Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

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Sub-Committee of Experts on the Transport of Dangerous Goods

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Recommendations made by the Sub-Committee on its forty-seventh, forty-eighth and forty-ninth sessions and pending issues: electric storage systems

Possible categorization of lithium batteries for transport according to their hazard and effects when reacting

Transmitted by the expert from France[1]

1. As pointed out in a series of documents such as ST/SG/AC.10/C.3/2016/84 from ICAO relating to the safe transport of lithium batteries by air, ST/SG/AC.10/C.3/2016/67 and informal document INF.22 (50th session) from RECHARGE and OICA relating to the transport of damaged/defective lithium batteries, dangerous events under normal transport conditions may result in a fire involving significant quantities of lithium batteries. Such events are numerous on transport by air as demonstrated by the recently updated review of incidents from FAA:

https://www.faa.gov/about/office_org/headquarters_offices/ash/ash_programs/hazmat/aircarrier_info/media/Battery_incident_chart.pdf

2. The expert from France propose to share some results concerning the way lithium batteries would behave in case of violent reaction. for the purpose of establishing some kind of ranking of lithium batteries (see ST/SG/AC.10/C.3/98, paragraph 73). These results rely on tests undertaken by the French laboratory INERIS investigating thermal power emitted and released gas nature and quantity of gases in case of thermal runaway of the batteries.

3. Two reports are attached under Annex 2 and 3, presenting extensive results of the investigations. Annex 2 presents test results concerning heat and gas emission of different types of batteries subject to fire or thermal runaway. Annex 3 contains numerical simulations of the effects of loads of various goods (dangerous or not dangerous goods) transported on road vehicules when subject to fire.

4. A brief summary of these results from INERIS are presented in Annex 1.

5. Although these results are yet restricted to one transport mode only and could be completed by several results concerning other modes, it doesn't appear impossible in the near future to assess the effects of batteries reacting in an accident and their intensity, with the goal of proposing a ranking i.e. a categorization of lithium batteries according to their behavior when reacting more or less violently. This would allow to define a series of adapted provisions depending on the allocated category. This comprises a definition of relevant tests for classification purpose in this categories.

6. It is proposed to add such work to the program for the next biennium. The lithium battery working group could be in charge coordination of this work.

Annex 1

I – Study of the effects of fire on different types of batteries

1. Several fire tests were performed at INERIS over the past years on Li-ion cells, modules and batteries of different chemistry (Nickel-Manganese-Cobalt, Lithium-Iron-Phosphate, ...) or geometry (cylindrical, prismatical, pouch).

2. The data (gas production, thermal power, …) were collected and compared in order to determine if, for the same energy, chemistry and/or geometry, every battery has the same behavior under fire conditions. Three effects were considered:

- toxic effect due to the gas release during the fire,
- thermal effect due to the heat produced during the fire,
- mechanical effect due to the projection of debris.

3. The results for the toxic effect are presented below. Each data point represents a sample tested at INERIS as a function of:

- geometry (Pouch: empty markers, Cylindrical: crossed markers, Prismatic: filled markers),
- chemical composition (NMC: triangle, LMO: circle, LFP: diamond).

In order to compare the data for the panel of tested batteries, the quantities of each gas measured during the tests are expressed in g/Wh using the following formula:

$$\frac{\textit{Mass of the gas measured during the fire test}}{\textit{Electrochemical energy of the tested sample}}$$

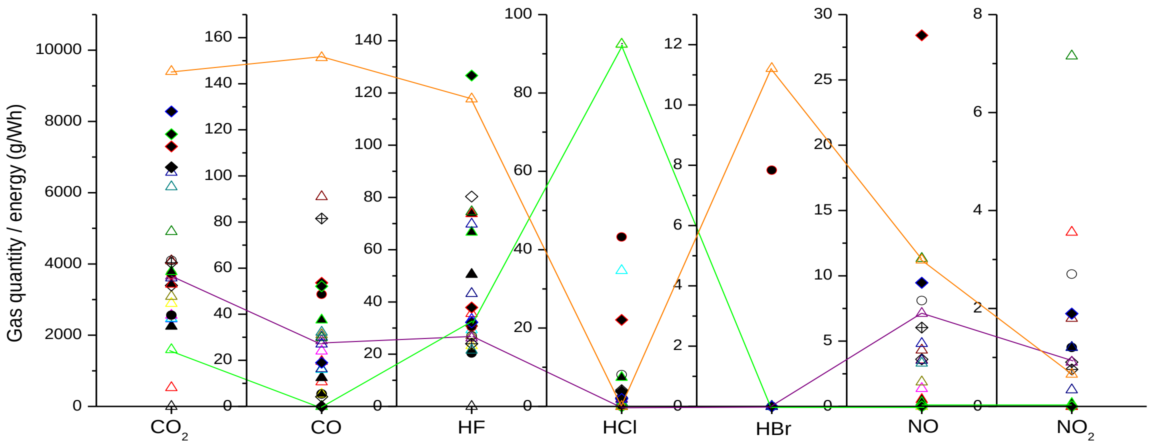

Figure 1: Quantities of gases measured during the fire tests performed at INERIS

The results show that the quantity of gases produced during a fire test depends not only on the energy of the tested sample but on a number of parameters. These parameters could be the chemical composition, the geometry, the state of charge, the architecture of the sample, ...

It can also be noted that for three samples with the similar geometry and chemistry (orange, green and purple lines in the Figure 1 above), the quantity of gases released can vary by a factor of almost 10, depending on the type.

4. The results for the thermal effect are presented below. Each data point represents a sample tested at INERIS as a function of:

- geometry (Pouch: empty markers, Cylindrical: crossed markers, Prismatic: filled markers),
- chemical composition (NMC: triangle, LMO: circle, LFP: diamond).

In order to compare the data for the panel of tested batteries, the radiated power measured during the tests are expressed in kW/Wh using the following formula:

$$\frac{\textit{Radiated Power of the fire}}{\textit{Electrochemical energy of the tested sample}}$$

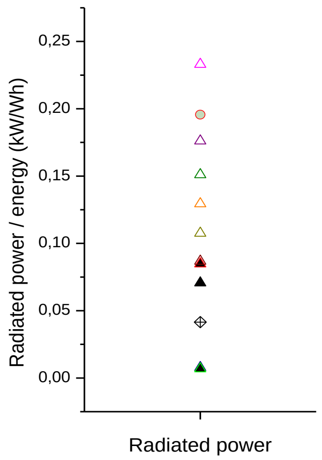

Figure 2: Fire radiated power during the fire tests performed at INERIS

The results show that the radiated power of the fire during a burning test depends not only on the energy of the tested sample but on a number of other parameters including chemical composition, geometry, state of charge, architecture of the sample, ...

It can be noticed that for several samples with the same geometry and the same chemical composition, radiated power can vary by a factor of almost 30.

5. Regarding the mechanical effects, during all the tests at INERIS, projections of debris were observed only for one sample with cylindrical cells. Furthermore, according to a report[1] published by the NFPA (National Fire Protection Association), this geometry possesses the higher risk of projections. But no conclusion can be made yet and this effect needs to be studied more deeply.

II – Comparison of the effects of different types of cargoes in fire

6. In part I, only results for batteries were presented. To go one step further, the thermal and toxic effects of fires of different types of road cargoes (classified or not as dangerous goods) were compared using simulation tools. This allowed to illustrate that the calculated effects of a lithium battery cargo subject to fire may be very variable, depending on the type, and sometimes lower than the effects of some non dangerous goods cargoes.

The cargoes considered are presented in Table 1 below:

Cargo type	Unit weight (kg)	Unit dimensions (L x w x h) m^3	Number of elements in the semi-trailer	Total weight of the loading (tons)
Battery packs N°1	**280**	**1.2 x 0.75 x 0.8**	**89**	**24.9**
Battery packs N°2	**232**	**1.3 x 0.68 x 0.4**	**107**	**24.8**
Pallets of aerosol cans	**500**	**1.2 x 0.8 x 2**	**33**	**16.5**
Pallets of DVDs (not DG)	266	1.2 x 0.8 x 1.8	33	8.8
Pallets of salads (not DG)	83	1.2 x 0.8 x 1.8	33	2.8
Pallets of 4 different plastics barrels (not DG)	120	1.2 x 0.8 x 1	66	7.9
Pallets of pesticides	**233**	**1.2 x 0.8 x 2**	**33**	**7.7**
Blocks of polyurethane (PU) foam (not DG)	100	1.9 x 1 x 1.55	26	2.6

Table 1: Cargoes considered in the study

The two batteries studied were taken randomly among the all amount of batteries tested at INERIS. The cargoes presented in red are those classified as dangerous goods.

[1] http://www.nfpa.org/research/fire-protection-research-foundation/reports-and-proceedings/hazardous-materials/other-hazards/lithium-ion-batteries-hazard-and-use-assessment
Report from July 2011

7. For the thermal effects, the results are presented in the Figure 3 below:

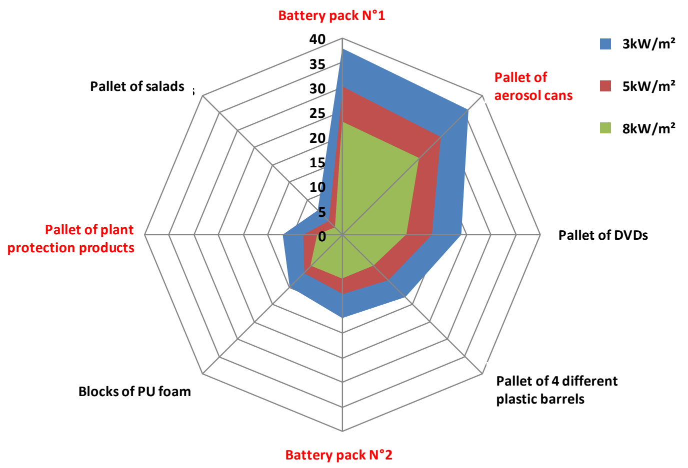

Figure 3: Thermal effects distances in meters for several thresholds (3, 5 and 8 kW/m²)

8. It can be noted that depending on the battery type, the thermal effects of a fire can be of the same order of magnitude of those relating to the fire of a cargo of aerosol (Battery pack N°1) or of a cargo of plastics barrels (Battery pack N°2).

9. For the toxic effects, the results are presented in the Table 2 below:

Cargo type	Equivalent toxicity of the emitted fumes at the source to reach irreversible effects (ppm)	Toxicity
Pallets of 4 different plastics barrels (not DG)	554	High
Pallets of pesticides	**989**	
Battery packs N°2	**4434**	
Blocks of polyurethane (PU) foam (not DG)	5309	
Battery packs N°1	**5834**	
Pallets of aerosol cans	**5850**	
Pallets of salads (not DG)	6520	Low
Pallets of DVDs (not DG)	14091	

Table 2 : Toxic effects thresholds

As for the thermal effects, the calculated equivalent toxicity of the emitted fumes is variable, depending on the battery type, ranking between the toxicity of pesticides and those of aerosol cans.

10. As a summary, the study of thermal and toxic effects that may be generated by fires of several cargoes (classified or not as dangerous goods) has determined that:

- the effects can vary greatly from one battery type to another,
- to the point that, for some batteries, these effects are lower than those for non dagerous goods, and for others they may be higher than those of dangerous goods such as flammable aerosols.

Annex 2

Document referenced Draft_DRA96_2014_OpérationA5_English

Annex 3

Document referenced Draft_DRA96_2015_OpérationA5_English

STUDY REPORT 14/01/2014

DRA-14-141820-13186A

Study on the relevance of a classification system for the transport of batteries and on the feasibility of a specification book

Study on the relevance of a classification system for the transport of batteries and on the feasibility of a specification book

Accidental Risk Division

People involved in the study: P. Goncalves

FOREWORD

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1 INTRODUCTION

Within the DRA-96 support program, operation A.5 focuses on the particular case of the transport of batteries. Work performed in 2013 detailed results obtained from various batteries during abuse testing and defined test specifications to potentially classify battery for transport.

In the present report, we will study, given past information learned, the relevance of having a classification of batteries for transport and will demonstrate the feasibility of the specifications proposed in 2013.

2 STUDY ON THE RELEVANCE OF HAVING A CLASSIFICATION OF BATTERIES FOR TRANSPORT

The ultimate goal of DRA 96 operation A5 is to end up with a classification system of batteries for transport based on the effects observed during abuse testing. In order to access such a classification, the 2013 report for operation A5 of the DRA 96 support program (DRA-13-133471-12328A) proposed to evaluate batteries' behavior when crushed, pierced or on a fire.

As fire was the last, and most dreaded, of many accidental scenarios (overload, short-circuit...), it was decided to focus on external fire testing in order to define this classification system.

2.1 CURRENT BATTERY MARKET

The idea of creating such a classification comes most notably from the great variety of battery types being transported in terms of their geometry, chemical composition and design which leads to varying behavior when batteries are subjected to accidental situations.

2.1.1 Geometry

In terms of cell geometry, four configurations[1] are currently used on the market (Figure 1):

- Cylindrical cell: generally used for small cells. It is constructed by superimposing anode-separator-cathode-separator bands which are coiled around a central pivot,

- Prismatic cell: used for capacity greater than 10Ah. Its housing is rigid with protective elements (e.g.: safety valve),

- Button cell: hardly used anymore for rechargeable lithium batteries,

- Pouch cell: have a soft housing which is sealed close to the electrode-separator stack and allows for potential warping due to internal cell pressure.

Figure 1: Various lithium cell formats: cylindrical, prismatic and pouch

[1] http://batteryuniversity.com/learn/article/types_of_battery_cells

2.1.2 **Chemical composition**

Regarding chemical composition, we will differentiate cathode and anode materials in the study below.

Currently, five[2] cathode materials are mostly present on the market:

- Cobalt Oxide, $LiCoO_2$ (LCO): a material still widely used in current batteries due to its high energy density, its low self-discharge, but high cost (due to the Cobalt) and low thermal stability (runaway risk),

- Nickel-Manganese-Cobalt Oxide, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (most widely used formula) (NMC): used more and more (particularly in electric vehicles), replacing cobalt oxide thanks to its greater thermal stability and lower cost,

- Nickel-Cobalt-Aluminum Oxide, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA): used more and more for stationary or mobile applications thanks to its high energy density and its long stability over time, but has a relatively high cost.

- Manganese Oxide, $LiMn_2O_4$ (LMO): used more and more thanks to its lower cost relative to cobalt oxide cathodes, but has long-term cyclability which is inferior to other chemistries,

- Iron Phosphate, $LiFePO_4$ (LFP): used more and more thanks to its very high thermal stability and its capacity to withstand high power levels, but has low energy density resulting from lower usage voltage than the preceding oxides.

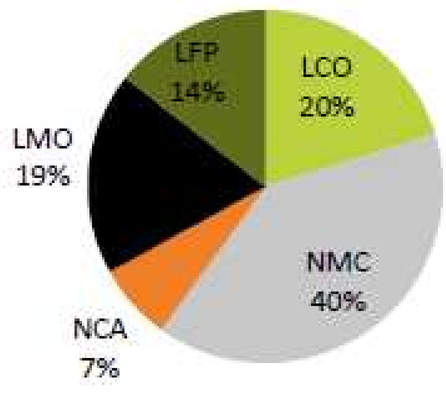

Figure 2: Lithium battery distribution forecast as relates to cathode material in 2020[3]

[2] N. Nitta, et al., Matter Today (2014)

[3] The Worldwide battery market 2011-2015, Avicenne Energy Presentation, Batteries 2012

As for anodes, two materials[2] are marketed on a large scale:

- Graphite: anode material present in the vast majority of current lithium batteries, thanks to its great abundance on earth, its low cost and strong thermal conductivity,

- Lithium Titanate, $Li_4Ti_5O_{12}$ (LTO): used more and more thanks to its high thermal stability, its capacity to withstand strong currents and its long life, despite a much higher cost and lesser energy density than graphite.

Instinctively, the chemical composition could, during an external fire test, have an influence on the effects observed. Indeed, depending, for example, on the quantity of electrolyte and on the chemical compounds used, the quantities of gases produced and the fire intensity could widely vary.

Another type of lithium battery that is worth mentioning is the Lithium-Metal-Polymer battery developed solely by Batscap and used in the BlueCar electric vehicle. This battery is made up of a metallic lithium anode and a vanadium oxide, carbon and polymer-based cathode.

