unstable phosphoryl fluoride POF_3. HF in particular can be evolved in large quantities, originating from the large inventory of fluorine-containing compounds used in Li-ion battery cells. These include the lithium hexafluorophosphate $LiPF_6$ which is a critical ingredient of the electrolyte, and PVdF (polyvinylidene fluoride or difluoride), a polymer typically used as a separator membrane.

Generation of HF and other toxic fluorine-containing compounds is therefore an unavoidable aspect of Li-ion battery electrochemistry. These fluorine-containing compounds and polymers are essential aspects.

HCN is a notoriously toxic substance though as a pure substance (a very low-boiling liquid) it has a Harmonised Classification only as H2 Acute Toxic. In a mixture however the classification is H1 Acute Toxic, which aligns with the majority of the Notified Classifications in the C&L Inventory (H1 for all forms). The H1 classification is found for mixtures in the authoritative GB Mandatory Classification and Labelling List.

HF has a dual classification as a H1 Acute Toxic gas by the dermal (skin attack) route, and also as a H2 Acute Toxic by the oral and inhalation routes. By Note 7, the lower Controlled Quantity applies, meaning a CQ of 5 tonnes in respect of HF.

POF_3 has no listed toxicity assessment, probably because it is too unstable to perform the testing. It is known to hydrolyse readily in water[60] generating three molecules of HF for each one of POF_3, so it is justifiable by Note 6 to assign a classification of H1 Acute Toxic (dermal), as it is a known precursor of HF.

Finally, carbon monoxide CO has been considered in the previous section as a "Physical Hazard" as it is a Flammable Gas classified as a P2 Physical Hazard. However it also a toxic gas, classified as H2 Acute Toxic, with a CQ of 50 tonnes. Moreover, the available data on HF and POF_3 were obtained in oxidising conditions in a full "fire test", and under oxidising conditions further evolution of CO is expected from partial combustion not only of the flammable "P2" hydrocarbons considered above, but also of the powdered graphite (carbon) used in large quantities as an anode material.

Evaluation of quantities and application of the Aggregation Rule for Health Hazards therefore requires estimates of the likely quantities of HCN, HF, POF_3 and CO generated in BESS fires.

Quantities of HCN: There is very little literature data, although concentrations of HCN were a contributory hazard to fire fighters in the 2019 McMicken incident. HCN probably arises from incidental nitrogenous polymers used in packaging or cell construction. For want of any other estimate, we may take the report[61] of measurements at the time, where "above 50 ppm" (HCN) and "above 500 ppm" (CO) were recorded. These are compounds with very similar molecular

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[60] *Wikipedia* entry for phosphoryl fluoride. [redacted]

[61] McKinnon, M B, DeCrane S, Kerber S (2020). "Four fire-fighters injured in Lithium-ion Battery Energy Storage System explosion – Arizona". Underwriters Laboratories report July 28, 2020. UL Firefighter Safety Research Institute, Columbia, MD 20145

weights, so a reasonable indicative estimate would be to assume that HCN may be generated at 1/10 of the quantity of CO. The cell type at McMicken was NMC, so the estimates from the previous section of 102 mg/Wh of CO are probably representative – at the "anoxic" stage of the incident[62]. A rough estimate of 10 mg/Wh of HCN is therefore justifiable on these figures.

This can only be taken as an order of magnitude. Further assessment requires measurements of HCN evolved in actual fire tests of representative cells complete with packaging, wiring etc.

Quantities of HF and POF_3: Literature sources document the evolution of these gases in fire tests of a variety of actual Li-ion cells. The leading source documenting HF and POF_3 releases in open fire tests is by Larsson[63] *et al.* who report HF releases from a variety of cell types but predominantly "pouch" format cells of the LFP cathode type. The test set included LCO (lithium cobalt oxide) cathodes and NCA-LATP (lithium nickel cobalt alumina – lithium aluminium titanium phosphate) but no examples of the NMC (nickel manganese cobalt) cathodes included by Golubkov. The latter evidence suggests that LCO and NMC cathode types are likely qualitatively similar, comparing mixed LCO-NMC and pure NMC.

Independent HF release estimates from other fire tests are given by Sturk[64] *et al.* Many experts[65] note that although LFP cathode cells are widely promoted as a "safer" technology (because of the higher thermal runaway threshold (Table 3), the lower temperatures reached in thermal runaway, and the generally slower "burn" in failure), the quantity of HF released in failures is significantly higher than for the mixed oxide (NMC, LCO etc) cathode types. LFP cathode cells are thus significantly *more* hazardous in terms of toxic emissions than NMC or other mixed oxide types.

Emissions vary according to State of Charge (SoC) and according to the packaging "form factor" (i.e. whether pouch, cylindrical or prismatic), so once again this points to the importance of actual fire tests on representative samples of the actual cells to be deployed in any installation. Quantities abstracted from Larsson *et al.* and from Sturk *et al.* are summarised in Table 6.

	Larsson *et al.*		Sturk[66] *et al.*	
Gas	LCO prismatic (25 Wh nominal)	LFP pouch cells (64 Wh nominal)	NMC (14 Ah taken as 50 Wh)	LFP (7 Ah taken as 22 Wh)
	(values in mg / Wh energy capacity)			
HF	20 – 25	170 – 200 (max. at 0% SoC)	6.2 – 19 (max. at 100% SoC)	50 – 132 (max. at 100% SoC)
POF_3	15 – 22	not detected	not measured	

Table 6: Fluoride gases generated from LFP cells compared to LCO or NMC cells from two sources.

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[62] There was no "fire" as such at McMicken, only a vapour cloud explosion. The "anoxic" conditions of the previous section are therefore reasonable for this purpose.

[63] Larsson F, Andersson P, Blomqvist P, Mellander BE (2017). Toxic fluoride gas emissions from lithium-ion battery fires. *Scientific Reports* **7**, 10018 doi: 10.1038/s41598-017-09784-z

[64] Sturk D, Hoffmann L & Tidblad AA (2015) Fire Tests on E-vehicle Battery Cells and Packs, *Traffic Injury Prevention*, **16:**sup1, S159-S164, DOI: 10.1080/15389588.2015.1015117

[65] Mrozik W, Rajaeifar M A, Heidrich O, Christensen P (2021) Environmental impacts, pollution sources and pathways of spent Li-ion batteries. *Energy Environ. Sci.*, 2021, **14**, 6099-6121. DOI: 10.1039/D1EE00691F

[66] Data from Table A4, online Supplementary Materials.

The Sturk quantities for NMC cells are somewhat lower than the results for the LCO cells reported by Larsson, though Sturk does not report POF_3 (a known HF precursor). The results for LFP cells are also lower in Sturk than the highest values reported in Larsson. There is no consistency regarding State of Charge. Generally speaking LFP cells behave differently from the other cathode chemistries, for which behaviour is qualitatively similar.

The Larsson data are more thorough than in Sturk; the Sturk data require estimates of terminal voltages (unstated) to derive energy capacities, and prudent conservatism in safety analysis demands that highest reported values be taken, so we will take the Larsson values for LFP pouch cells, with the LCO cells as a comparator, the type for which POF_3 emissions are reported. The comparison with Sturk shows that LCO cells are likely to be representative of NMC or other mixed transition metal cathodes.

Quantities of CO: For estimation of CO evolution it is no longer sufficient to consider anoxic conditions as in the Golubkov paper in the preceeding section. In an oxidising fire, all organic components of the cells and the significant inventory of graphite (carbon) used in the anodes will burn, although the degree to which combustion is complete will depend on circumstances. Also the composition by mass of the cells proposed is required.