2.2 STUDY OF THE RELEVANT EFFECTS FOR BATTERY CLASSIFICATION

During the various fire tests performed at INERIS, the following effects were observed:

- Toxic effect due to the emission of gases produced during combustion,

- Thermal effect due to heat released by the burning battery,

- Mechanical effect due to material spatter.

In light of the results obtained at INERIS, the effect of overloading does not seem relevant and need not be taken into account. Battery carriage classification could therefore be done according to relevant criteria (e.g.: emitted heat flux...) for the 3 effects listed above.

To determine the relevance of reaching a classification, the external fire tests previously done at INERIS must be analyzed to see if relevant classification criteria exist and to precisely define them. The following tests were done:

- At the cell, module, module stack or pack level,

- On items of varying chemistries (NMC, LFP...),

- On items of varying geometries (cylindrical, prismatic...).

2.2.1 **Toxic Effect**

Since the amount of gas emitted is an extensive variable, a first thought regarding toxic effects toxic effects is that they are greatly dependent on the amount of energy of the sample sample subjected to the external fire test (

Figure 3).

Indeed, within the framework of battery transport, the values of energy transported can vary enormously and are in the order of:

- Watt-hours for transport of a few button-type or 18650 batteries,
- Up to several Megawatt-hours for, for example, a truck fully loaded with car batteries.

Any prospective classification will therefore need to take into consideration the amount of energy transported.

Figure 3 shows the amounts (in g) of carbon monoxide (CO) and hydrogen fluoride (HF) measured during the tests performed at INERIS as a function of:

- The energy of the tested sample,
- The geometry (*pouch: full markers, prismatic: empty markers and cylindrical: locked markers*),
- The chemical composition (*NMC: triangle, LMO: round and LFP: diamond*).

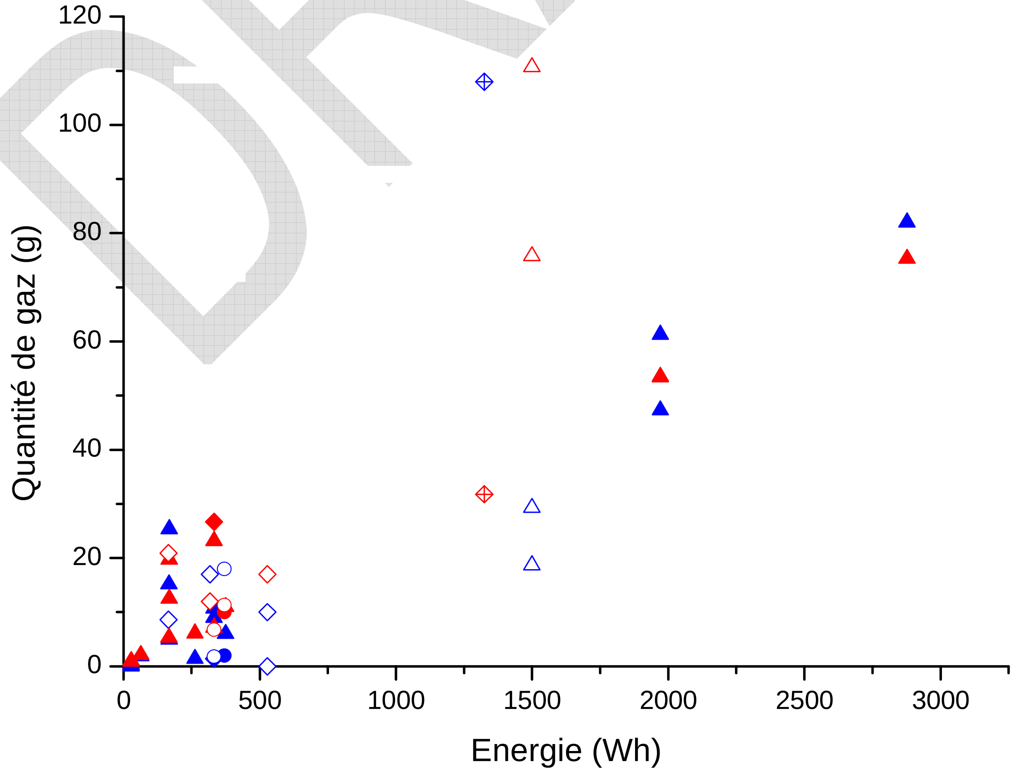

Figure 3: Amounts of CO (blue) and HF (red) emitted by the samples subjected to an external fire test at INERIS

As expected, the analysis shows a strong disparity between total amounts of gas emitted during the various external fire tests performed at INERIS. Of particular note is the dependence of the amount of gas emitted on the energy of the sample subjected to fire.

In light of this result, a classification of batteries for transport as a function of their toxic effect during a external fire test could at first appear to be relevant. Indeed, the amount of transported energy will directly affect the amount of toxic fumes emitted during an accidental event and the transported load would be considered toxic or not depending on this amount of energy.

However, it would be overly simplistic to consider only the amount of transported energy as a factor influencing a battery's toxicity when subjected to fire. To illustrate this, Figure 4 shows the various amounts of gas measured during the external fire tests performed at INERIS, expressed in energy units (mg/Wh).

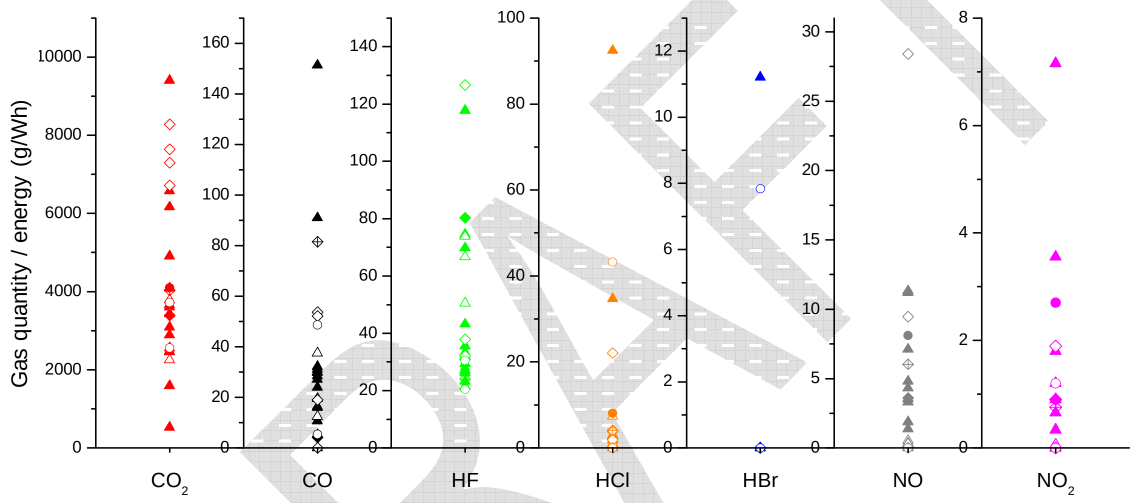

Figure 4: Amounts of various gases emitted, in energy units, during the cell, module or pack fire tests at INERIS

The results analysis shows a strong heterogeneity in the values of amount of gas emitted during an external fire test. A battery's toxic effect therefore strongly depends on a large number of parameters such as the amount of energy of the tested sample, the chemical composition, the sample structure, the tested batteries' various states of charge... One notices that for two samples sharing the same chemistry and geometry, the amount of gas emitted can vary by a factor of 10.

A classification of transported batteries as a function of their toxic effect according to the results of a external fire test therefore seems conceivable and relevant.

Future work within DRA 96 operation A5 will consist of:

- defining a reliable and sound test protocol to be able to test batteries and gather data needed to evaluate their toxic effect,
- identifying the parameters relevant to classification,
- for these parameters, defining one or more thresholds that will allow the classification of batteries according to one or more toxicity classes.

2.2.2 **Thermal effect**

During external fire tests, the study of a battery's thermal effect is done using a fluxmeter placed at a certain distance from the tested sample. The value obtained from this measurement is a heat flux value (in kW/m²) received by the fluxmeter. By nature, this value is very dependent on the distance at which the fluxmeter is placed. Since all external fire tests done at INERIS were not performed according to the same protocol (different clients, different tested sample sizes...), the distance of the fluxmeter varied tremendously and the measured flux value could not be taken at face value to make a comparison between the batteries' thermal effects.

To be able to make such a comparison, one must be able to trace back to the power emitted by the flame produced by the tested battery. To do this, one must choose a model. The point source model[4] where the flame is equivalent to a point source, centered on its axis, radiating with power equivalent to that of the entire flame (Figure 5) is a relevant model for this study.

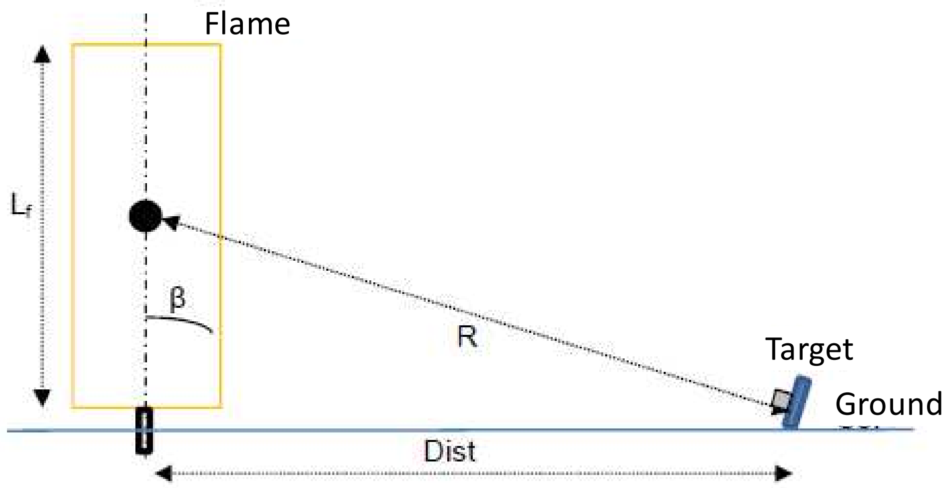

Figure 5: Point source model schematic

[4] Report n° DRA-14-133133-02917A: Knowledge and tool formalization in the major risk area (DRA-76); Ω-8; Torch Fire: http://www.ineris.fr/centredoc/referentiel-omega8-final1-couverture-1395914430.pdf

Radiative thermal flux density, Φ_c, received by a target placed at a distance R from the flame and perpendicular to the radiation at the point source is given by the following formula:

$$\Phi_c = a \frac{P_r}{4\Pi R^2}$$ Equation 1

with:

Φ_c	=	Flux received by the target, [W/m²]
P_r	=	Power radiated by the flame, [W]
R	=	Distance between the center of the flame and the target, [m]
a	=	Atmospheric transmissivity or atmospheric attenuation factor, [-]
$4\Pi R^2$	=	Solid angle of sphere with radius R centered on the point source, [-]

In our case study, the atmospheric attenuation value will be equal to 1 (upper-bound case) by making the following hypotheses:

- The fluxmeter is placed very close to the flame (a few meters),
- The tests are done in a closed and ventilated vessel chamber, therefore condensation in the air is considered to be non-existent.

During the external fire tests done at INERIS, the measured flux values are not constant with time and vary significantly. For our study, it was therefore decided to take the maximum value measured during the test. The power radiated by the flame with therefore be equal to:

$$P_r = \Phi_c(max) * 4\Pi R^2$$ Equation 2

As in the toxic effect study, a first thought regarding thermal effects is that they are greatly dependent on the amount of energy of the sample subjected to the external fire test.

Indeed, within the framework of battery transport, one can recall that values of transported energy can vary drastically and are in the order of:

- Watt-hours for transport of several button-type or 18650 batteries,
- Up to several Megawatt-hours for, for example, a truck fully loaded with car batteries.

Figure 6 shows the values of power radiated by the flame as measured during the test as a function of:

- The energy of the tested sample,
- The geometry (*pouch: full markers, prismatic: empty markers and cylindrical: locked markers*),
- The chemical composition (*NMC: triangle, LMO: round and LFP: diamond*).

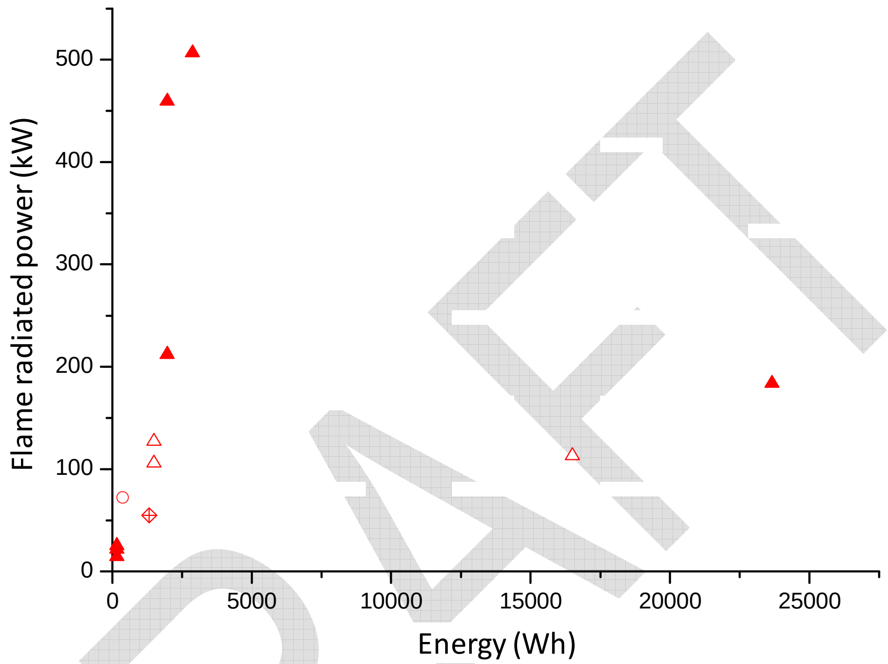

Figure 6: Power radiated by the flame of samples subjected to the external fire test at INERIS

Indeed, the analysis shows a dependence of the power radiated by the flame as a function of the energy of the sample subjected to fire. However, this dependence is much more pronounced at low energy levels (< 5000 Wh) than at high energy levels. Because the two samples were full battery packs and had energy levels above 15,000 Wh, it is likely that the fact that the active material (i.e. the modules) was isolated from the flame by an exterior metal casing caused the radiated power during these tests to be inferior to what would be expected at such energy levels. **In order to create a classification for battery transport, it therefore seems essential to handle single cell or module transport separately from full battery pack transport.**

In light of this result, a classification of batteries for transport as a function of their thermal effect during an external fire test could at first appear to be relevant. Indeed, the amount of energy and the type of merchandise transported (pack, cell, ...) will directly affect the amount of radiated power during an accidental event, and a transported load may or may not be considered a thermal risk depending on this energy.

However, it would be overly simplistic to consider only the amount of transported energy as a factor influencing a battery's radiated power when subjected to fire. To illustrate this, Figure 7 shows the various amounts of gas measured during the external fire tests performed at INERIS, expressed in energy units (mg/Wh).

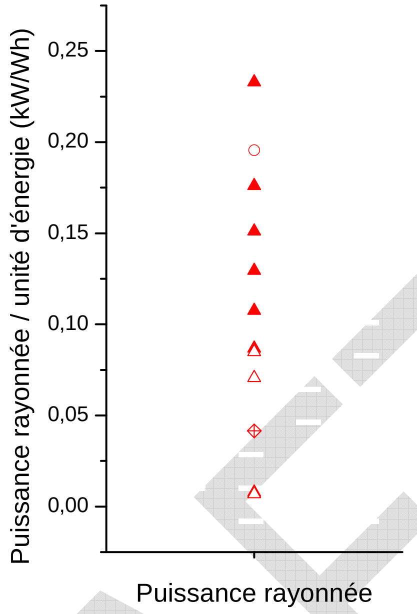

Figure 7: Emitted radiated power, in energy units, during the cell, module or pack fire tests at INERIS

The results analysis shows a strong heterogeneity in the values of amount of radiated power emitted during a external fire test. A battery's toxic effect therefore strongly depends on a large number of parameters such as the amount of energy of the tested sample, the chemical composition, the sample structure, the tested batteries' various states of charge... One notices that for two samples sharing the same chemistry and geometry, the radiated power per energy unit can vary by a factor of 20.

Significantly varying behavior was also observed as a function of the samples subjected to fire: single active elements (cells or modules) or full battery packs.

A classification of transported batteries as a function of their thermal effect according to the results of an external fire test therefore seems conceivable and relevant.

Future work within DRA 96 operation A5 will consist of:

- Defining a reliable and sound test protocol to be able to test batteries and gather data needed to evaluate their thermal effect,

- Identifying the parameters relevant to classification,

- Defining one or more thresholds that will allow the classification of batteries according to one or more classes of thermal effect.

/!\ In light of the results above, the protocol and/or the thresholds which will be defined in the classification for battery transport may vary as a function of the type of item to be transported (cell, module, pack).

2.2.3 **Effect of material spatter**

During the INERIS external fire tests, only one tested sample projected material at significant distances. The sample for which the spatter effect was observed is the only sample of cylindrical geometry subjected to an external fire test at INERIS, which can lead to believe that this particular geometry is more prone to spattering. Furthermore, according to a report[5] published by the NFPA (National Fire Protection Association), this geometry presents the most risk for projectile danger. A more in depth study of this effect must therefore be done through the test campaign which INERIS will undertake within the scope of DRA 96 operation A5 to demonstrate, or not, the impact of this geometry.

At first glance, a battery transport classification as a function of spatter effects according to the results of an external fire test seem relevant nonetheless, and future work within this operation will be to:

- Define a reliable and sound test protocol to be able to test batteries and gather data needed to evaluate the spatter effect,

- Identify parameters relevant to classification,

- If possible, define one or more thresholds that will allow the classification of batteries according to one or more classes of spatter effects.

[5] http://www.nfpa.org/research/fire-protection-research-foundation/reports-and-proceedings/hazardous-materials/other-hazards/lithium-ion-batteries-hazard-and-use-assessment

2.3 CONCLUSION

The study of INERIS external fire test results indicates classification of batteries for transport as a function of their toxic and thermal effects as being particularly relevant. A test protocol and reference threshold values will have to be defined however to carry out this classification.

Regarding a classification as a function of spatter effects, a more in depth study will have to be done within the operation A5 of the DRA 96 to demonstrate the relevance of this criterion and to define a test protocol which would allow gathering all information required for a prospective classification.

No over-pressure effect was detected during the various tests performed at INERIS. This effect therefore does not appear to be relevant for the aimed classification.

3 SPECIFICATIONS FEASIBILITY

As recalled in §2, the ultimate goal of DRA 96 operation A5 is to be able to end up with a classification of batteries for transport in accordance with the effects observed during abuse testing. In order to achieve such a classification, the 2013 report for DRA 96 support program operation A5 (DRA-13-133471-12328A) proposed to evaluate batteries' impact resistance, behavior when pierced and when on fire.

As fire was the final and most dreaded scenario of many accidental situations (overload, short-circuit...), it was decided to focus on external fire testing in order to define this classification system.

3.1 FUTURE METHODOLOGY

Paragraph 2 clearly demonstrates that the effects observed on batteries subjected to fire, in particular thermal and toxic effects, and to a lesser extent, spatter effects, should allow the establishment of a classification method.

Within DRA 96 operation A5 in 2015, a methodology will be implemented to come up with such a classification.

Firstly, relevant parameters must be selected for each effect defined above. These parameters must be selected for their appropriateness as regards the goal of this exercise, which is to come up with a classification system for battery transportation. As the principles for current tests in the testing and criteria manual of Recommendations for carriage of hazardous material are such that they can be carried out by a large number of laboratories, the parameters selected for a prospective classification must also be easily measurable.

After having defined the relevant parameters for classification, threshold values must be recommended. These values will allow the classification of batteries according to one or more classes with regards to toxic, thermal or spatter effects.

For toxic effects, we may rely on what is done in the classification for the transport of toxic and infectious substances (Class 6)[6]. Indeed, the classification of the substances is realized by using, as reference parameter, the gas concentration in the ambient air for a defined exposure time of 60 minutes.

For thermal or spatter effects, we may rely on the work done in the classification for the transport of explosives materials (Class 1). Indeed, for the study of the thermal effect, an external fire test[7] is performed using the thermal flux as the parameter used for the classification of the various samples tested.

[6] *Class 6: Toxic and infectious substances.* "Recommendations on the transport of dangerous goods, Model Regulations."

[7] Test 6 (c): External fire (bonfire) test. "Recommendations on the transport of dangerous goods, Manual of Tests and Criteria."

For the study of spatter effects, the external fire test[7] was performed using three aluminum screens (size and type of aluminum were clearly defined) placed 4 m from the edge of the tested samples as a means of measuring the spatter effect.

Moreover, for toxic or thermal effects, the parameters chosen for the transport classification (gas concentration and thermal flux) are the same as the ones defined on a ministerial decree[8] and used for industrial site hazard studies in France. Therefore, theses parameters seem very relevant.

3.2 BROAD PRINCIPLES OF THE TEST PROTOCOL

As defined in the previous paragraphs, the protocol to be implemented in order to come up with a prospective classification of batteries for transport must:

- Be sound, to allow the results to be reproduced,
- Be as simple as possible to implement in order to allow a maximum number of laboratories to carry it out,
- Allow the gathering of all data required to calculate relevant parameters to be defined within the classification context.

Preliminary thoughts on this test protocol are described in the paragraphs below.

3.2.1 **Tested samples**

Batteries are already subjected to a number of tests prior to authorization for transport:

- T1: Altitude
- T2: Thermal stability
- T3: Vibrations
- T4: Shock
- T5: Short-circuit
- T6: Impact
- T7: Overcharge
- T8: Forced discharge

[8] Order of 09/29/05 related to the evaluation and the accounting for the probability of occurrence, the kinetics and the intensity of the effects, and the severity of consequences of potential accidents in the hazard studies of classified installations and subjected to authorization

All these tests are performed on batteries (cell, module or pack) without packaging. Nevertheless, during the external fire tests performed for the classification of other dangerous goods, the samples are tested with their transport packaging. Therefore, the test campaign at INERIS could be performed on batteries inside their packaging.

3.2.2 **Fuel**

As the external fire tests aim to achieve a classification for battery transport, the fuel to be used for the test must be consistent with this objective. Therefore, an automobile fuel (diesel or gasoline) will be used for the test.

3.2.3 **Exposure time**

In order to be the most representative of a most critical case, the battery will be completely on fire for the external fire test. The fuel fire will therefore be maintained under the tested sample until the battery is fully combusted. The end of combustion will be determined with the absence of flames on the sample.

3.2.4 **Gas analysis**

Gas analyses can be performed in several ways in order to reach a final total amount of gas:

- Continuous analysis: physiochemical methods, FTIR...

- Discontinuous analysis: bubbling...

To demonstrate measurement reliability during the tests to be performed at INERIS, continuous and discontinuous gas analyses will be done measuring the various gases, known to be toxic, that may be emitted during a battery fire: CO_2, CO, HF, NO_x …

3.2.5 **Thermal flux measurement**

The thermal flux emitted by the battery fire will be measured with a fluxmeter placed at a certain distance from the tested sample. As the thermal flux value can vary greatly depending on the sample being tested, the distance at which the fluxmeter will be placed may also vary. However, to be able to assume the point source model (see §2.2.2), the distance must be greater than five times the equivalent diameter of the tested sample.

During the INERIS test campaign, several fluxmeters will be placed at different distances in order to verify that the different values measured will allow reverting back to an identical radiated power.

3.3 INERIS TEST CAMPAIGN

3.3.1 Test campaign objectives

INERIS has already completed a large number of external fire tests (see §2). However, in order to be able to come up with a battery transport classification, a test campaign must be carried out because, during the previous tests:

- The procedures used were not all identical and varied by client (fuel, battery state of charge...)
- Few tests were done with a fluxmeter to measure the thermal effect and most were done on cells which all had the same composition and geometry (pouch cells with NMC chemistry)
- No test was performed with a means to analyze spatter effects
- Very few tests were performed on cylindrical cells which make up a large part of the current battery market (especially for portable applications) and which are prone to spatter effects.

The goals of the future INERIS test campaign are therefore:

- To test the protocol to be implemented and prove that it is sound, reliable and that it will gather all the required data by repeating it several times on a same sample,
- To modify the protocol if it does not meet one of the conditions listed above and to test the new protocol, once again, on several identical samples,
- To study the impact of the battery state of charge on its response to the external fire test in order to define the state of charge to be used for the classification test protocol,
- To conclude on the impact of the battery's geometry and chemical composition by using a same test protocol for all tests,
- To check the impact of the tested sample's energy value on the batteries' toxic, thermal and spatter effects. This relationship will allow to conclude, or not, through a battery carriage classification test, on the possibility of performing a test on a sample whose energy level is inferior to the amount transported,
- To demonstrate that the cylindrical cells are indeed more prone than other geometries to spatter effects and to conclude on the relevance of including this effect in a prospective classification,
- To perform tests on a wide variety of batteries while being very exhaustive regarding the data measured (thermal flux, continuous gas analysis...), to define, once the data is gathered, the parameters most relevant to classification (thermal power or energy, total or kinetic amounts of gases...).

3.3.2 **Supply of batteries**

To perform this test campaign, batteries must be supplied. With the goal of obtaining a sound classification for lithium battery transport, the tests must be performed on a representative current market sample, specifically in terms of chemistry and geometry (see §2.1). To perform the tests and to be able to observe the effects (specifically thermal or toxic), it was decided that the tested samples must have an energy level of at least 300 Wh.

Thanks to the study in §2.1, it seems that to represent actual market conditions, it is appropriate to obtain batteries with

- Cylindrical, prismatic and pouch geometries,

- Cobalt Oxide, Nickel-Manganese-Cobalt Oxide, Nickel-Cobalt-Aluminum Oxide, Manganese Oxide and Iron Phosphate cathode materials,

- Graphite and Lithium Titanate anode materials.

Access to a supply of Lithium-Metal-Polymer batteries is rendered difficult by the fact that these batteries are marketed by Batscap for internal use only.

There are five cathode chemical compositions, two anode chemical compositions and three cell geometries to be tested. In order to be the most representative and the most exhaustive possible, and to reach the goals defined in the preceding paragraph, the following test sequence is proposed:

- Three tests with one same cell (cathode 1, anode 1 and geometry 1) with the same energy value to demonstrate the soundness and reliability of the test protocol. Here, we are assuming that the protocol will be modified twice and that the total number of tests for this sequence is nine.

- Five tests with the same cell as previously (cathode 1, anode 1 and geometry 1), but with varying states of charge in order to determine the state of charge value to use during the tests. Each test will be repeated twice, for a total of ten tests,

- Two tests with the same cell as previously (cathode 1, anode 1 and geometry 1), but with different energy assemblies to demonstrate, for the same cell, the relationship between the thermal and toxic effects and the energy of the sample subjected to fire. Each test will be repeated twice, for a total of four tests,

- Four tests on cells of varying cathode chemical composition (cathode 2, 3, 4 and 5) but with the chemical composition of anode 1 and the same geometry 1 to verify the impact of chemical composition on the effects. Each test will be repeated twice, for a total of eight tests,

- One test on a cell with a different anode chemical composition (anode 2) but with the chemical composition of cathode 1 and the same geometry 1 to verify the impact of chemical composition on the effects. This test will be repeated twice,

- Two tests on cells with the same chemical composition (to be defined) but with different geometries (geometry 2 et 3) to verify the impact of geometry on the effects. Each test will be repeated twice and will be performed on three selected chemical compositions, for a total of twelve tests,

Forty-five tests are to be performed in order to represent current market conditions for lithium batteries and to reach the goals defined in the preceding paragraphs.

3.3.3 **Budget allocation**

After some research, we found that we could easily stock up on:

- Cylindrical, pouch and prismatic batteries for the $LiFePO_4$ cathode and a graphite anode,
- Cylindrical and pouch batteries for $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ and $LiCoO_2$ cathodes and a graphite anode,
- Pouch batteries for a $LiMn_2O_4$ cathode and a graphite anode,
- Cylindrical batteries for a $Li_4Ti_5O_{12}$ anode and a $LiFePO_4$ cathode.

The cost of cells, taking into consideration unforeseen events and the tests to be performed with the above-mentioned cells, is approximately € 20,000.

For the 2015 DRA 96 A5 operation, a new search will have to be done to stock up on:

- Prismatic cells for two different cathode materials other than $LiFePO_4$ and a graphite anode,
- Cylindrical or pouch cells with a graphite anode and a $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode,
- Cylindrical cells with a graphite anode and a $LiMn_2O_4$ cathode.

In order to perform all the tests, the total cost of cell provisioning will therefore be approximately € 30,000.

Considering the budget allocated for the operation and the equipment test availability, it seems more reasonable to allow a work program over 2, maybe even 3 years. According to the budget anticipated for the 2015 DRA 96 A5 operation, € 10,000 worth of cells could be ordered and six tests could be performed in 2015. The final cell order and the performance of the remaining tests would be done in the following years.

The cost of developing the protocol and the performance of the tests within three test campaigns is estimated at € 160,000.

Processing the data from these tests is estimated at € 120,000.

The total operation is therefore estimated at € 310,000.

4 CONCLUSION

Following the meeting held on December 9, 2014 at the Ministry of Ecology, Sustainable Development and Energy and the discussions held in relation to this report, the MTMD requested to define an external fire test protocol, the expected result of which is the destruction of the sample. The effects produced by this destruction will be analyzed in order to attempt to establish a classification.

The analysis of the external fire tests previously done at INERIS allowed to determine that the effects one can observe during those tests were thermal, toxic and spatter effects (although the latter was only observed once). The test protocol and the tests that will be performed within the operation A5 in 2015 must allow to gather reliable data to then define threshold values for the various expected effects which will be used to establish a prospective classification.

The current use of test methods, technical personnel assigned to the battery tests, and the cost of performing the tests does not allow for the completion of the entire program within one year. One must count on three years of execution to obtain a complete sample group.

The test protocol as well as an interim report on results of tests performed will be provided in 2015.

STUDY REPORT 01/05/2016

DRA-16-148820-00064A

COMPARISON OF THERMAL AND TOXIC EFFECTS Of THE FIRE OF BATTERIES AND OTHER GOODS IN TRANSPORT BY A HEAVY GOODS VEHICLE

Comparison of thermal and toxic effects of the fire of batteries and other goods in transport by a heavy goods vehicle

Accidental Risk Division

People involved in the study: Guillaume LEROY, Philippe GONCALVES

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1 INTRODUCTION

1.1 CONTEXT

As part of the DRA-96 support program, operation A.5 relates to the case of the transport of batteries. Since 2013, consideration is being given as part of this operation to assess the relevance of categorizing batteries in order to, if such categorization proves relevant, propose evolutions in regulations for the transport of dangerous goods.

Work conducted in 2013 allowed detailing of the results obtained on different batteries during abusive testings, and to define test specifications in order to arrive at a possible classification of batteries for transport. It was proposed (Report No. DRA-13-133471-12328A), in order to get to this categorization, to evaluate the resistance to crush, the behavior in case of a nail penetration and battery fire. Fire being the final scenario of many accidental situations (overload, short circuit, ...) and the most feared, it was decided, to set this categorization, to move towards the external fire test.

In 2014, we studied, given the feedback of INERIS, external fire tests performed on batteries, the relevance to lead to a categorization of batteries for transport, and we demonstrated the feasibility of the specifications to build the test campaign for the categorization of batteries. It has been shown (Report No. DRA-14-141820-13186A) that, because of the wide variety of batteries currently on the market (particularly in terms of chemistry, geometry and design), thermal and toxic effects during a fire behavior test could vary (for the same amount of energy) by a factor of up to 20. However, only the case of the batteries was studied and, despite the great disparity in results (suggesting a relevance of the categorization), it is necessary, in order to conclude, to demonstrate that:

- The effects measured on batteries are not consistently larger than on goods classified as dangerous,
- The effects measured on batteries are not systematically lower than on goods classified as non-dangerous.

We have also identified battery suppliers, the cost of buying batteries, supply possibilities and the duration and cost of testing.

In 2015, we therefore modeled the thermal and toxic effects of a fire in a transport of several types of goods (classified as dangerous or not) during transport by heavy goods vehicles, to position two types of batteries, compared to a set of products.