An outline composition for the chemicals content of a whole site of BESS cells of 26.3 MWh capacity is given in a memorandum by D. Haigh of Golder Associates[67] (UK) Ltd written for a BESS applicant (SYNERGY) in relation to a Planning Consent granted for a BESS at Kells, Co. Antrim, Northern Ireland[68]. This gives a composition for the entire site abstracted in Table 7.

		structural component	Mass (tonnes) per 26.3 MWh	tonne / MWh
Cobalt oxide	CO	cathode active materials	19.1	0.726
Manganese dioxide	MnO_2		19.1	0.726
Nickel oxide	NiO		19.1	0.726
carbon	C (graphite)	anode active material	38.1	1.449
electrolyte	$LiPF_6$ in organic carbonates	active electrolyte	28.6	1.087
PVdF	Polyvinylidene fluoride	separator	9.5	0.361
Aluminium foil	Al	cathode support	19.1	0.726
Structural aluminium	Al	housings	21	design-dependent
Copper foil	Cu	anode support	17.2	0.654
			Mass functional substances per MWh :	6.456
			Energy density (Wh/kg) :	155

Table 7: Tonnages of active substances at an actual 26.3 MWh BESS in Northern Ireland

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[67] Attenborough House, Browns Lane Business Park, Stanton-on-the-Wolds, Notts NG12 5BL

[68] Obtained by a Freedom of Information application to Antrim and Newtownabbey Borough Council, December 2021

Although the chemical technology is evolving continuously, the energy density for the cells implied in Table 7, around 150 Wh/kg, is consistent with literature reports elsewhere. For estimation of the potential for generating Carbon Monoxide, the Carbon-containing components need to be identified. The organic solvents used in the electrolytes are a minority but significant part of the total Carbon content, which is dominated by the graphite used in the anodes. The Carbon content of the whole electrolyte can be estimated on the basis of typical compositions of the solvents and concentrations of the $LiPF_6$ salt found in the technical literature. The resulting Carbon composition of the cells in mg / Wh is given Table 8.

substances	Mass fraction of solvent in electrolyte, 1.2 mol L^{-1} solution[69]	Mass fraction[70] of Carbon in solvent	Mass Fractions of Carbon in component (electrolyte, or anode material)	Mass (mg / Wh) of Carbon, for BESS in Table 7
Organic solvents in electrolyte (dimethyl-, ethyl-methyl-, ethylene- and propylene carbonates)	85.8 %	41.1 – 41.5 %	35.57 %	386.6
PVdF membranes ($C_nH_nF_n$)			37.5 %	135.4
Graphite anodes	-	-	100 %	1449
				1971

Table 8: Estimated carbon content of Li-ion cells used in the BESS in Table 7.

Finally, the approach taken in the Golder memo was to estimate the CO_2/CO ratio in combustion in fire from actual fire tests published by the insurer F M Global[71]. The source is important as one of very few sources to provide actual mass measurements in full scale fire tests of burning batteries. Key parameters used in Golder are given in Table 9.

CO_2 / CO mass ratios	Equivalent CO_2 / CO mole ratios	Mole fraction CO in gas mixture	C-content of BESS anodes	“Worst case” CO generation
43 – 71	27.4 – 45.2	3.52 – 2.16 %	38.1 tonne	3.1 tonne

Table 9: CO_2/CO ratios in open fire tests reported by F M Global and application to Table 7 BESS

This will be representative of conditions in an uncontrolled fire with free supply of oxygen or air. However this will not necessarily be the case if air supply is restricted by enclosure design, conditions at the site, or especially by the deployment of so-called “clean agent” or AFC (aerosol-forming composite) fire suppression systems which attempt to smother a fire and restrict air

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[69] Typical for Li-ion battery cells. See: Logan E R, Tonita E M, Gering K L, Li J, Ma X, Beaulieu L Y, Dahn J R (2018). A Study of the Physical Properties of Li-Ion Battery Electrolytes Containing Esters. *J Electrochem Soc* **165**(2) A21-A30 [DOI: 10.1149/2.0271802jes]

[70] From various solvent compositions in the Golubkov study. Different compositions do not differ greatly in Carbon mass fraction.

[71] F M Global (2013) Flammability characterization of Li-ion batteries in bulk storage. Available at [redacted]

supply. The assumptions of the Golder memo (taking the worst case CO_2 / CO ratio in open fire tests) cannot therefore be said to be conservative for the formation of Carbon Monoxide (CO).

The Golder assumptions and the lowest CO_2/ CO mass ratio from the F M Global source provide only a lower estimate of the potential for Carbon Monoxide generation in fire, for the purposes of the HSC Regulations. The argument taken in Golder was the opposite, that the "worst case" CO_2 / CO was conservative because complete consumption of all Carbon containing components was unlikely, and the "worst case" CO_2 / CO ratio was derived from actual fire tests.

However this is to misunderstand the HSC Regulations, where, as argued above, it is the mere presence on the site of controlled substances which are regulated; the likelihood of accidents and of their extent is not relevant. For the purpose of the HSC Regulations, the substances "S" which are regarded as hazardous in "loss of control" are *any* substances which may generate *listed* hazardous substances (Parts 1 or 2) under loss of control. Carbon monoxide is certainly a Parts 1 and 2 hazardous substance which is *known* to be generated in loss of control situations; the regulated "substances S" that *may* generate CO are the polymers, the organic solvents, and the graphite in the anodes. As remarked above, it is readily conceivable that actual CO proportion might be *worse* than the so-called "worst case" from F M Global, if air supply is restricted, for any reason. The quantity derived from the figures in Table 9 is therefore *not* conservative, as claimed by Golder.

Both the Golder assumption and the complete conversion assumption are given in Table 10, for the carbon containing components.

Source of Carbon	Mass of Carbon in components (Table 8)	CO generated: as 3.52 mole % of combustion products	CO generated: as 100 mole % of combustion products	
	(mg / Wh)	(mg / Wh)	(mg / Wh)	tonne (26.3 MWh)
solvents	386.6	31.8	**902**	23.7
PVdF	135.4	11.1	316	
anodes	1449	119	3381	
totals	1971	**161.9**	4599	

Table 10: Mass of CO generated from carbon-containing components of a 26.3 MWh BESS, under two assumptions for mole fraction of CO in combustion products.

The result for 100% conversion of the organic solvents in the 26.3 MWh BESS in Table 7 is shown explicitly, because this assumption appears to have been made in Golder, for the organic solvents only[72], whilst the 3.52% mole fraction used for the combustion of graphite.

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[72] The figure in Table 2 of Golder is 22.5 tonne CO generated from the organic carbonates only. The difference from the 23.7 tonne in Table 10 is readily explained by different assumptions (or knowledge) for the electrolyte composition conjectured in Table 8.

For the purposes of this paper, shall take the 3.52% mole fraction of CO in the carbon oxides combustion gases as a rational minimum CO generated in fire situations. This is not necessarily conservative as argued above.

Because 100% conversion of organic solvents to CO has been used in one evaluation of CO generation from a BESS fire (by consultants acting for an Applicant), we shall take this as a conjectural upper figure for estimation purposes. As before, further evaluation can only come from actual fire tests under various representative conditions of air supply or partial smothering.

Toxic gas generation from BESS in fire situations is summarised in Table 11. LFP cells are contrasted with "Mixed Oxide" cells taking data for the LCO cells in Table 6, and for a range of estimated CO quantities derived from the preceeding considerations in Table 10. For the lower limit, we take 3.52 mole % of CO in combustion gases for a typical inventory (Table 7) of carbon-containing materials. For the upper limit, we use the figure assuming 100% conversion of the organic solvents to CO (Table 10), as used in one prior BESS fire assessment submitted to a Planning Authority (Golder). As discussed above (Table 6) the fluoride gas data from Larsson for LCO cells was the first to report POF_3. Generally LCO cells appear to be similar to NMC and other mixed oxide cathode types in their breakdown behaviour, in contrast to the qualitatively different LFP behaviour, especially for fluoride emissions.

As in Table 5, toxic gas generation is scaled to a Reference Case 50 MWh of energy storage, and their contributions to the summation in the Aggregation Rule (for Health Hazards) are shown in the right-most columns, for the two cell types. The energy storage at which the Aggregation Rule sums to unity is also given, in MWh, using both ends of the range given for CO.

We conclude from the data given in the cited sources, that BESS based on Mixed Oxide cathodes would trigger a HSC assessment at a storage capacity between 34.5 – 68.5 MWh, based on the Aggregation Rule. For a BESS based on LFP cells, the assessment threshold is significantly lower, between 16.7 – 22.1 MWh. The range is also smaller, as the estimates for LFP cells are dominated by the fluoride gases, whereas the estimates for the LCO cathodes are more sensitive to the assumptions made regarding CO.

Moreover, the LFP cells exceed the CQ for H1 acute Toxics on the basis of HF alone, at 25 MWh, without requiring any assumptions regarding completeness of combustion in generation of CO.

We remark under Table 5, that further accuracy in the "Physical Hazards" assessment could only be obtained from actual *closed container* (anoxic conditions) tests on representative samples of the actual cells to be installed. Similarly, we could only obtain further accuracy in the Toxic Gases assessment, by actual fire tests on representative samples of the cells to be installed, under a range of scenarios regarding air supply (which could affect the mole fraction of carbon monoxide in combustion products).

substance	HSC Hazard Category	Controlled Quantity (tonnes)	Masses (mg / Wh) (equivalent kg/ MWh)		Masses (tonne / 50 MWh)		Contribution to Aggregation Rule	
			LCO	**LFP**	**LCO**	**LFP**	**LCO**	**LFP**
HCN	H1 Acute Toxic	5	10	10	0.5	0.5	0.1	0.1
HF	H1 Acute Toxic (dermal)	5	25	200	1.25	10	0.25	2.0
POF_3	H1 Acute Toxic (provisional, Note 6)[73]	5	22	-	1.1	-	0.22	-
CO	H2 Acute Toxic, Category 3, inhalation	50 [74]	162 – 902 [75]		8.1 – 45.1		0.162 – 0.902	
Aggregation Rule sums for 50 MWh Reference Case:							0.73 – 1.5	2.26 – 3.0
Storage (MWh) at which Aggregation Rule for **Health** Hazards > 1 : (upper case for CO generation)							34.5 MWh	16.7 MWh
Storage (MWh) at which Aggregation Rule for **Health** Hazards > 1 : (lower case (3.52 mole % CO) for CO generation)							68.5 MWh	22.1 MWh

Table 11: Toxic gases generated from BESS in oxidising conditions for two contrasting cell types, and a range of quantities of CO generated from carbon-containing components.

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[73] Larsson *et al.* comment: “Judging from its chlorine analogy POCl3/HCl, POF3 may even be more toxic than HF”.

[74] As H2 Health Hazard rather than as P2 Physical Hazard, where the CQ is 10 tonne.

[75] From Table 10, boldface figures. Note maximum CO generated in anoxic conditions (Table 5) is 218.8 mg / Wh, reported for LCO-NMC cells by Golubkov.

3.4 Routes to generation of Part 1,2 Hazardous Substances in loss of control accidents in BESS: (III) inhalable Nickel compounds.

A final consideration for Li-ion BESS using some mixed oxide cathodes containing nickel oxides is the possibility of generating dust or smoke containing "Nickel compounds in inhalable powder form", which are Named Hazardous Substances in Part 2 of Schedule 1 to the HSC Regulations (entry number 11)[76]. The inhalable powders referred to specify the oxides and sulphides of nickel listed in Table 12.

Clearly these cannot be a concern if Nickel oxides are absent from the cell types deployed, but NMC cells and LCO-NMC mixed oxide cells do contain Nickel, and the BESS in Table 7 is stated to contain an inventory of 19.1 tonnes nickel oxide NiO for 26.3 MWh storage capacity[77].

The requirement for this to become a Named Hazardous Substance in Part 2 is that they be present in "inhalable powder form", so the question arises of release of nickel oxides in fires, as inhalable dust or smoke. The form in which they occur in the Li-ion cells is already nanoporous; all that would be needed is release from the aluminium foil support with mechanical disruption in thermal runaway accidents.

The question is an important one for health protection, and the operation of the HSC Regulations, because the Controlled Quantity is particularly low, only 1 tonne.

The total inventory of NiO in a modest-sized BESS (26.3 MWh) in actual practice, as reported to a Local Planning Authority, is already 19.1 tonnes (see Table 7), well in excess of the Controlled Quantity.

If it is "reasonable to foresee" the "fixed" form of NiO within the Li-ion cells becoming released in "inhalable powder form" e.g. in fires or thermal runaway events, then even quite small BESS (around 1.4 MWh capacity) may require HSC, by exceeding the CQ of a Part 2 Named Hazardous Substance. Moreover, the parallel entry in the COMAH Regulations appears in Column 3 of the Schedule to the COMAH Regulations [78], so such a site would be classified as an "upper-tier" COMAH site as soon as the threshold is exceeded, without any "lower-tier" categorisation.

Compound:	formula	Hazard Codes	Controlled Quantity (Named substance, Part 2)
nickel monoxide	NiO	H350 carcinogen by inhalation	1 tonne
nickel dioxide	$ONiO$	H350i	
dinickel trioxide	Ni_2O_3	H350i	
nickel sulphide	NiS	H350i, H400, H410	
trinickel disulphide	Ni_3S_2	H350i, H400, H410	

Table 12: specified Nickel compounds that are Part 2 Named Hazardous Substances if present in "inhalable powder form", being known or suspected carcinogens by inhalation

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[76] https://www.legislation.gov.uk/uksi/2015/627/schedule/1/made

[77] This was the reference case for the cited memo. The actual BESS in development is about double this size.

[78] https://www.legislation.gov.uk/nisr/2015/325/schedule/1

3.4.1 Evidence for the generation of inhalable Nickel Oxides in loss of control accidents

Whether the generation of nickel oxides from Li-ion battery cells is possible depends on the cathode chemistry type. Clearly, if nickel is not a component of the Li-ion cell, then significant generation of nickel oxides is impossible. However the NMC and NMC-LCO cell types do contain Nickel, many BESS already installed use the NMC type, and in at least one Planning application[79] in process, the developer has stated that the cells may be either LFP or NMC.

Evidence for the generation of inhalable nickel oxides comes from the video records of controlled failures made by Christensen already referred to in Section 3.2.1 above.

Figure 3 (d) (page 27) shows the stage of an explosion of a 1.7 kWh module destroyed in a field test where a cloud of initially black smoke emerges from the disrupting module. In this test the ignition of flammable gases followed immediately upon the explosive disruption in a "deflagration event".