1.2 STRUCTURE OF THE REPORT

This report is organized around the following four points:

1) Description of the implementation methodology for evaluating the distances of the thermal and toxic effects associated with the burning of a heavy goods vehicle carrying different loads,
2) Description of the characteristics of the heavy goods vehicle and the various loads studied. A wide spectrum of loads is designed to position the hazard potential of a heavy goods vehicle carrying batteries compared to that associated with other loads whose effects have already been characterized by INERIS.
3) Characterization of the source term. This chapter attempts to characterize the source terms of the fire loads described in 2). These source terms come in two aspects:
    - The thermal source term for the characterization of the flame,
    - The toxic source term associated with the nature and flow of fumes emitted by the combustion reaction.
4) Modeling of the distances of thermal and toxic effects from the source terms previously established and the methodology described in 1).

2 APPLIED METHODOLOGIES

This chapter presents the general methodologies used to determine the thermal and toxic effects associated with the fire of a heavy goods vehicle.

2.1 DETERMINATION OF THERMAL EFFECTS

The analysis of the basic parameters that influence the thermal flux received by a target has identified simple and conservative estimation methods. The obtained results represent a good approach to evaluate the magnitude of the phenomenon.

The proposed method to quantify the thermal flux received by a target subjected to thermal radiations, is based on the fact that the flux received depends on the position of the target compared to the volume occupied by the flames.

To evaluate the received flux, the flux emitted by the flame surface must first be established. The thermal source term is defined through:

1) The geometrical characteristics of the flame,
2) The power of fire (Section 4.1.1).

These two parameters allow defining the emitting power of the flame also called emittance (paragraph 4.1).

The combination of the geometry of the flame and its emittance is then used to estimate the flux received as represented by Figure 1.

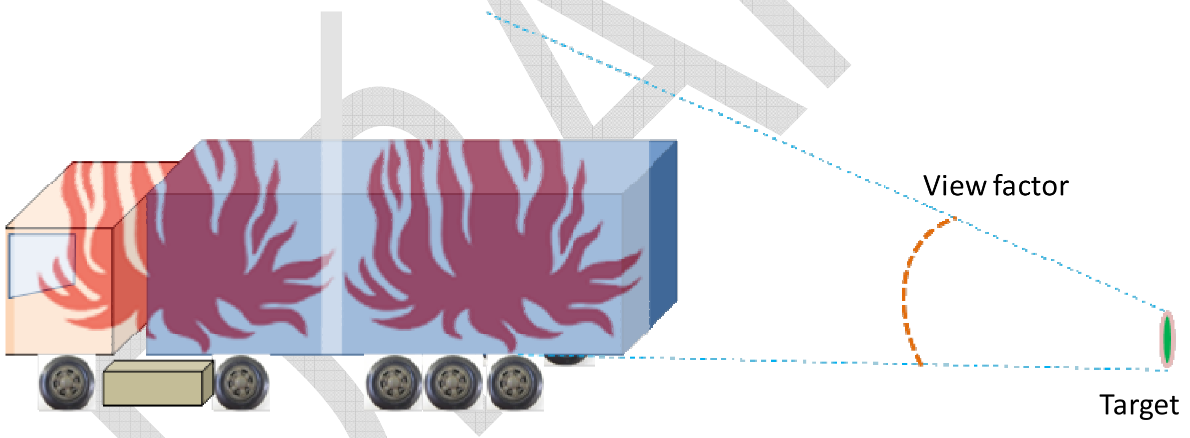


Figure 1: Illustration of the view factor

The flux received by the target will therefore increase with the view factor and the emittance. One objective of this study is therefore to compare the propensity of the various loads to generate major fires leading to high flame heights and significant emittance.

The hypothesis of considering only the effects associated with the flame radiation is justified as long as the target is away from the seat of the fire. Thermal radiation is indeed the privileged mode of transfer of heat from a certain distance from the fire. However, it should be noted that the results given for the radiative thermal effects are generally not relevant in the immediate environment of the flame, for which the effects related to convective transfer mode cannot be neglected. It is therefore appropriate to retain that in the vicinity of flames, it is not relevant to reason only in radiated flow. Therefore, the model used will no longer be valid for a distance less than a few meters.

2.2 DETERMINATION OF TOXIC EFFECTS

During a fire, large amounts of fumes are generated as a result of the combustion of the substances involved. These fumes are characterized by the formation of a plume above the flames whose dimensions depend in particular on the burning surface and the nature of the products involved.

In addition to their visual impact, these fumes can also have an impact on the environment and on people because of their toxicity.

The toxicity of the fumes can be estimated by determining the composition of smoke i.e., from a theoretical point of view from the elemental composition of the products involved, if known to be from an experimental side with tests carried out on a large scale. The latter determination is usually more accurate because it can integrate the presence of residues, while the theoretical approach generally assumes full conversion of the elements. It should be reminded that, as of today, in ranking the transport of dangerous goods, toxic effects of a fire of that transport are not considered. This parameter is therefore not considered for current classifications.

The interaction between the fire and the environment is shown in Figure 2; it is comprised of mainly three steps.

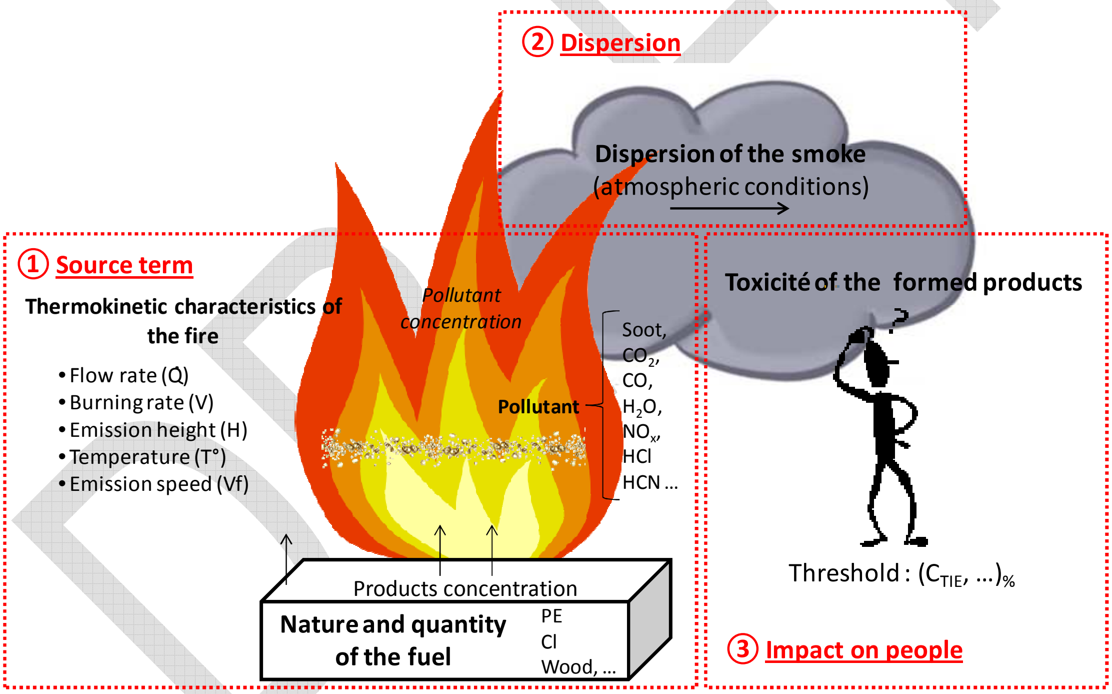


Figure 2: Schematic representation of the emission of pollutants generated by a fuel storage fire

The principle of calculating the dispersion of fire fumes is based on the following steps:

- Calculating the flow of the fumes inherent to the fire and the concentration of gases in these fumes (§ 5.1.2 and 1.1.1),
- Calculation of the atmospheric dispersion (§ 5.2.1)
- Comparison of the concentrations obtained in the previous step with the effect thresholds (§ 5.2 and 5.3).

3 DESCRIPTION OF COMBUSTIBLE ELEMENTS

This chapter introduces the combustible elements that may be involved in the fire of a heavy goods vehicle composed of a tractor and different loads.

3.1 DESCRIPTION OF THE HEAVY GOODS VEHICLE

The modeled carrier vehicle is a 38-tonne heavy goods vehicle consisting of a tractor and a trailer as shown in Figure 3. Its loading occupies the entire volume of the trailer.

Figure 3: Heavy goods vehicle studied

The heavy goods vehicle has the following general characteristics:

Maximum mass (tonnes)	38
Tractor mass (tonnes)	6
Empty trailer mass (tonnes)	7
Loading mass (tonnes)	25
Length (m)	16.5
Width (m)	2.5
Height (m)	4

Table 1 : Characteristics of the heavy goods vehicle studied

The maximum mass seen in Table 1 is the GVWR: Gross Vehicle Weight Rating.

The heavy goods vehicle studied is broken down into several components, namely:

- Wheels and mud guards,
- A tractor consisting of a cabin, a tank holding up to 0.82 m3 of diesel and a back deck for attachment of the trailer,
- A loaded trailer.

The unit mass of the elements composing the vehicle, excluding load, is presented in Table 2.

Part	Element	Unit mass (kg)	Number	Total mass (kg)
Road tractor	Wheel + mud guard	88	4	352
	Cabin	4 933(1)	1	4 933
	Diesel tank	680	1	1
Trailer	Trailer	Not useful(2)	1	Undefined
	Wheel + mud guard	88	12(3)	1056

Tableau 2 : Unit mass of the elements composing the vehicle

(1) Only the mass of the cabin is included in the total mass of the tractor as the rear platform of the tractor is comprised primarily of non-combustible metallic elements.

(2) The trailer being composed primarily of metallic materials and therefore non-combustible, its mass will not be useful in calculating the power generated by the burning of the heavy goods vehicle.

(3) The number of trailer wheels is usually doubled.

3.2 DESCRIPTION OF THE CONSIDERED LOADS

The objective is to compare the thermal and toxic effects related to the burning of heavy goods vehicles loaded with batteries, with fires of shipments of goods classified as hazardous as well as classified as non-hazardous. The list of the various loads selected is described in the following chapters. The different classes of dangerous goods are described in Appendix A.

3.2.1 **Battery Packs of 2 different types**

In the context of transport, this load is currently considered as dangerous goods and belongs to Class 9 "Miscellaneous Dangerous Goods." The technical characteristics of the two battery packs used in the study are described below:

- <u>Battery 1:</u> Capacity: 66.6 Ah; Energy: 23.7 kWh; SOC: 100%; Initial Tension: 398.4 V; Pouch Cells; Cathode: NMC; Anode: Graphite
- <u>Battery 2:</u> Capacity: 50 Ah; Energy: 16.5 kWh; SOC: 100%; Initial Tension: 355 V; Prismatic Cells; Cathode: NMC; Anode: Graphite.

A description of the different geometries and chemistries of the cells currently on the market is present in Appendix B, and the safety sheets of batteries tested at INERIS are presented in Appendix C.

3.2.2 **Pallets of Aerosols**

In the context of transport, this load is currently considered dangerous goods and belongs to Class 2.1 "Flammable gases". The technical characteristics of aerosols used for the study are described below:

- Packaged products: foam or shaving gel, body care product, household product or automobile maintenance product,
- Composition of Aerosols: liquid containing the active ingredient in a solvent and a gas propelling the product.

A safety sheet of a type for an aerosol tested at INERIS is presented in Appendix C.

3.2.3 **Pallets of salads**

In the context of transport, this load is not currently considered as dangerous goods.

3.2.4 **Pallets of DVDs**

In the context of transport, this load is not currently considered dangerous goods.

3.2.5 **Pallets of various plastic drums**

The different considered types of plastics are: rubber, textile, polyethylene and polyvinyl chloride. In the transport sense, this load is not currently considered dangerous goods.

3.2.6 **Pallets of pesticides**

In the context of transport, this load is currently considered as dangerous goods and belongs to Class 9 "*Miscellaneous Dangerous Goods*". The technical characteristics of the tested items are described below:

- Different pesticides (e.g. 2-pyridine sulfonamide) and herbicides (e.g. chlorsulfuron).

A safety sheet for a type of product tested at INERIS is presented in Appendix C.

3.2.7 **Polyurethane foam blocks**

In the context of transport, this load is not currently considered as dangerous goods.

These loads are selected to compare a broad spectrum of fires and to use reliable data from the experiment. The different loads considered in the study are described in Table 3. They have all undergone fire tests at INERIS.

Nature of the load	Unit mass (kg)	Unit dimension (L x w x h) m^3	Number of items in the trailer	Total mass of the load (ton)	Reference
Battery pack N°1	280	1.2 x 0.75 x 0.8	89	24.9	INERIS Tests[1]
Battery pack N°2	232	1.3 x 0.68 x 0.4	107	24.8	INERIS Tests[1]
Pallets of aerosols	500	1.2 x 0.8 x 2	33	16.5	INERIS Tests[2]
Pallets of DVDs	266	1.2 x 0.8 x 1.8	33	8.8	INERIS Tests[3]
Pallets of salads	83	1.2 x 0.8 x 1.8	33	2.8	INERIS Tests[4]
Pallets of 4 drums containing various plastics	120	1.2 x 0.8 x 1	66	7.9	INERIS Tests[5]
Pallets of pesticides	233	1.2 x 0.8 x 2	33	7.7	INERIS Tests[6]
Polyurethane (PU) foam blocks	100	1.9 x 1 x 1.55	26	2.6	INERIS Tests[7]

Table 3: Loads considered in the study

The number of elements in the trailer is chosen so they occupy the entire volume of the trailer under the condition that the total mass of the load does not exceed 25 tonnes.

Given the dimensions of the components carried, a possible arrangement of the different loads in the heavy goods vehicle could be summarized in Figure 4. This is, in a major way, to occupy all available space in the trailer.

[1] Combustion tests on battery packs [Reference FIVE]

[2] INERIS – Omega 4 - Modeling a fire affecting a storage of aerosol generators - September 2002

[3] Combustion tests on a DVD pallet – [Reference Flumilog Tests]

[4] Combustion tests on a pallet of salads – [Reference Flumilog Tests]

[5] Combustion tests on a pallet of plastic drums – Confidential tests

[6] Combustion tests on a pallet containing pesticides – Confidential tests

[7] Combustion tests on polyurethane foam blocks – Confidential tests

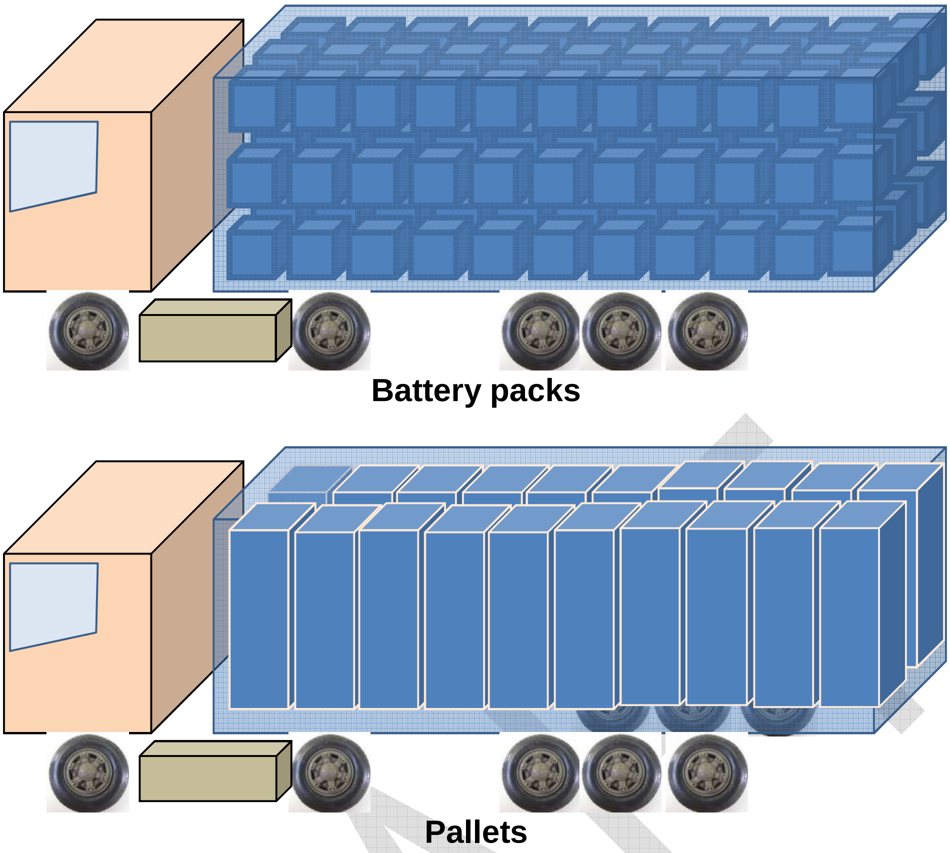


Figure 4: Loadings arrangement in the heavy goods vehicle

Concerning the pallets of plastic drums, they are small pallets of a height of 1 m that will therefore be disposed on the trailer on two levels.