Other experiments by Christensen are shown in the same lecture source[80] in which the ignition is not in fact immediate. Christensen summaries the possible course of events in the "flowchart" of Figure 4 below. Whether the ignition of flammable gases and vapours is immediate or delayed depends on circumstances, notably the relative concentrations of flammable gases and air (or oxygen). Delayed ignition (likely to encouraged, not inhibited, by aerosol-based fire suppression systems) is in many ways more dangerous, as no flame need be involved until an explosive mixture is generated, leading on contact with a hot surface to a Vapour Cloud Explosion.

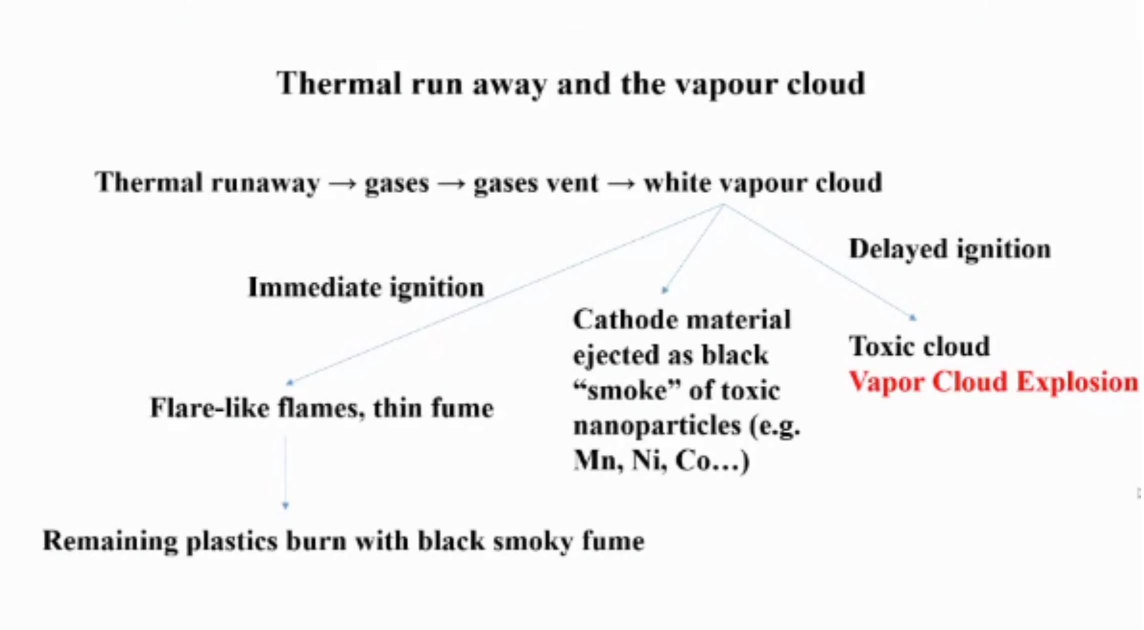

Figure 4. Summary of possible courses of events in a BESS "thermal runaway" event. From lecture by Prof Paul Christensen.

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[79] Letter from Sunnica to Mrs Lucy Frazer QC MP

[80] PV Magazine "Insight", online conference 14 October 2021, Presentation 6 "Rundown on thermal runaway" by Prof Paul Christensen (Professor of Pure and Applied Electrochemistry, University of Newcastle) [redacted]

An example of a thermal runaway event *without* immediate ignition, also from Christensen's work, is shown in Figure 5, where the concentration of flammables in air was such that the mixture never ignited during the test[81]. This parallels the situation known to have occurred in the heavily-analysed[82] explosion at McMicken, Arizona in 2019, where no flame was involved until a "deflagration event" which left first-responders with life-limiting injuries. Various stages in the generation of a vapour cloud are shown in panels (b) (c) and (d). Figure 5(a) repeats Figure 3(d) for comparison of the "black cloud" stage.

Figure 5(a). Same as Figure 3(d), showing the early emergence of a "black cloud" before a "white cloud" likely to be dominated by droplets of organic solvents. In this test the ignition followed shortly thereafter.

Australia 2021 | Part 1

If the gasses ignite immediately, long flare-like flames can result.

Hammer + nail weighs ~ 23kg!!!

Single EV module 1.7 kWh at 100% SOC, nail penetration.

Figure 5 (b). Initial failure of a 1.67 kWh module in a low State of Charge (SoC) (40%). The black cloud (said by Christensen to be "cathode material") emerges in the first fraction of a second.

If the vapour cloud does not ignite…..

gazine Insight Australia 2021 | Part 1

Nail penetration of a 1.67 kWh module, 40% SoC.

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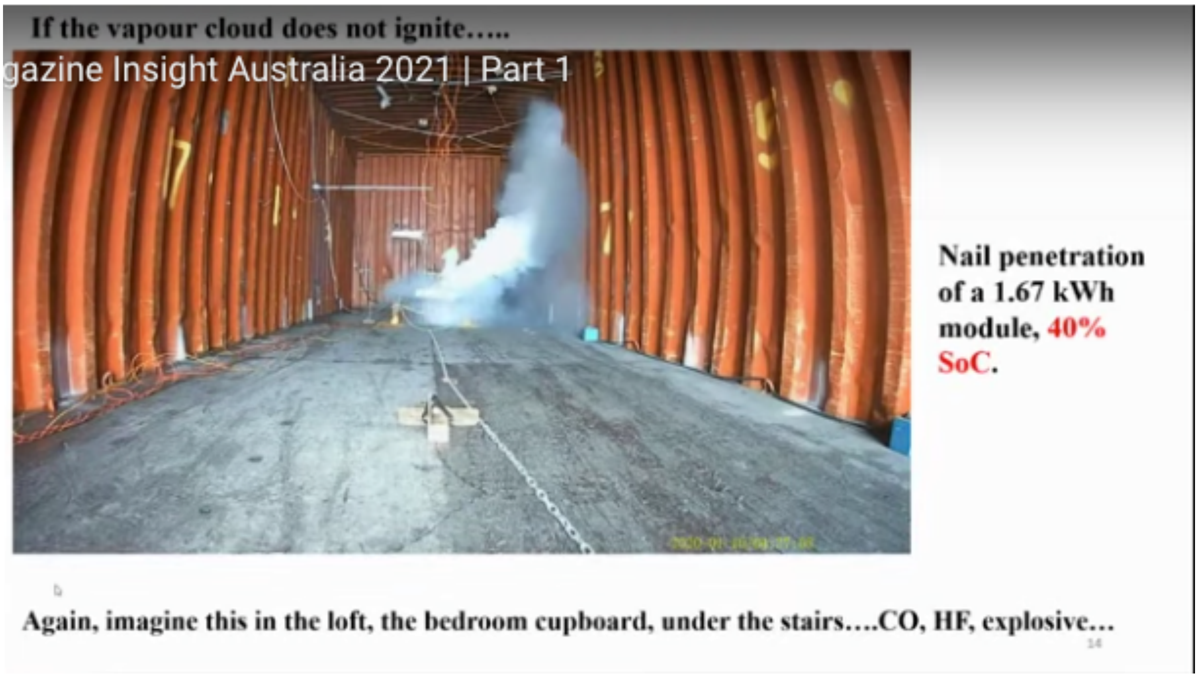
[81] PV Magazine "Insight", online conference 14 October 2021, Presentation 6 "Rundown on thermal runaway" by Prof Paul Christensen (Professor of Pure and Applied Electrochemistry, University of Newcastle) [redacted] Later in same lecture.