4 THERMAL EFFECTS

4.1 SOURCE TERM

This part aims to characterize the thermal source term of the loads fire described in §3.2. This heat source term is associated to the geometric characteristics of the flame as well as its emittance.

The next step is to define the parameters that characterize the thermal source term of a fire, namely:

1) The total power of the fire,
2) The emittance of flame,
3) The flame height.

4.1.1 Power of the fire

4.1.1.1 APPLIED METHODOLOGY

First, the evaluation of the fire propagation kinetics in the loaded heavy goods vehicle is made using an INERIS tool developed to model the total power of the fire from a propagation model. The methodology consists of adding the power of the fire of the different components of the heavy goods vehicle:

1) The wheels,
2) The cabin,
3) The diesel slick,
4) The load.

To take into account the inertia of fire spread from one element to the other, it is considered that:

1) The propagation is performed only between two adjacent elements,
2) The fire of an element begins when the power of the fire of the adjacent element is at its maximum.

The methodology is applied by considering a fire starting at the loading level, a scenario which leads, according to the results, to the kinetics of the fastest fire.

The methodology is detailed in Figure 5.

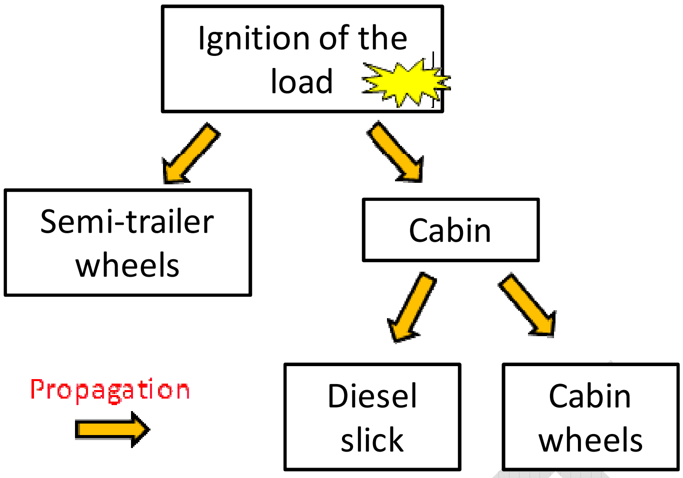
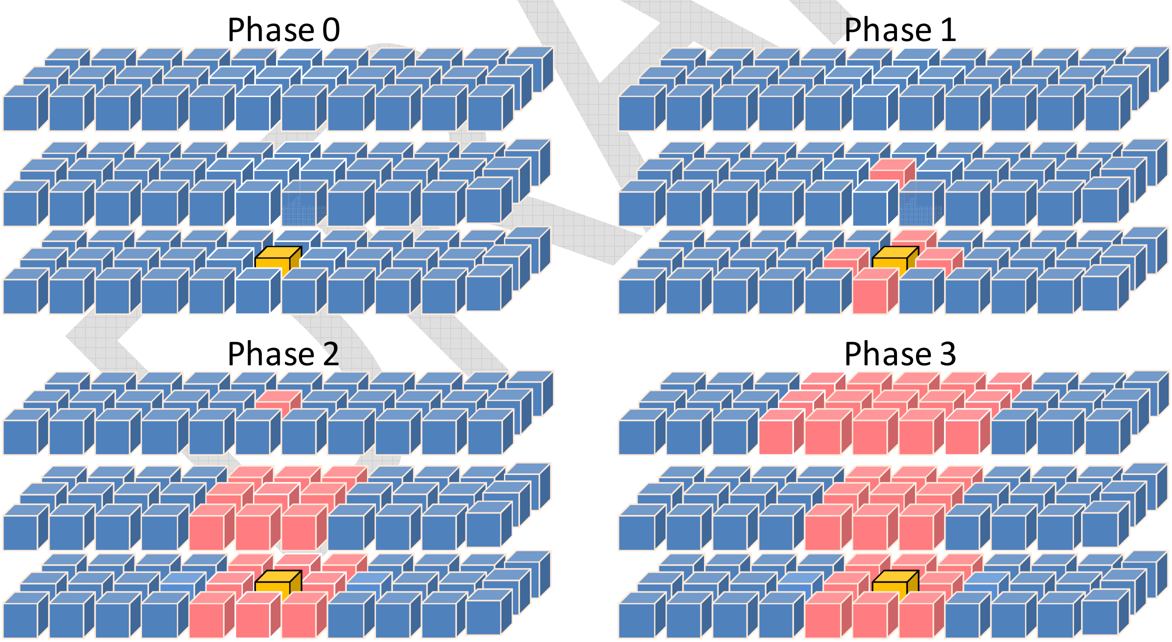


Figure 5: Applied methodology – fire starting at the load level

The spread in the load consisting of pallets follows the same law, meaning that the fire spreads gradually (from one element to its neighbors). However, the spread of fire in loads arranged over several levels (batteries or small pallets) follows a different law. A split view of the load of battery packs allows to better understand the fire spread process inside the load. Considering a fire starting in the center of the trailer, on the 1st level (majoring position in terms of kinetics) the evolution of the fire can be summarized in Figure 6.



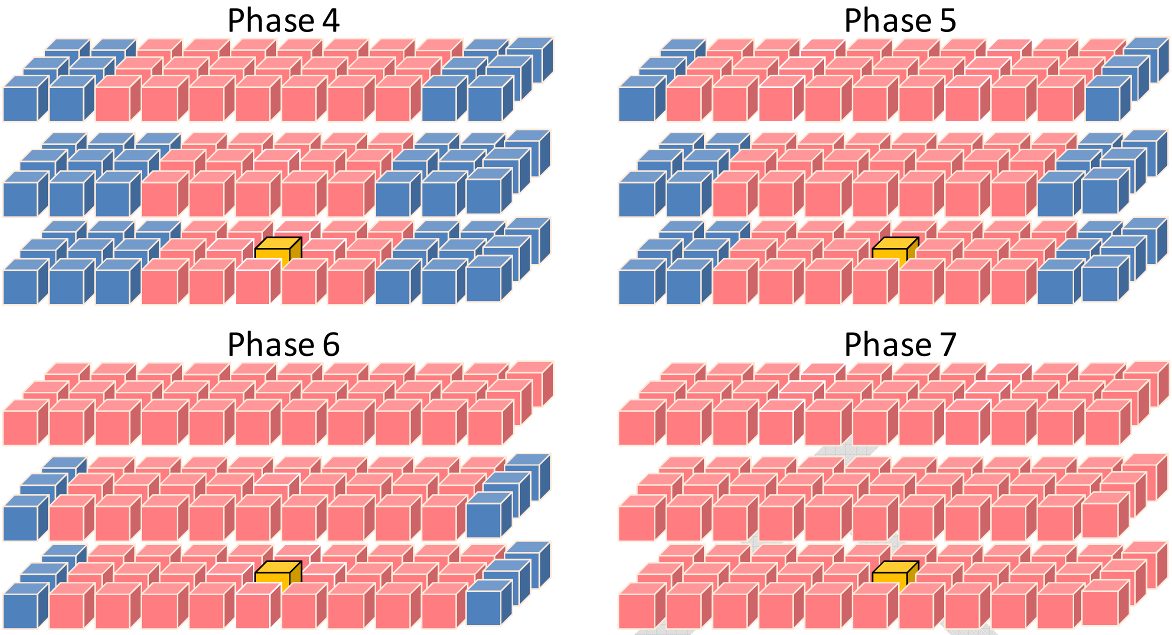


Figure 6: Mapping the spread of fire in a load of battery packs

Phase 0 is the inflammation of the first pack. The fire spreads from place to place by radiation and convection (phases 1 and 2), and takes the form of a V, which is characteristic of a load (phase 3). Then, when the fire reaches the upper batteries, the total power of the fire is stabilized because the flames then propagate in both directions (phases 4, 5 and 6). Eventually, the batteries at the ends of the load burn (phase 7), putting an end to the burning of the load.

The spread of the fire in a load of battery packs will therefore be likely to grow faster than a pallet storage because of the arrangement on several levels that promotes the spread of fire.

4.1.1.2 Power of single elements

The powers of single elements come from tests conducted at INERIS. They are represented in Figure 7.

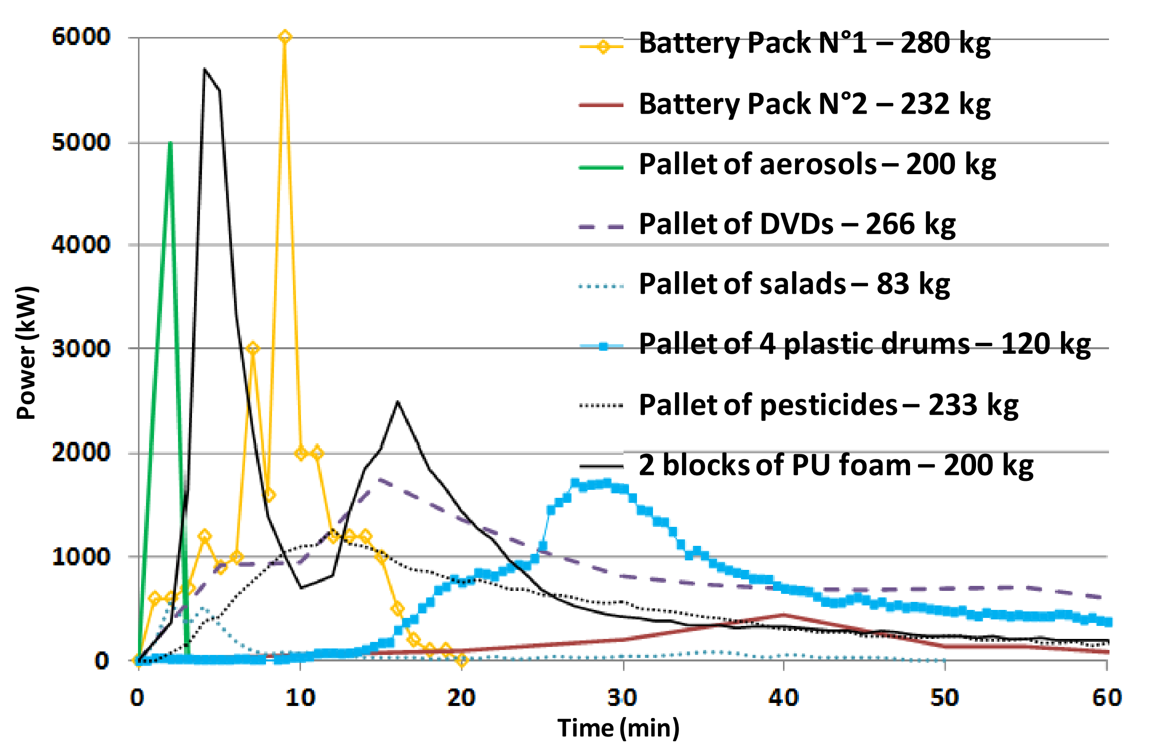


Figure 7: Power of the fire of single elements studied

The maximum power generated by the fire of battery pack N°1 (Figure 7) is similar to those developed by a pallet of aerosols and a 200 kg PU foam block. The observed order of magnitude is 5000 kW.

Similarly, pallets of DVDs, pallets of plastic drums, and pallets of pesticides with a maximum power of about 1750 kW are classified in the same power class.

Finally, the fire of battery pack N°2 develops a maximum power similar to that of light pallets of salads, that is to say approximately 500 kW.

These powers can be classified into three very distinct levels, detailed in Table 4 below.

XXX: Battery

XXX: Merchandise classified as dangerous goods

XXX: Merchandise not classified as dangerous goods

Maximum thermal power level (kW)	Merchandise classified as dangerous goods	Merchandise not classified as dangerous goos
5000 - 6000	**Battery pack N°1** **Pallet of aerosols**	**2 PU foam blocks**
1200 - 1750	**Pallet of pesticides**	**Pallet of DVDs** **Pallet of plastic drums**
400 - 600	**Battery pack N°2**	**Pallet of salads**

Table 4: Classification of the maximum powers of the fires of single elements

It is noted that for each power level, we find products classified as hazardous merchandise and others not classified. We especially note that, for the same type of product (in this case the batteries), the level of maximum power generated by a fire can vary by a factor of about ten. In order to refine the comparison, it is necessary to take into account the maximum power value generated per unit of energy (kW_{fire} / $kWh_{battery}$). The values obtained are therefore:

- 0,25 kW/kWh for battery pack N°1,
- 0,03 kW/kWh for battery pack N°2.

Thus, even reduced to a value per unit of energy, the maximum power developed by a fire of batteries may vary by a factor of about eight.

To help understand the parameters that are responsible for this difference of behavior, it is necessary to identify the characteristics of each pack that can influence the results of a fire behavior test. Table 5 below summarizes the similarities and differences between the two battery packs tested at INERIS (in bold, the characteristics which are different from one pack to another).

Characteristics	Battery pack N°1	Battery pack N°2
Pack exterior casing	**Aluminum + Steel**	**Steel + Thermoplastic**
Battery architecture	**Vertical**	**Horizontal**
Initial SOC	100%	100%
Capacity	**66 Ah**	**50 Ah**
Electrochemical energy	**23.7 kWh**	**16.5 kWh**
Cell chemistry	Cathode: NMC Anode: Graphite	Cathode: NMC Anode: Graphite
Cell geometry	**Pouch (plastic envelope)**	**Prismatic (steel envelope)**
Cell safety device	**None**	**Safety vent in case of overpressure**

Table 5: Characteristics of the two battery packs tested at INERIS

In the case of thermal effects, the characteristics that could impact the power generated by the fire are:

- The battery architecture: the spread of fire between two elements is much faster vertically than horizontally,
- The cell geometry: the plastic envelope pouch of the cells burns very easily and thus helps increase the overall power of fire,
- The amount of on-board electrochemical energy in the battery,
- The safety devices: a vent allows, in case of internal cell overpressure, to release the gases present, a part of which might not burn,
- The outer casing pack: the presence of a plastic casing burning easily, can significantly increase the power of the fire.

Because of the presence of plastic in the composition of the battery pack N°2 casing, we could have expected a maximum radiated power much more important (due to the combustion of the plastic). Actually, we have observed, at the end of the test, that a part of the plastic casing of this pack melted but no major combustion is observed. This demonstrates that it is not possible to make any conclusion as to the power that will be generated by a battery fire based solely on its composition.

On the one hand, the thermal effect of a battery is highly dependent on many parameters such as the amount of energy of the sample test, the sample structure, the chemical composition of samples, the architecture of the pack, etc. On the other hand, for two samples having the same chemistry and an electrochemical energy of the same order of magnitude, the power radiated per unit of energy can vary by a factor of eight.

4.1.1.3 Power of the full load

Although the power of the fire of the single element provides guidance on potential violence of the fire, it is necessary to compare the powers of loaded heavy goods vehicle fires considering:

- The energy contribution of the fire in the cabin, the tires of the heavy goods vehicle and the diesel fuel in the tank,
- The number of items that can be stored in the trailer based on their volume unit (battery pack, pallet or PU foam block)
- The kinetics of the burning load.

The power of the fire of the loaded heavy goods vehicle, estimated using the approach detailed in paragraph 4.1.1.1, is shown in Figure 8, for the various loadings described in the preceding paragraph. The number of items carried in the trailer is indicated in the figure.