[82] Hill, D. M. (2020). McMicken Battery Energy Storage System Event: Technical analysis and Recommendations. Report from DNV-GL to Arizona Public Service. Doc. No. 10209302-HOU-R-01. 18 July 2020,

Figure 5 (c): The white vapour cloud follows a fraction of a second later. The light-scattering material creating the opaque white material is likely to be the organic solvents from the cell.



If the vapour cloud does not ignite…..

gazine Insight Australia 2021 | Part 1

Nail penetration of a 1.67 kWh module, 40% SoC.

Again, imagine this in the loft, the bedroom cupboard, under the stairs….CO, HF, explosive…

Figure 5 (d). The vapour cloud eventually fills the container, without ignition, during the test.

If the vapour cloud does not ignite…..

gazine Insight Australia 2021 | Part 1

Nail penetration of a 1.67 kWh module, 40% SoC.

An example of vapour cloud formation before an actual BESS explosion[83] (the September 2020 Liverpool explosion and fire) is shown in Figure 6 from actual CCTV records shortly before the explosion. A black cloud analogous to Figures 3(d) and 5(a) is not captured, but as seen from the recordings this is typically an initiating event rapidly superseded by the emergence of a white cloud.

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[83] Merseyside Fire and Rescue Service, Fire Investigation Report 132-20, Incident Number 018965, Carnegie Rd, Liverpool, September 2020. Report dated February 2022.

Figure 6 (a). From internal CCTV, seconds before the Liverpool explosion. Figure 15 of report.

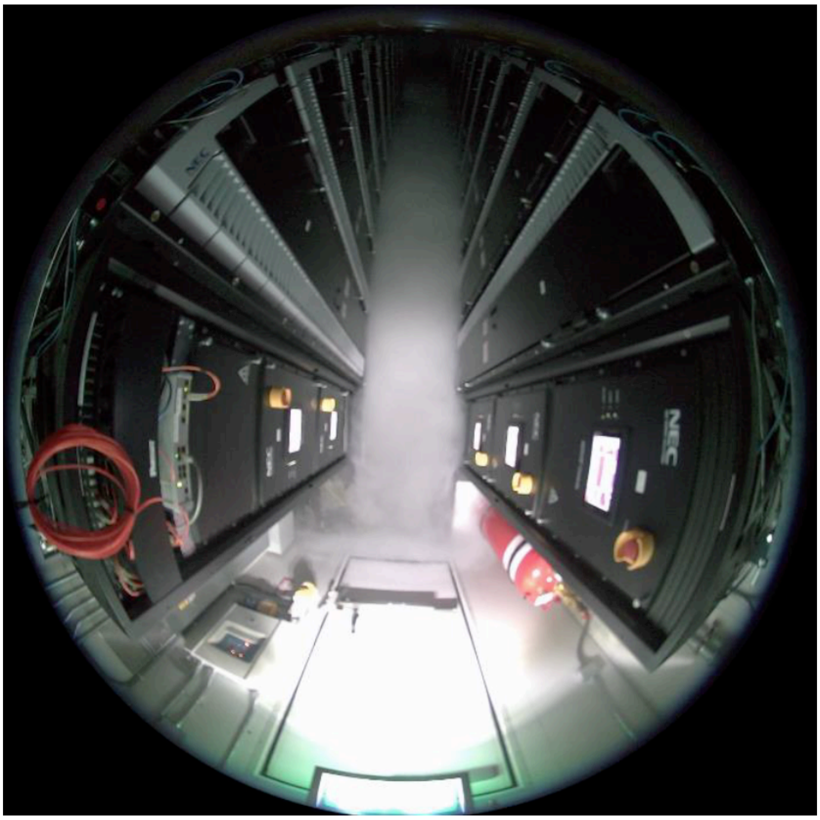
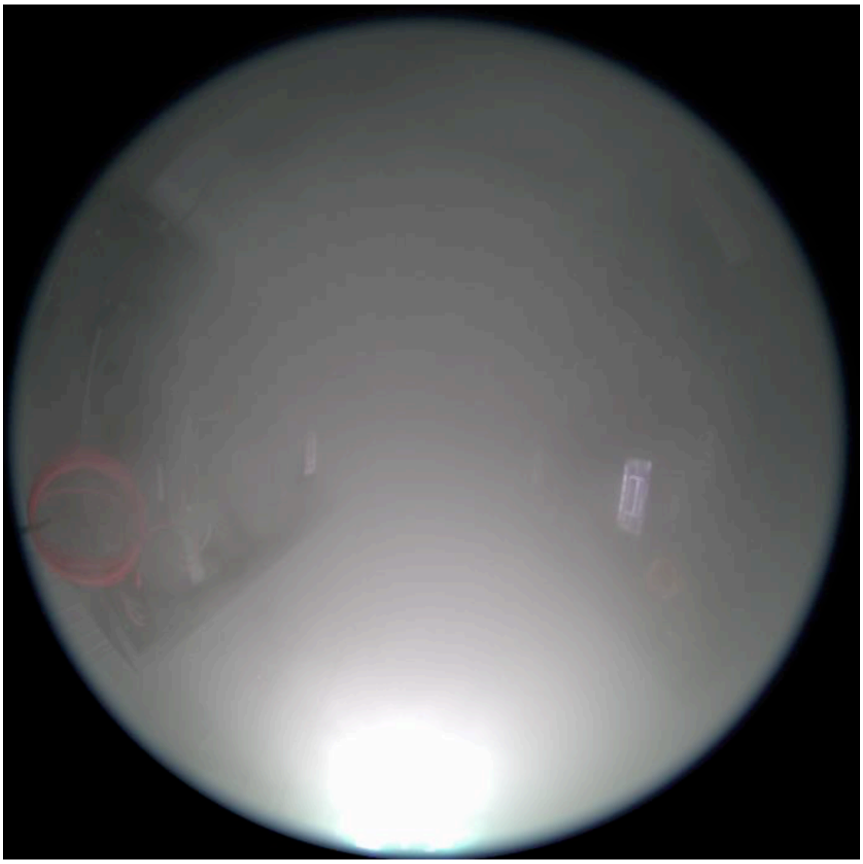


Figure 6(b). The vapour cloud fills the local region of the container before ignition. Figure 16 of report.



Christensen states at several points (including the notes in Figure 4) that the “black cloud” seen very early in Figures 5(a) and 5(b) is “cathode material” and likely to consist of toxic heavy metal nanoparticles, including manganese, cobalt and nickel (which are all used in the cathode, in NMC cells). The occurrence as nanoparticles is not surprising since the cathode material is already nanoporous in its deposition.

The nanoparticles emitted are likely to include oxides, since the cathode material in so-called “NMC” cells is a mixed nickel-manganese-cobalt *oxide.* Metallic oxide nanoparticles (MO-NP) form readily and nanoporous MO are already present in the cathodes. Metallic nanoparticles (MNP) can be stable and might also be present, though Christensen confirms[84] that the oral description of “toxic heavy metal nanoparticles” should have been of “metal *oxide* nanoparticles”.

As smoke, this is patently an “inhalable” form, likely to survive as smoke or dust in any subsequent fire or explosion. If Christensen is correct, that the “black cloud” emerging in these failure records contains nanoparticles of the “cathode material” (the component containing Nickel in NMC cells), then it is likely that these images demonstrate, for NMC and related cathode types, the presence of “Nickel Oxides in inhalable powder form” which is a Named Hazardous Substance in Part 2 of the Schedule to the HSC and COMAH Regulations.

The chemical composition of the vapour clouds (both “black” and “white”) emerging in failure of NMC and other Nickel-containing cell types is therefore important from a regulatory perspective, and should therefore be definitively confirmed. If the “black smoke” is confirmed to contain Nickel Oxides, then Nickel-containing cell types would probably require Hazardous Substances Consents at energy storage capacities as low as 1.4 MWh.

3.4.2 Other literature evidence for inhalable Nickel Oxides from NMC Li-ion failure.

Multiple literature sources in fact confirm the likely presence of Nickel Oxide particles, or particulates containing complex mixed oxides including Nickel, and at inhalable particle sizes. Bergström *et al.* claim[85] to be the first (2015) to analyse “soot” or particles collected from smoke generated in cell failure, detecting nickel compounds (by ICP-MS) from NMC cells.

Recent (2020) peer-reviewed literature[86] concludes that the ejected powders consist of carbon, organics, carbonates, metal and <u>metal oxides</u> i.e. including Nickel oxides. Although the majority component of the collected “soot” is carbon, these were closed cell tests gathering all particulates generated, which could well have included graphite from the anodes. The same source (Chen, 2020) details the chemical decomposition of the NMC cathode into first Ni_2O_3 and then NiO (both specified in Table 12) with evolution of free oxygen, an exothermic reaction explained elsewhere[87] in the context of fire behaviour dependent on State of Charge. The earlier (Ouyang, 2018) source details how the NMC cathode decomposes first into the nickelous oxide Ni_2O_3 and the analogues

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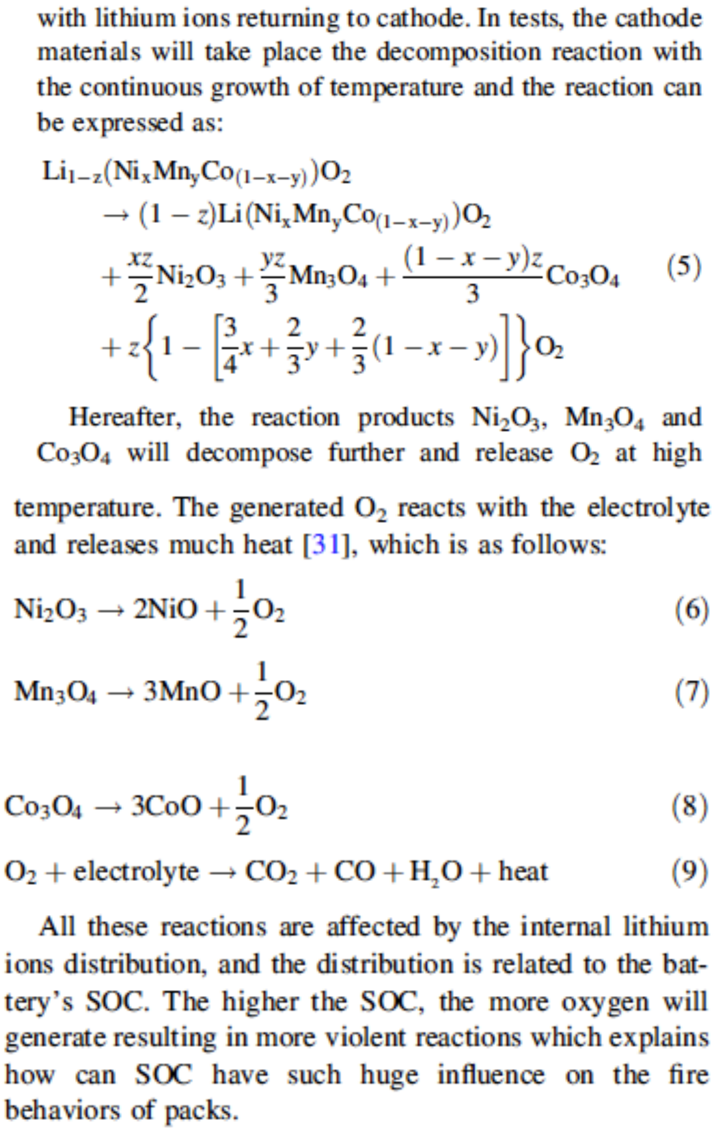
[84] Christensen, P. June 2022. Private communication with EJF.

[85] U. Bergström *et al* (2015), “Vented gases and aerosol of automotive Li-ion LFP and NMC batteries in humidified nitrogen under thermal load” [redacted]

[86] S. Chen, Z. Wang and W. Yan (2020) “Identification and characteristic analysis of powder ejected from a lithium ion battery during thermal runaway at elevated temperature”, *J. Haz. Mat.*, 400, 123169 DOI: 10.1016/j.jhazmat.2020.123169

[87] Ouyang, D., Chen, M & Wang J. (2018) Fire behaviours study on 18650 batteries using a cone calorimeter. *J. Thermal. Analysis and Calorimetry* Doi: 10.1007/s10973-018-7891-6

Mn_3O_4 and Co_3O_4 from the manganese and cobalt content, with release of oxygen, followed by further reduction to NiO, MnO and CoO with yet further release of oxygen, all dependent on internal distribution of Lithium ions, and the higher to SoC, the more oxygen is generated internally, explaining the increasing violence of “fires” with increasing SoC.



with lithium ions returning to cathode. In tests, the cathode materials will take place the decomposition reaction with the continuous growth of temperature and the reaction can be expressed as:

$$\begin{aligned} &Li_{1-z}(Ni_xMn_yCo_{(1-x-y)})O_2 \\ &\quad \rightarrow (1-z)Li(Ni_xMn_yCo_{(1-x-y)})O_2 \\ &\quad + \frac{xz}{2}Ni_2O_3 + \frac{yz}{3}Mn_3O_4 + \frac{(1-x-y)z}{3}Co_3O_4 \\ &\quad + z\left\{1 - \left[\frac{3}{4}x + \frac{2}{3}y + \frac{2}{3}(1-x-y)\right]\right\}O_2 \end{aligned} \quad (5)$$

Hereafter, the reaction products Ni_2O_3, Mn_3O_4 and Co_3O_4 will decompose further and release O_2 at high temperature. The generated O_2 reacts with the electrolyte and releases much heat [31], which is as follows:

$$Ni_2O_3 \rightarrow 2NiO + \frac{1}{2}O_2 \quad (6)$$

$$Mn_3O_4 \rightarrow 3MnO + \frac{1}{2}O_2 \quad (7)$$

$$Co_3O_4 \rightarrow 3CoO + \frac{1}{2}O_2 \quad (8)$$

$$O_2 + \text{electrolyte} \rightarrow CO_2 + CO + H_2O + \text{heat} \quad (9)$$

All these reactions are affected by the internal lithium ions distribution, and the distribution is related to the battery’s SOC. The higher the SOC, the more oxygen will generate resulting in more violent reactions which explains how can SOC have such huge influence on the fire behaviors of packs.