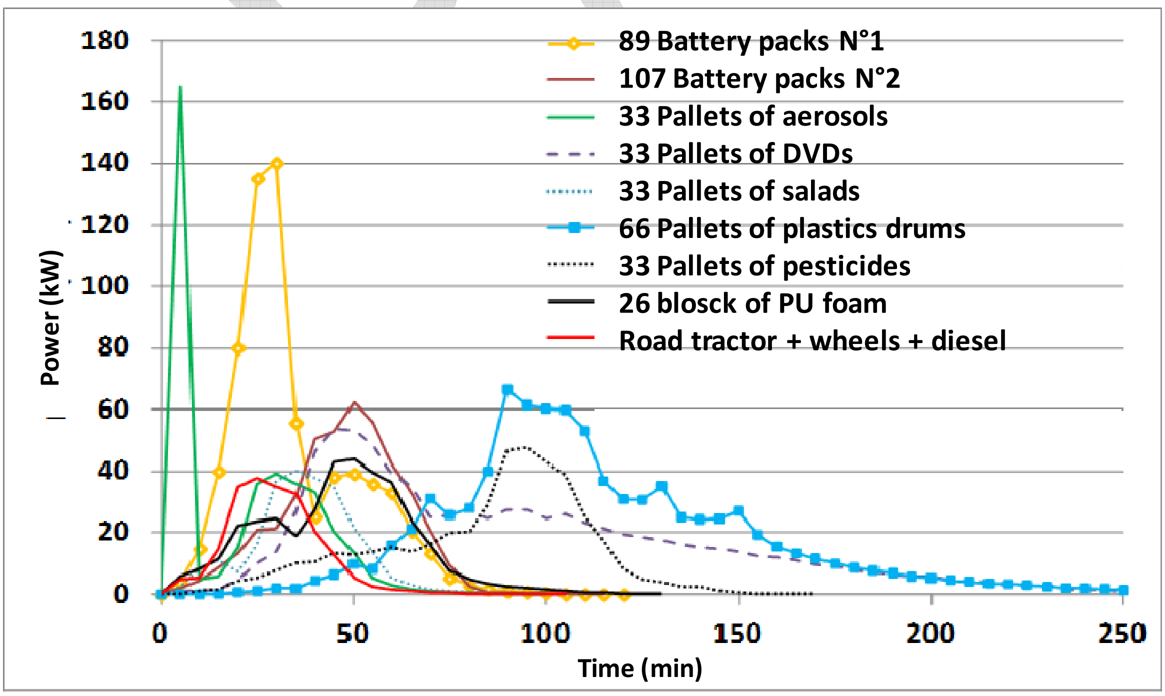
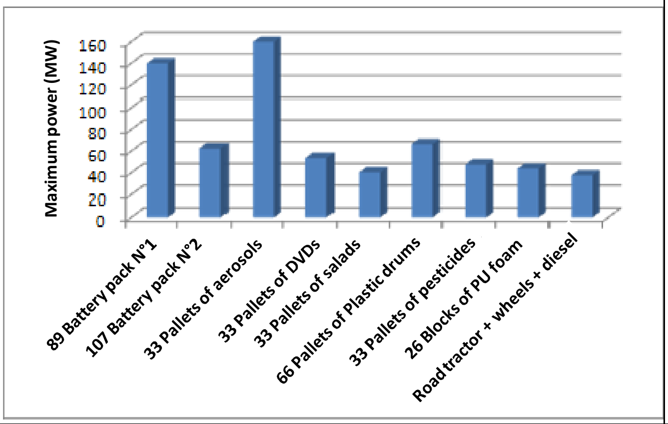


Figure 8: Total power of the fire of the Heavy Goods Vehicle depending on the type of loading. The data is summarized in Figure 9.

Maximum power of the fire (MW)



Duration of the fire (min)

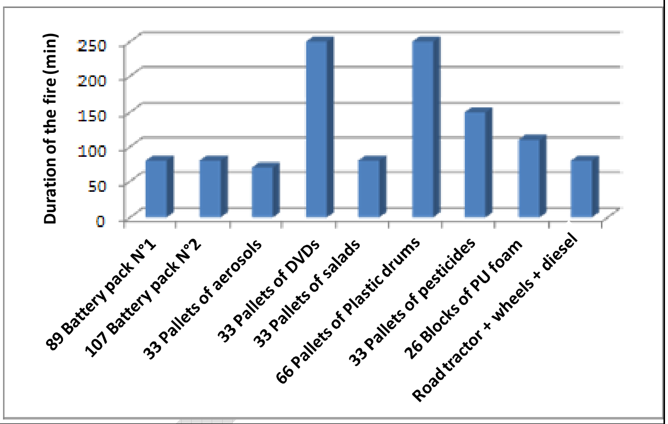


Figure 9: Comparison of the maximum power of the fire and the duration of the fire depending on the type of loading

1) The power peaks of heavy goods vehicles fires loaded with battery packs N°1 and aerosol pallets are of the same order of magnitude, i.e. around 150 MW.
2) The power of heavy goods vehicle fire containing the other elements is between 38 and 66 MW, values 2-4 times lower than those associated with aerosols and battery packs N°1.
3) The duration of heavy goods vehicles fires loaded with pallets of DVDs and plastic drums are the most important (about 250 min) for powers not exceeding 60 MW. Although potentially at risk because of that duration, thermal effects will be limited regarding the effects associated with the burning of a heavy goods vehicle loaded with battery packs N°1.
4) The power peak related with the fire of plastic drums and pesticides occurs later (about 100 minutes after the ignition of the heavy goods vehicle) and does not exceed 60 MW. This slow kinetics of the fire would allow emergency services to circumscribe or even extinguish the fire before the occurrence of the peak power.
5) The power linked to the fire of salads pallets is of the same order of magnitude as that associated with the burning of the tractor. Indeed, the energy contribution of the salads pallets is low (less than 500 kW). This also applies to a wide range of water based foods.

Considering the scale effect between the single elements and the whole load is not likely to significantly change the previous conclusion except that only two distinct power classes could be proposed:

Maximum thermal power level (MW)	Merchandise classified as hazardous	Merchandise not classified as hazardous
140 - 160	Battery pack N°1 Pallet of aerosols	
35 - 70	Pallet of pesticides Battery pack N°2	Pallet of DVDs Pallet of plastic drums 2 PU foam blocks Pallet of salads

Tableau 6: Classification of the maximum powers of the fires of full loads

It is therefore observed that, for battery packs with energies and masses of the same order of magnitude, the maximum power developed during a fire of a full load can:

- Be higher or lower than values for fires of dangerous goods loads,
- Be higher or lower than the values for fires of non-dangerous goods loads.

In addition, given the characteristics of the two packs described in Table 5, it is not possible to conclude, based solely on the composition (external or internal) of the pack, on the amount of energy transported, etc. Many parameters are involved and influence the thermal behavior of a fire of a full load.

Based on this preliminary information, a categorization of batteries according to their thermal effect according to the results of an external fire test therefore seems feasible and justified.

4.1.2 **Flame emittance and height**

After determining the maximum power values emitted during fires of various loads, it is necessary, in order to be able to define the thermal source term of these fires, to determine the flame emittance and height.

The flame emittance is defined by the surface radiative power of the fire. It is an essential parameter to estimate the flux received by the target present in the flame environment and thus calculate the effect distances.

The flame emittance can be estimated using the following equation:

$$\phi_0 = \frac{\eta_r P_{tot}}{S_{fl}}$$ Equation 1

P_{tot} = Maximum total power emitted by the loading fire (kW)

S_{fl} = Outer flame area (m²)

η_r = Radiative fraction (-)

To evaluate the flame area, the latter is considered, for simplification, as a parallelepiped having for floor area the loading area (13.5 x 2.5 m²). Its height is estimated using an empirical correlation called Thomas correlation[8].

For all loads except the load of aerosols pallets, the value of the radiative fraction is taken inclusively at 30%.

Table 7 shows the flame characteristics for each type of load at the power peak of the fire.

Nature of the load	Max burning rate (g/m²/s)	Max flame height (m)	Maximum total power emitted by the load fire (kW)	Flamme surface (m²)	Max flame emittance (kW/m²)
89 Battery packs N°1	167	11.9	140	421	100
107 Battery packs N°2	90	8.2	62.5	303	62
33 Pallets of aerosols	Undefined	10.0	165	361	100
33 Pallets of DVDs	78	7.5	53.7	280	57
33 Pallets of salads	60	6.4	40.4	246	49
66 Pallets of 4 drums containing various plastics	69	6.9	66.5	263	76
33 Pallets of pesticides	67	6.8	47.7	258	55
26 Polyurethane (PU) foam blocks	50	5.7	44	223	59

Table 7: Flame characteristics of various loads

[8] Thomas, The size of flames from natural fires, 9th international symposium on combustion, p 844-859, 1963

4.2 CALCULATION OF THE DISTANCES OF THERMAL EFFECTS

The characterization, made in the preceding paragraphs, for each load, of the source term defined with the maximum power emitted by the fire, the emittance of flame and the flame height, allows subsequently, through a modeling tool, to calculate the distances of thermal effects for various thresholds effects on people.

4.2.1 Selected effect thresholds

The results are expressed in the form of effects distances on human health related to radiative flux generated by a fire. Thus, the calculations include the thermal flux which may be received by an individual located at a certain distance from the flame front, on the perpendicular bisector of the front concerned, for an exposure time greater than 2 minutes.

The selected values are those recommended by the French Ministerial Decree of September 29, 2005 on the evaluation and consideration of the probability of occurrence, kinetics, intensity effects and severity of the consequences of potential accidents in the danger studies of classified facilities subject to authorization.

The main thermal effects thresholds are:

- **8 kW/m²: Significant Lethal Effects Threshold:** corresponds to the flux received over which one could observe 5% mortality in the exposed population[9],
- **5 kW/m²: Lethal First Effects Threshold:** corresponds to the flux received over which one could observe 1% mortality in the exposed population,
- **3 kW/m²: Threshold for Irreversible Effects:** corresponds to the received flux, above which irreversible effects might occur in the exposed population.

[9] The notion of "population at risk" does not include "hypersensitive" subjects

4.2.2 **Thermal effects thresholds of the different types of loads studied**

The thermal effects distances associated with fires of heavy goods vehicles carrying various loads are shown in Table 8 and in decreasing order.

Load	Effect distance in meters at the threshold of …		
	3kW/m²	5kW/m²	8kW/m²
Battery pack N°1	38	30	23
Aerosols	36	28	22
Pallets of DVDs	24	18	13
Pallets of plastic drums	18	13	9
Battery pack N°2	17	12	9
PU Blocks	15	11	9
Pallet of pesticides	12	8	5
Pallets of salads	7	4	2

Table 8: Thermal effects distances obtained for the various loads

Figure 10 illustrates the results obtained.

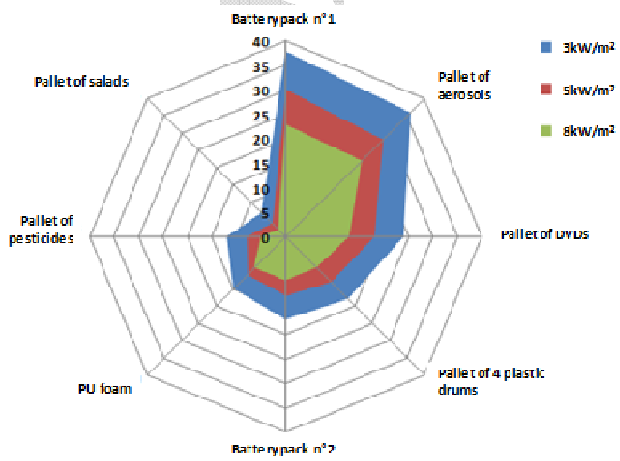


Figure 10: Thermal effects distances

Thermal effects distances related to the fire of a load of battery packs N°1 are of the same order of magnitude as those relating to the fire of a load of aerosol. They are 1.5 times higher than the effects distances related to the burning of a load of pallets of DVDs and between 2 and 3 times higher than those associated with loads of plastic drums, polyurethane foam blocks, pesticides and battery packs N°2. They are finally about 7 times higher than a fire of a load of salads.

4.3 CONCLUSION ON THE THERMAL EFFECTS

Regarding the data obtained from this study, we can conclude that:

- Modifying one or more parameters of the design of the battery (architecture, external and internal components, etc.) can induce strong variations in the maximum power generated by the fire,
- Depending on the battery tested, the measured thermal effects may be lower or higher than the measured effects on certain goods classified as dangerous by mean of transport (e.g. aerosols),
- Depending on the battery tested, the measured thermal effects may be lower or higher than the measured effects on certain goods classified as NOT dangerous by mean of transport (e.g. DVDs or plastic drums),
- Information on the constitution of a battery does not allow to conclude, without prior tests, on the violence of the measured thermal effects. For example, in our case, the presence of plastic on the battery pack N°2 casing causes one to suspect a much greater power of the fire.

This information allows us to conclude that a categorization of batteries for transport according to their thermal effect during a fire behavior test is relevant.

Future work in the context of the operation A5 of DRA 96 will therefore be:

- To define a reliable and robust testing protocol to be able to test batteries and retrieve data needed for the evaluation of the thermal effect,
- To identify the relevant parameters for the categorization,
- To define one or more thresholds that will allow categorization of the batteries into one or more classes of thermal effect.

5 TOXIC EFFECTS

5.1 SOURCE TERM

This section aims to characterize the toxic source term of the fire of the loads described in §1. This toxic source term is associated with the nature and the flow of gaseous effluents emitted by the combustion reaction.

The source term, determining the toxic effects, consists of:

1) The speed of the fumes at the emission point,
2) The height of emission,
3) The flow of the fumes and the concentration of the various gases present in these fumes.

5.1.1 **Emission speed and height**

In the case of fires such as those considered in this study, the fumes are generated in the upper part of the volume formed by the flames. The first step in order to characterize the emission is to determine the height of the fumes emission. To do this, there are many empirical formulas published in the literature. We used the formula proposed by Heskestad[10] for this study. The height *h* obtained from the relationship proposed by Heskestad corresponds to the average height of the flames because, in reality, the latter are animated by an intermittent movement.

In the case of liquid hydrocarbon fires, Heskestad[10;11] showed that, at the height *h*, the average temperature difference between the fumes of the fire and the ambient air is close to 250 K. In addition, this same author provided an empirical correlation for determining the average speed of the fumes elevation to the height *h* depending on the amount of heat convected by the fumes. Experimental measurements show that at least 70% of the thermal power generated by a fire is convected.

5.1.2 **Flow of fumes**

After determining the speed and height of the emission of fumes, it is necessary, in order to determine the source term, to calculate the speed of the fumes emitted.

The fumes are composed of gases produced by burning the stricken heavy goods vehicle and the air driven by updrafts generated by the flames. The total flow of fumes is obtained by means of a formula proposed by Heskestad[10] and varies, depending on the power of the fire.

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[10] G. Heskestad - « Engineering Relations for Fire Plumes », Factory Mutual Research Corporation, Fire safety Journal, 7, 1984, pp 25-32

[11] G. Heskestad - « Fire Plume Air Entrainment according to two Competing Assumptions », Factory Mutual Research Corporation, 21th Symposium on Combustion/ the Combustion Institute, 1986/ pp 111-120

5.1.3 Determination of the concentrations of gaseous effluents present in fumes

Finally, to complete the determination of the source term, the mass concentration of each gaseous effluent in the combustion fumes must be determined. This concentration is characterized as the ratio of the emission rates of gaseous effluents by the total flow of fumes.

We must therefore first determine the emission rate of gaseous effluents based on the total mass of gaseous effluents emitted from the combustion of the loaded heavy goods vehicle.

The total mass of gaseous effluents emitted by the combustion of the heavy goods vehicle depending on the various loads is presented in Table 9.

	Combustible element	Total production of gaseous effluents (kg)							Reference
		CO	CO_2	HCl	HF	HCN	NO_2	SO_2	
Loading	89 Battery N°1 pack	174.17	12422.84	9.19	48.49	0.32	10.5	0	INERIS Tests[1]
	107 Battery N°2 pack	204.1	9772.51	14.34	49.26	0.32	7.59	0	INERIS Tests[1]
	33 Pallets of aerosols	140.44	2865.66	3.85	1.32	0.32	1.6	0	INERIS Tests[2]
	33 Pallets of DVDs	239.44	16280.16	6.69	1.32	0.32	6.02	0	INERIS Tests[3]
	33 Pallets of food type products (lettuces)	203.14	4083.36	3.85	1.32	0.32	1.6	0	INERIS Tests[4]
	66 Pallets of plastic	497.5	15154.86	578.05	608.52	0.32	9.39	14.78	INERIS Tests[5]
	33 Pallets of pesticides	259.24	10620.66	20.68	1.32	19.46	47.8	1023	INERIS Tests[6]
	26 Polyurethane (PU) foam blocks	195.77	5749.06	3.85	1.32	8.43	6.95	0	INERIS Tests[7]

Table 9: Total mass of gaseous effluents depending on the transported combustible elements

These data are from tests conducted by INERIS on each of the combustible elements. The test reference is entered in the last column of Table 9.

The mass of gaseous effluents from the burning of the cabin and tires is added to each load fire. These data are also derived from INERIS tests[12].

[12] Light vehicle combustion tests - [Reference FIVE]

The gaseous effluent emission rate is obtained from the power of the fire such as:

$$D_i(t) = \frac{P_i(t)}{P_{max}} \alpha_i \qquad \text{Equation 2}$$

$$M_{tot_i} = \alpha_i \int_0^{Tfinal} \frac{P_i(t)}{P_{max}} dt = \alpha_i * \frac{E_{tot}}{P_{max}} \qquad \text{Equation 3}$$

With:

$D_i(t)$	=	Rate emission of the gaseous effluent *i* (kg/s)
$P_i(t)$	=	Fire power (W)
P_{max}	=	Maximum total power (W)
α_i	=	Factor associated to the gaseous effluent i (kg/s)
E_{tot}	=	Fire's final total energy (J)
M_{tot_i}	=	Gaseous effluent total mass i (kg) from Table 9

The α_i coefficient used to calculate the emission rate of a gaseous effluent in Equation 2 is derived from Equation 3.

This coefficient is therefore a constant, which implies that each effluent's emission rate is proportional to the power of the fire. However, the concentration of each gaseous effluent in the fumes remains fixed throughout the duration of the fire. This can be explained by the fact that the total flow of fumes also varies in proportion to the power of the fire according to §5.1.2.

To illustrate this, the CO and HCl emission rates obtained in time for the burning of heavy goods vehicles containing battery packs are shown in Figure 11. Note that in a safe approach, the diesel tank is considered empty in order to limit the power of the fire and increase the toxic effects on the ground.

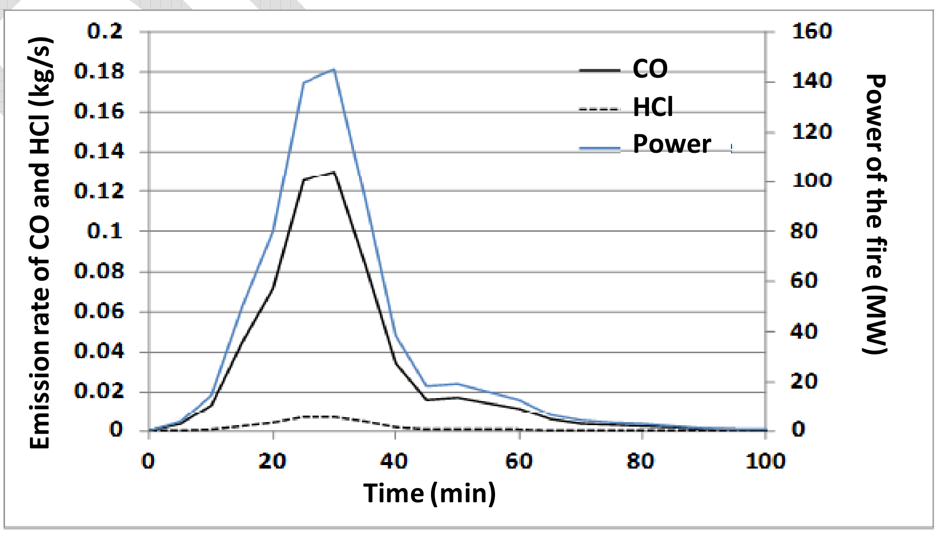

Figure 11: Emission rate of CO and HCl and power depending on time for the fire of a heavy goods vehicle carrying battery packs N°1

5.2 CALCULATION OF OPEN FIELD TOXIC EFFECT DISTANCES

5.2.1 **Atmospheric dispersion**

To understand free field toxic effects, elements of atmospheric dispersion are reviewed in this paragraph.

5.2.1.1 COMPUTING CODE

Atmospheric dispersion of gaseous effluents is modeled using the Phast computing code, version 6.53.

5.2.1.2 ATMOSPHERIC CONDITIONS

Meteorological conditions are described by numerous parameters, of which the main ones are tied, on the one hand, to atmospheric turbulence, and on the other, to wind speed. These two parameters, that characterize meteorological conditions, will not be dealt within this document. Similarly, for information regarding Pasquill classes, the reader is referred to the INERIS guide on dispersion, available on the INERIS website at: www.ineris.fr[13]

The most unfavorable results, regarding the effects likely to be felt, can be obtained when:

- the atmosphere is rather stable;
- wind speed is maximal.

However, each class of stability was indexed to the wind speed. Therefore, a wind speed of 10 m/s is not usually associated with stability class A. According to Pasquill[14], class B, for example, is associated with a maximum wind speed of 5 m/s.

[13] INERIS - OMEGA 12 - Atmospheric Dispersion (Computational mechanisms and tools) - DRA - December 2012

[14] “Atmospheric Diffusion”. 1974, Ellis Horwood.

In order to encompass the largest possible sample group of meteorological conditions, INERIS retained, as prescribed, 9 Pasquill[14] classes whose characteristics can be found in Table 10.

Atmospheric stability	Wind speeds considered (m/s)
A	3
B	3 and 5
C	5 and 10
D	5 and 10
E	3
F	3

Table 10: Retained meteorological conditions

The roughness parameter which allows taking into account the impact of ground roughness on fume dispersion was set at 0.1, which corresponds to a flat, sparsely inhabited environment.

5.2.2 Used toxic thresholds

The approaches used are:

- Additivity law of thresholds[15],
- Application of ISO 13 571[16] standard that allows to distinguish the effect of irritant gases from asphyxiating gases on people's capacity to evacuate a hazard zone.

5.2.2.1 Additivity law of thresholds

In order to characterize fume toxicity, the threshold to retain is not specific to one gas, but to a mix of gases. In such a case, if the mix is made up of n pollutant gases denoted by P_1, P_2, P_3 …, the equivalent threshold is estimated using Equation 4.

$$\frac{1}{Threshold_{equivalent}} = \sum \frac{[Concentration \cdot of \cdot pollutant \cdot P_i]}{Threshold \cdot of \cdot pollutant \cdot P_i} \quad \text{Equation 4}$$

The previous expression allows taking into account the specific toxicity of each gas on the one hand, and to "add" their respective toxicities on the other, in a simplified fashion.

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[15] INERIS - Omega 16 - Toxicity and dispersion of fumes from a fire - Phenomenology and modeling of effects - ref: 57149 - 2005

[16] ISO 13571 – TC92 SC3 N335 International Standard – Life-threatening components of fire – guidelines for the estimation of time available for escape using fire data – 2007

It is clear that such an approach does not allow taking into account all potential synergistic or antagonistic effects caused by the simultaneous presence of various gases.

In France, a methodology[17] for determining acute toxicity thresholds was developed by INERIS, published in 2003 and revised in 2007: it allows fixing acute toxicity thresholds in the case of an accidental emission of a toxic substance into the atmosphere by an industrial facility. The main toxic effect thresholds developed for exposure periods of 1 to 60 minutes are the following:

- **Threshold for Significant Lethal Effects**: corresponds to the concentration in the air for a given exposure period above which one could observe 5% mortality at the edge of the exposed population[18],
- **Threshold for the First Lethal Effects**: corresponds to the concentration in the air for a given exposure period above which one could observe 1% mortality within the exposed population,
- **Threshold for Irreversible Effects**: corresponds to the concentration in the air for a given exposure period above which irreversible effects[19] could show up within the exposed population.

In our restricted environment study, the threshold considered is the Threshold for Irreversible Effects (TIE) at 60 min.

The Threshold for Irreversible Effects (TIE) retained for various products prone to being emitted by truck fires are given in Table 11 for an exposure time of 60 min.

Gaseous effluent	TIE 60 min (ppm)
CO	800
CO_2	50,000
HCl	40
HF	100
HCN	41
NO_2	40
SO_2	81

Table 11: Irreversible threshold values for each toxic gas

[17] French methodology for determining acute toxicity values in the case of an accidental emission of chemical substances into the atmosphere. INERIS 2007

[18] The idea of “exposed population” does not take into account “hyper-sensitive” subjects (for example, those with respiratory issues)

[19] Within the framework of this methodology, irreversible effects include: lesions with no functional repercussions (chemical burn), with functional repercussions (pulmonary fibrosis, loss of smell...) and irreversible functional injury (asthma).

5.2.2.2 APPLICATION OF ISO 13571 STANDARD

FED concept

The fractional effective dose is an asphyxiating gas model that allows the evaluation of asphyxiating effects of toxic fumes on the human body as a function of exposure time. It is expressed as follows:

$$X_{FED} = \sum_{t0}^{t1} \frac{CO}{35000} \Delta t + \sum_{t0}^{t1} \frac{HCN^{2,36}}{1.2x10^{6}} \Delta t \qquad \text{Equation 5}$$

With:

CO	=	CO concentration (ppm)
HCN	=	HCN concentration (ppm)
Δt	=	Time step (min)
$t1$	=	Exposure time of individual (min)

It is to be noted that the increased absorption rate of the asphyxiating gases due to hyperventilation is taken into account in Equation 5.

FEC concept

Fractional effective concentration allows evaluating the effects of irritant gases as a function of their concentrations in fumes[15].

$$X_{FEC} = \sum_{i=1}^{n} \frac{C_i}{Threshold_i} \qquad \text{Equation 6}$$

With:

C_i	=	Pollutant concentration i [ppm]
$Threshold_i$	=	Effect threshold for pollutant i [ppm]

Table 12 below provides threshold values for each irritant gas prone to being present in the combustion fumes. These values are taken from ISO 13571 standard[15].

Toxic gas	$Threshold_i$ [ppm][15]
HCl	1,000
HF	500
NO_2	250
SO_2	150

Table 12: Threshold values for each toxic gas

Retained criterion

Knowing that a threshold criterion of 1 for FED and FEC statistically serves to protect only half of the exposed population, and that the relationship between these indicators and the percentage of the population likely to suffer irritant or asphyxiating effects follows a log-normal distribution, INERIS retains a threshold criterion of 0.3 for the two indicators, which translates statistically to 11.4% of the population likely to suffer compromised tenability conditions. This value therefore allows, in a prudent fashion, to ensure the absence of the effect on 90% of the population. It is to be noted that an FED or FEC of 0.3 allows reverting back to concentrations greatly inferior to thresholdsof irreversible effects.

5.2.3 Open field toxic effect thresholds of various types of loads studied

The concentration of gaseous effluents is set such that the FEC or the FED does not exceed 0.3.

Table 13 shows:

- the equivalent threshold (§5.2.2.1) for an exposure of 60 min,
- the different concentrations of gaseous effluents obtained for an FEC or FED of 0.3 for various loads, ranked in increasing order (§5.2.2.2).

The lower the threshold value, the greater the toxic effects.

	Gaseous effluent threshold concentration (ppm) for the two approaches	
Loading	**Additivity law of TIE**	**ISO 13,571 approach**
33 pallets of pesticides	**43,873**	**727**
66 pallets of plastic barrels	**35,039**	**879**
26 blocks of PU foam	**375,109**	**1,662**
33 pallets of salads	**305,800**	**1,671**
33 pallets of DVD's	**891,283**	**1,880**
33 pallets of aerosol containers	**787,507**	**2,174**
107 Battery packs N°2	**321,340**	**2,392**
89 Battery packs N°1	**422,201**	**5,346**

Table 13: Open field gaseous effluent threshold concentrations

The additivity law leads to high thresholds which leads to low effect distances. This approach will not be applied in the report follow-up.

The threshold concentrations required to obtain a FEC or FED of 0.3 for a fire of pallets of pesticides are of the same order of magnitude as those for a fire of a load of plastic barrels. They are between 2 times weaker than for fires of blocks of PU foam, pallets of salads and pallets of DVDs, and approximately 3 times lower a fire of aerosols or of battery packs N°2. They are approximately 7 times lower for a fire of battery packs N°1.

We may note that, although the amounts of each gaseous effluent produced by the fire of a load of battery packs are greater than those of a fire of a load of aerosols, the toxic effects are less significant (greater concentration threshold). This is the due to the fume flow rate parameter (§5.1.2) which is much more significant in the case of a fire of battery packs.

The lowest threshold concentration of gaseous effluents is therefore the one associated with a fire of a load of pallets of pesticides, which therefore constitutes the envelope load in terms of toxic effects.

Figure 12 presents the various plumes obtained at the threshold isoconcentration for the load of pallets of pesticides for various atmospheric conditions. This means that inside the plume, the concentration of gaseous effluents exceeds the threshold concentration and may constitute a hazard for a person standing inside that zone.

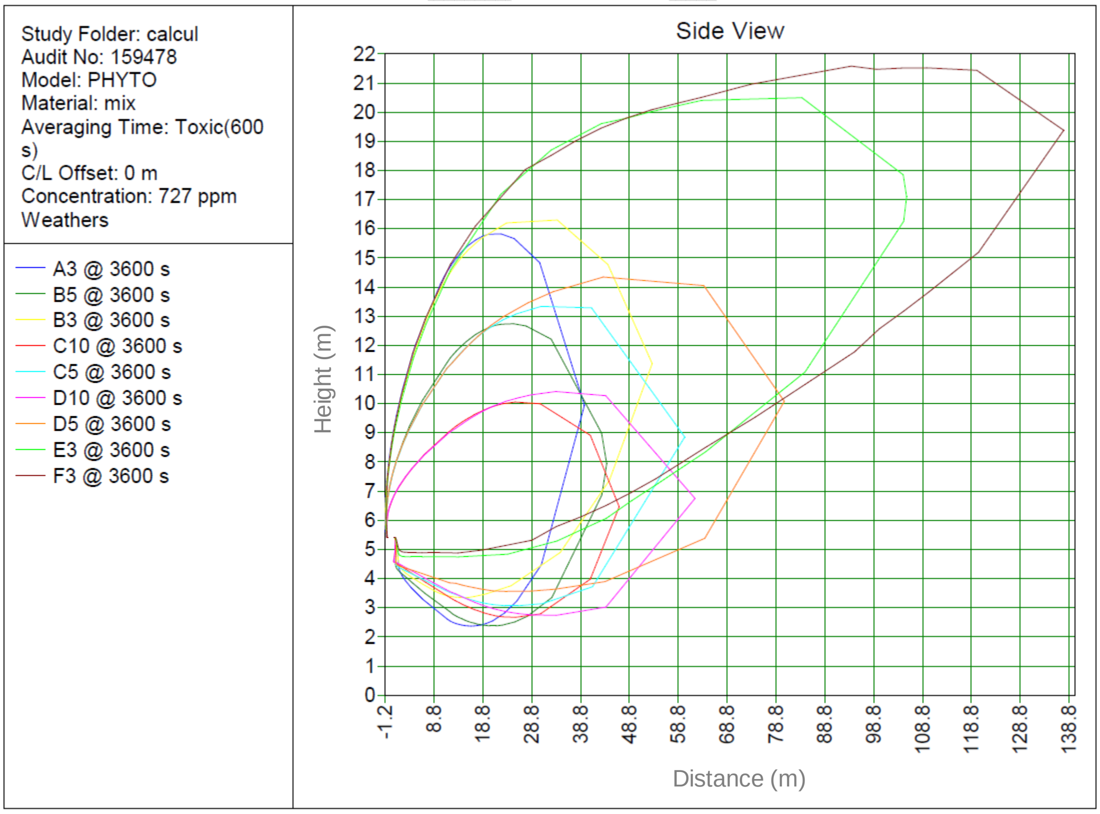

Figure 12: Smoke plumes at the threshold isoconcentration for various atmospheric conditions - pallets of pesticides

No matter the atmospheric conditions studied, no toxic effect at chest height was observed for a fire of pallets of pesticides. As the threshold concentrations of gaseous effluents calculated for the other loads were higher, a truck fire containing these various previously described loads will therefore not lead to toxic effects at chest height either.

5.3 CONFINED SPACE CALCULATION OF TOXIC EFFECT DISTANCES

5.3.1 Retained effect thresholds

It is to be noted that the study of toxic effects related to a vehicle fire in a confined space cannot be generalized since it is dependent on the geometric characteristics of the space (tunnel, parking lot...) and ventilation conditions. These specific studies are therefore performed on a case by case basis, using field study codes.

One qualitative approach that allows prioritizing toxic effects related to various loads in confined spaces would be to compare the amount of gaseous effluents emitted by the fires, for each load type, without taking into account the air entrainment which would depend on the ventilation of the confined space.