Other 2020 papers[88] analyse the collected powders finding particles with “huge amounts of Nickel” and confirm that with the majority of particles are smaller than 10 μm^2 (measured as cross-sectional area in SEM images) they “*can therefore be inhaled deeply into the lungs*”. Detected elements included Al, F and Ni and the particles are stated to be “*carcinogenic and respirable for humans*”. The same source also details modes of failure, depending on State of Charge, and estimates the mass loss from failed cells undergoing thermal runaway. The particle size analysis in this paper (Essl, 2020) confirms unambiguously the generation of nickel-containing particulates in “inhalable powder form”, meeting the description of Item 11 of the Part 2 “Named Hazardous Substance”.

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[88] Essl, C., Golubkov, A. W. et al. (2020) Comprehensive hazard analysis of failing automotive Li-ion batteries in overtemperature experiments. *Batteries*, **6**,30 DOI: 10.3390/batteries6020030

More recent (2022) studies[89] confirm that the soot generated from EV fires consists of "*metal oxides of the cathode material, lithium and fluoride compounds*". The same source concludes that NMC cells in thermal runaway produce "*soot consisting mainly of heavy metal-oxides of Nickel, Manganese and Cobalt (each 18-20% by mass)*". These results are from deposition of "fire soot" in tests conducted in enclosed spaces mimicking vehicle parking facilities. These deposits were found to consist largely of the metal oxides. The carbon soot reported in Chen (2020) was not found at distance, presumably because these were actual fire tests in oxidising conditions, where fine carbon dust would be expected simply to burn to CO or CO_2. Moreover this "heavy metal oxide soot" is transported over long distances (up to 100 metres) and deposited on surfaces. The same metal oxides as in the dry powder were also found dissolved (or dispersed) in fire sprinkler water.

This paper has not carried out a comprehensive literature review, but the above sample of sources suggests that, over the period 2015 to 2022, a rapidly accumulating body of knowledge of chemicals released during Li-ion battery cell failure has emerged. In addition to the gaseous substances detailed in Sections 3.1 (Flammables) and 3.3 (Toxics), substances generated in Li-ion thermal runaway accidents definitely do include respirable dusts, transportable over distances of 100 m, definitely inhalable, and do include Nickel Oxides where the originating cell type contains Nickel (typically NMC, a common chemistry in the EV industry). Essl (2020) clearly states that "*Particles should be considered as additional toxic hazard*" (i.e. additional to Flammable and Toxic gases), and moreover points out that the overall mass loss of cells tested (44%) comprises 74 g of vent gases, but 300 g particulates (35% of original cell mass). Hence particulate emissions are in fact dominant by weight.

Quantities of respirable Nickel Oxide dusts generated in battery failures remain unclear. The emerging literature reports many different situations and measurement techniques, and is often inconsistent. Estimates may be possible from mass loss measurements documented by Essl *et al.* (2020), who found that mass loss in the form of collected particulates comprised 35% of the original cell mass. The total electrode mass (cathode plus anode plus Al collector foil) in the cell comprised 68.5% of the original, suggesting that around half of the electrode material is emitted in the form of particulates. Because some of the anode graphite may be expected to burn, cathode material (43.5% of the original mass) is likely to predominate, though the particulates analysis in Essl (2020) was not quantitative for composition.

An *a priori* estimate of 50% cathode material being lost in the form of inhalable dusts is therefore not unrealistic, and may not be conservative i.e. conceivably larger fractions of the cathode oxides may emerge as respirable dusts, smoke, or powders. Taking the data for an actual commercial BESS in Table 7 (0.726 tonne/MWh NiO) , a "worst case" generation of respirable dust would be 100% of the NiO quantities listed, with 50% a credible first estimate of particulates generation based on Essl (2020). This would mean generation of inhalable NiO dust of about 0.363 tonne/MWh. The Controlled Quantity of "reasonably foreseeable" generation of the Part 2 Named Hazardous Substance (CQ of 1 tonne) is breached at an energy storage capacity of 2.75 MWh.

This implies that even a single container BESS of the NMC cell chemistry would require HSC, based on exceeding the Controlled Quantity of a Part 3 Hazardous Substance (the cells), generation of over 1 tonne of a Part 2 Named Hazardous Substance being "reasonable to foresee in loss of control of the processes".

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[89] Held, M., Tuchschmid, M. *et al.* (2022) Thermal runaway and fire of electric vehicle lithium-ion battery and contamination of infrastructure facility. *Renewable and Sustainable Energy Reviews* **165**, 112474 DOI: 10.1016/j.rser.2022.112474

3.5 Routes to generation of Part 1,2 Hazardous Substances in loss of control accidents in BESS: (IV) Generation of E1 Hazards to the Aquatic Environment in firefighting operations

After Physical and Health Hazards, the remaining Hazard Class to be considered is that of substances hazardous to the aquatic environment in Category “Acute 1” or “Chronic 1” (E1 Environmental Hazard, CQ 100 tonnes) or in Category “Chronic 2” (E2 Environmental Hazard, CQ 200 tonnes).

Specific examples of substances that may be generated in fire or thermal runaway have been discussed already in previous sections and listed in Table 2, which is not exhaustive. Transition metal compounds in general, and compounds of copper, cobalt and nickel in particular, are all known or potential toxins in the context of the aquatic environment.

The quantities estimation required by the HSC Regulations under Hazard classes E1 or E2 requires a minimum quantity of 100 tonnes; however this easily generated in fire-fighting operations where water is used as an extinguishant (the only extinguishant recommended for thermal runaway in Li-ion batteries).

A quantity 100 tonnes of contaminated water is readily conceivable in fire-fighting: this is equivalent to 100 m^3, or 100,000 litres, or 26,420 U.S. gallons. A rough marker is that a Tesla Model S (battery capacity 100 kWh) that caught fire in Houston, Texas in April 2021 reportedly required 30,000 U.S. gallons to control, already in excess of the 100 m^3 threshold for an E1 Environmental Hazard, for a fire in a battery miniscule in size compared to the capacity of grid-scale BESS.

So it is almost inevitable during effective fire-fighting a quantity of potentially contaminated water in excess of the CQ for a E1 Hazard will be generated “if control of the processes is lost”.

The other requirement is that the contaminated fire water falls into the Categories “Acute 1” or “Chronic 1” (for toxicity to the aquatic environment) or in Category “Chronic 2” (for an E2 Hazard).

As argued above, this is again readily conceivable if copper oxides are generated from the anode foils in fires; these oxides are conceivable from all current Li-ion battery types (even LFP) and carry a M-factor of 100 (Harmonised Classification, either oxide, see Table 2) for the “Acute 1” hazard.

This would be the governing factor determining the concentration in contaminated fire water that would classify such fire water as a E1 hazard; applying the M-factor and the “Summation Method”[90] then under the rule in Table 4.1.1 of Annex I to the CLP Regulation[91] the contaminated fire water is classified as “Acute Category 1” if the concentration of copper oxides dispersed in the fire water exceeds just 0.25% by weight, requiring just 250 kg of copper (I or II) oxides in 100 m^3 of fire water, to exceed the Controlled Quantity of an E1 Environmental Hazard.

With a typical BESS containing 654 kg copper foil per MWh of energy storage (Table 7), this could burn to create 736 kg copper (II) oxide, per MWh energy storage. This is already (at just 1 MWh), well in excess of the quantity required to create a E1 Environmental Hazard from fire water.

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[90] Annex I to the CLP Regulation, section 4.1.3.5.5. See Guidance document https://echa.europa.eu/documents/10162/23036412/clp_en.pdf/58b5dc6d-ac2a-4910-9702-e9e1f5051cc5

[91] Rule defined in Table 4.1.1 of Annex I to the CLP Regulation, also in the above Guidance document.

Similarly any generation of Cobalt compounds would, under the Summation Principle, further reduce the concentrations of individual toxic compounds that would classify the resulting mixture as “Acute” or “Chronic” Toxic to the aquatic environment, in Category 1.

These considerations show that detailed appraisal of the possibility of generating E1 or E2 Environmental Hazards in fire water is warranted; the Controlled Quantity is readily exceeded by relatively modest fire-fighting operations.

The data that appear to be lacking for full application of the Regulations are data on those transition metal compounds classified as toxic to the aquatic environment, their generation in fire or thermal runaway accidents tackled with water, and their aquatic eco-toxicology (including M-factors) where not already listed in the ECHA databases or the parallel UK databases.

These data are required first of all for the operation of the Summation Principle in the CLP Regulation. This should not be confused with the “third application” of the “Aggregation Rule” (Note 5) required under the HSC Regulations, which in this instance would “aggregate” quantities of E1 and E2 Hazards below the Controlled Quantities (there are no Part 2 Named Hazardous Substances in the Environmental Hazard category that are relevant to BESS).

Although the application of the Note 5 Aggregation Rule is in principle required, it is likely that most fire-fighting operations would use in excess of the Controlled Quantity in any case, hence the Aggregation Rule is unlikely to be the controlling factor from the perspective of the HSC Regulations; the summation Principle of the CLP Regulation is in this case more important, for classifying a complex mixture of compounds potentially present in the fire water.

It would appear however that the quantities of copper, cobalt, or nickel compounds likely to classify contaminated fire water as “Acute Toxic Category 1” are quite small, and well within the potential to be generated from typical compositions of Li-ion BESS in fires or thermal runaway. For example, copper oxides at a concentration of just 0.25% (w/w) are an “Acute Toxic Category 1” contaminated fire water. This is readily conceivable.

A precautionary approach requires the assumption that such toxic compounds will be generated in fire, and any fire-fighting operation using in excess of 100 m^3 fire water will then exceed the CQ for a E1 Environmental Hazard.

Because these consequences are “reasonable to foresee if control of the processes is lost”, the copper foil content of Li-ion BESS should be regarded as a Part 3 hazardous substance, and potentially the cathode oxides in mixed oxide Li-ion battery chemistries.

One must again remark that actual fire tests, with water extinguishing and chemical analysis of the resulting fire water, and establishing the eco-toxicology of compounds found, are required to refine the above considerations.

4.0 Conclusions:

The significance of Table 5 (Physical Hazards) and Table 11 (Health Hazards) for the purposes of evaluation requirements for HSC are compared in Table 13, which summarises the threshold in energy storage capacity at which a HSC assessment is likely to be required, under various cell types and assumptions regarding CO generation in fire. Included are the conjectured thresholds for requirements based on inhalable nickel compounds, and on generation of contaminated fire water, for which further information is required for the assignment of fully evidence-based thresholds.

The central conclusion of Table 13 is that a 50 MWh BESS is almost certain to require a HSC assessment, regardless of electrode type or the assumptions made regarding CO. LFP cells are widely promoted as “safer” than other chemistries because of their “slower” behaviour in thermal runaway, but generate larger quantities of toxic fluorides. At 25 MWh, they are likely to require HSC on the basis of HF generation alone, irrespective of assumptions regarding CO. NMC or other mixed oxide cathodes may generate smaller quantities of toxic fluorides but including CO may still trigger the Aggregation Rule on Health Hazards, and are almost certain to trigger the Aggregation Rule on Physical Hazards, derived from anoxic conditions, similarly requiring no assumptions regarding completeness of combustion.

The generation of inhalable nickel oxides, now widely reported in the technical literature, appears to impose a particularly stringent threshold on BESS using nickel-based cathodes i.e. complex oxides such as the NMC, NMC-LCO and NCA chemistries. The Controlled quantity of inhalable Nickel Oxides, a Part 2 Named Hazardous Substance, is only 1 tonne, and this is also the Qualifying Quantity for *Upper-tier* COMAH (there is no “lower tier” for this Part 2 Named Substance). Based on a realistic (reasonable to foresee) estimate of 50% of the tonnage of NiO in an exemplar commercial BESS, we estimate Controlled Quantities being exceeded for the Nickel-containing cathode types at just 2.75 MWh, well within the capacity of a single container BESS. No progression of a thermal runaway accident to adjacent containers is required for the CQ to be exceeded.

For the smaller BESS, of non-Nickel cathode chemistries, there may be credible margins of uncertainty. For BESS installations of 50 MWh or above, it is almost inconceivable that one or other of the thresholds in Table 13 would *not* apply. Therefore, BESS at 50 MWh energy storage are almost certain to require HSC, irrespective of cell type, and disregarding thresholds dependent on an uncertain CO_2/CO ratio in fire.

As remarked at multiple points, these thresholds are based on evidence available in the published literature for representative cell types and conditions. Controlled and independently verified tests on representative samples of actual cells proposed to be installed would be necessary to establish legal thresholds more thoroughly than the *a priori* estimates set out here. These tests should include (i) closed container tests to establish quantitatively generation of P2 Flammable Gases (ii) open fire tests to establish H1 Acute Toxic fluorides, HCN, HCl and especially CO, under different degrees of oxygen supply or deprivation, and (iii) fire tests with chemical analysis of smoke, dust and contaminated fire water to establish Health and Environmental hazards from nickel oxide dusts or contaminated fire water more precisely than can be done at present (iv) consideration of the tests for “Explosive article” behaviour mandated in the UN MTC to determine of BESS cells in a high SoC behave as Division 1.3 or Division 1.2 explosives.

Storage capacity estimated at threshold	cell cathode type and conditions	governing reason for HSC
1 MWh (text, E1 Hazards)	*any, fire conditions with water extinguishant > 100* m^3	*CuO-contaminated fire water exceeds CQ of E1 Environmental Hazard*
2.75 MWh (text, Sect. 3.4.2, re Table 12)	Nickel oxide cathodes (NMC, or NMC-LCO, or NCA), in fire, generating smoke or dust	NiO in “inhalable powder form” exceeds CQ of Named HS in Part 2
15.5 MWh (text, Explosives)	any (with adjustment for energy density), at high SoC	Active materials exceed CQ for P1a Explosive Articles
16.7 MWh (Table 11)	LFP, high case for CO	Aggregation Rule > 1 for Health Hazards (H1 or H2 Acute Toxic Gases)
22.1 MWh (Table 11)	LFP, low case for CO	
25 MWh (text, re Table 11)	LFP, HF alone	HF exceeds CQ as H1 Acute Toxic
28.3 MWh (Table 5)	LCO-NMC, anoxic conditions	Aggregation Rule > 1 for Physical Hazards (P2 Flammable Gases)
34.5 MWh (Table 11)	LCO-NMC, high case for CO	Aggregation Rule > 1 for Health Hazards (H1 or H2 Acute Toxic Gases)
45.7 MWh (text, re Table 5)	LCO-NMC, anoxic conditions	CO exceeds CQ as P2 Flammable Gas

Table 13: Summary of energy storage capacity thresholds below 50 MWh likely to trigger a requirement for HSC, for contrasting cathode chemistries and CO assumptions. *Italicized entry* requires further data on behaviour of Li-ion cells in fire and of eco-toxicology of contaminated fire-water, for a fully evidence-based threshold.