In our confined space study, we will use a data item which allows taking into account all the toxic elements present in the fumes. This data item is the TIE equivalent and is obtained using Equation 7.

$$\frac{1}{Threshold_{\text{equivalent}}} = \sum_{i=1}^{n} \frac{Csource_i}{Threshold_i} \qquad \text{Equation 7}$$

With:

$Csource_i$ = Fraction of pollutant *i* at the source [ppm]

$Threshold_i$ = Effect threshold for pollutant i [ppm]

This approach resembles the additivity law approach for thresholds described in paragraph 5.2.2.1 with the exception that the concentrations considered are those of source pollutants, having no information on the amount of air entrainment by the fire.

5.3.2 Confined space toxic effect thresholds of the various types of loads studied

Table 14 shows the volumetric concentrations of various gaseous effluents contained in the fumes for each load calculated on the basis of the test results presented in Table 9 as well as various TIE equivalents at the source of the various loads studied. The TIE equivalent at the source for a given load corresponds to the total concentration of the produced gaseous mix's gaseous effluents produced by the load fire and required to give rise to irreversible effects on people in 60 min. The various TIE equivalents at the source are ranked in increasing order, which means that the lower the value, the more significant the toxic effects.

	Combustible element	Volumetric concentration of gaseous effluents in fumes (-)							TIE equivalent at the source (ppm)
		CO	CO_2	HCl	HF	HCN	NO_2	SO_2	
Loading	**66 pallets of plastic drums**	4.35E-02	8.42E-01	3.87E-02	7.44E-02	2.90E-05	4.99E-04	5.64E-04	**554**
	33 pallets of pesticides	3.44E-02	8.97E-01	2.11E-03	2.46E-04	2.68E-03	3.86E-03	5.94E-02	**989**
	107 Battery packs N°2	3.14E-02	9.56E-01	1.69E-03	1.06E-02	5.11E-05	7.10E-04	0	**4,434**
	26 Blocks of polyurethane (PU) foam	5.06E-02	9.45E-01	7.63E-04	4.78E-04	2.26E-03	1.09E-03	0	**5,309**
	89 Battery packs N°1	2.13E-02	9.69E-01	8.64E-04	8.32E-03	4.07E-05	7.83E-04	0	**5,834**
	33 pallets of aerosols	7.13E-02	9.26E-01	1.50E-03	9.39E-04	1.69E-04	4.93E-04	0	**5,850**
	33 pallets of salads	7.23E-02	9.25E-01	1.05E-03	6.59E-04	1.18E-04	3.46E-04	0	**6,520**
	33 pallets of DVDs	2.26E-02	9.76E-01	4.84E-04	1.74E-04	3.13E-05	3.45E-04	0	**14,091**

Table 14: Volumetric concentrations and TIE equivalents for each load studied

Figure 13 compares equivalent TIEs at the source obtained for various loads. To help understand this, the data presented in this figure for each load result from the following formula:

$$\frac{Threshold_{\ equivalent\ \ \max}}{Threshold_{\ \mathrm{equivalent}}} \qquad \text{Equation 8}$$

This formula implies that the greater the value, the greater the toxic effect.

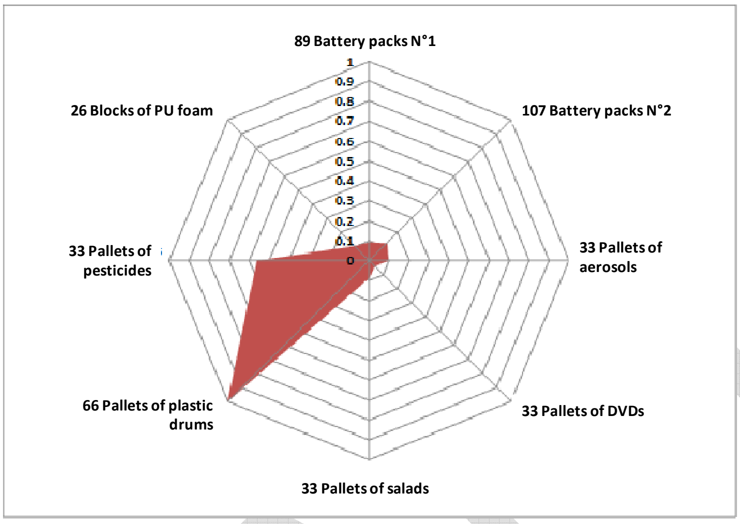

Figure 13: Qualitative analysis of toxic effects in confined spaces

The loads of pesticides products and plastics drums have the weakest TIE equivalents. Fire of these loads in a confined space will therefore lead to envelope toxic effects in comparison with other loads, and through experience, in comparison to all other load types not studied in the present study. Fire of loads of batteries, aerosols, salads and PU foam will lead to intermediate toxic effects, and fire of pallets of DVDs, to lower toxic effects. As a reminder, this qualitative approach only allows prioritizing toxic effects tied to the fires of the various loads studied.

These various threshold values can therefore be classified according to three distinct levels, detailed in Table 15.

TIE equivalent at the source (ppm)	Classified as hazardous goods	Not classified as hazardous goods
500 - 1,000	**Pallets of phytosanitary products**	**Pallets of plastic drums**
4,400 - 6,500	**Battery packs N°2** **Pallets of aerosol containers** **Battery packs N°1**	**Pallets of salads** **Pallets of PU foam**
14,000 - 15,000		**Pallets of DVD's**

Table 15: Classification of TIE equivalents for fires of various loads studied

It is noted that for each potency level, with the exception of the 14,000 - 15,000 ppm level, we find products classified as dagerous goods and others that are not.

It is therefore observed that for battery stacks with energy and mass of the same order of magnitude, the TIE equivalents developed during a fire of a full load can:

- Be higher or lower than values for fires of dangerous goods loads,
- Be higher or lower than the values for fires of non-dangerous goods loads.

Moreover, in comparison to the characteristics of the two packs described in Table 5, it is impossible to conclude on the amount of energy transported, *etc.*, based solely on the composition (external or internal). A great number of parameters come into play and influence the toxic behavior of a full load fire.

According to this preliminary information, a classification of batteries as a function of their toxic effect according to the results of an external fire test therefore seems conceivable and justified.

5.4 CONCLUSION ON TOXIC EFFECTS

In view of the data obtained from this study we can conclude that:

- None of the studied loads show any toxic effect at chest level in an open field fire,
- Modifying one or more parameters in the design of the battery (architecture, external and internal components, etc.) may induce changes in the amount of gases produced,
- Toxic effects measured in a fire of a battery packs load can be lower or higher than measured effects on certain goods classified as dangerous in the transport sense (in our case, aerosols and pesticides),
- Depending on the battery tested, the toxic effects measured in confined spaces can be lower or higher than measured effects on certain goods classified as NOT dangerous in the transport sense (i.e. polyurethane foams),
- Information on the constitution of a battery does not permit a conclusion, without performing a test, about the importance of measured toxicity. For example, in our case, the presence of plastic on the battery pack N°2 casing causes one to suspect a much more important production of gaseous effluents (including CO and CO_2).

However, it is difficult to conclude on the relevance of the categorization of batteries for transport according to their toxic effects during an external fire test. Indeed, although this effect has been compared to other types of loading, none of these loads is classified as dangerous **for the toxic effects of these fumes**.

In addition, the likelihood of fire parameter has not been considered in this study. Now, although the toxic effects of batteries are, for example, equal to those of polyurethane foam, the likelihood of a fire starting, induced by the loading, is much higher in the case of batteries. It stresses that, for an equivalent toxicity, batteries, due to their higher fire probability, are more dangerous, in terms of toxicity, than a large number of loads.

Future work in the context of the operation A5 of the DRA 96 will then consist in:

- Identifying the relevant parameters to categorization,
- Setting, for these parameters, one or more thresholds that will allow to categorize batteries in one or more classes of toxicity,
- Defining a reliable and robust testing protocol in order to test batteries and retrieve data needed for the evaluation of the toxic effect.

6 GENERAL CONCLUSION

The study of thermal and toxic effects that may be generated by fires of several goods loads classified or not as dangerous to transport (including two types of battery packs) and based on tests previously conducted at INERIS has determined that:

- The effects can vary greatly from one battery type to another,
- The effects of battery loadings fires can be, depending on the battery type selected, lower or higher than fires of goods laodings classified as dangerous to transport as well as loads classified as NOT dangerous.

A testing protocol will be drafted and the first tests in the context of the operation will be undertaken in 2016. They are used to retrieve data and subsequently to define threshold values for different effects expected to be used to try to establish a categorization. An example of a final diagram illustrating a potential categorization procedure of a battery in a given class is presented in Appendix D.

The test protocol and a progress report on the results of the first tests carried out will be provided in 2016.

TABLE OF APPENDICES

APPENDIX A:
VARIOUS CLASSES OF DANGEROUS GOODS

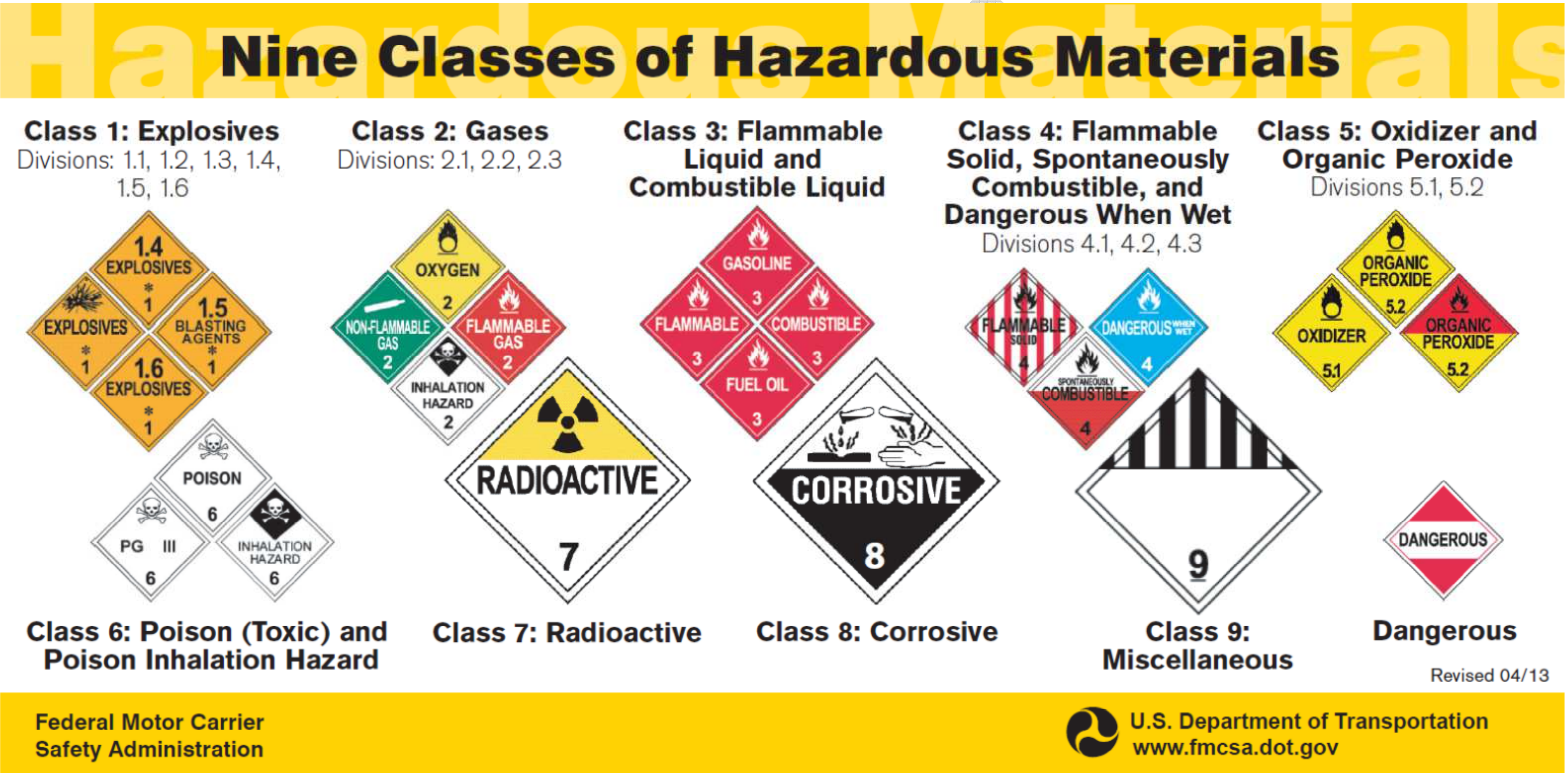

Figure 14: Nine classes of hazardous materials

APPENDIX B:
DESCRIPTION OF VARIOUS CELL GEOMETRIES AND CHEMISTRIES

A.i GEOMETRY

As far as cell geometry goes, four[20] types are currently used in the market (Figure 15):

- cylindrical cell: generally used for small cells. It is constructed by superimposing anode-separator-cathode-separator bands which are coiled around a central pivot
- prismatic cell: used for current greater than 10Ah. It's housing is rigid with protective elements (e.g.: safety valve)
- button cell: hardly used anymore for rechargeable lithium batteries
- pouch cell or: have a soft housing which is sealed close to the electrode-separator stack and allows for potential warping due to internal cell pressure.

Figure 15: Various lithium cell formats: cylindrical, prismatic and pouch

A.ii CHEMICAL COMPOSITION

Regarding chemical composition, we will distinguish between cathode and anode materials in the study below.

Currently, five[21] cathode materials are mostly present on the market:

- Cobalt Oxide, $LiCoO_2$ (LCO): material still widely used in current batteries due to its high energy density and its low auto-discharge, but has a higher cost (due to the Cobalt) and low thermal stability (runaway risk)
- Nickel-Manganese-Cobalt Oxide, $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (most widely used formula) (NMC): used more and more (particularly in electric vehicles), replacing cobalt oxide thanks to its greater thermal stability and lower cost.

[20] http://batteryuniversity.com/learn/article/types_of_battery_cells

[21] N. Nitta, et al., Matter Today (2014)

- Nickel-Cobalt-Aluminum Oxide, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA): used more and more for stationary or mobile applications thanks to its high energy density and its long stability over time, but has a relatively high cost.
- Manganese Oxide, $LiMn_2O_4$ (LMO): used more and more thanks to its lower cost relative to a cobalt oxide cathode, but has long-term cycleability which is inferior to other chemistries.
- Iron Phosphate, $LiFePO_4$ (LFP): used more and more thanks to its very strong thermal stability and its capacity to withstand high power levels, but has low energy density resulting from lower usage voltage than the preceding oxides

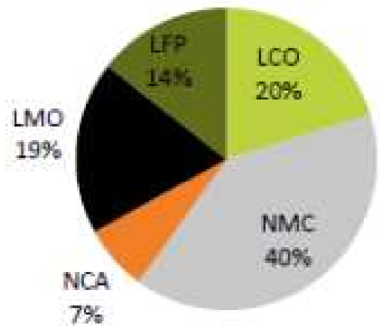

***Figure 16: Lithium battery distribution forecast as relates to cathode material in 2020*[22]**

For anodes, two materials[21] are marketed on a large scale:

- Graphite: anode material present in the vast majority of current lithium batteries, thanks to its great abundance on earth, its low cost and strong thermal conductivity
- Lithium Titanate, $Li_4Ti_5O_{12}$ (LTO): used more and more thanks to its strong thermal stability, a capacity to withstand strong currents and long life, and despite a much higher cost than graphite as well as a lesser energy density.

Another type of lithium battery that is worth mentioning is the Lithium-Metal-Polymer battery developed solely by Batscap and used in the BlueCar electric vehicle. This battery is made up of a metallic lithium anode and a vanadium oxide, carbon and polymer-based cathode.

[22] The Worldwide battery market 2011-2015, Avicenne Energy Presentation, Batteries 2012

APPENDIX C:
EXAMPLES OF SAFETY DATA SHEETS FOR VARIOUS HAZARDOUS LOADS STUDIED

A.iii BATTERIES

MATERIAL SAFETY DATA SHEET March 7th, 2012

SECTION 11 – TOXICOLOGICAL INFORMATION

Routes of Entry:

Skin Contact: NO Skin Absorption: NO Eye contact: NO
Inhalation: NO Ingestion: NO

Acute Exposure

Skin:	No effect noticed in routine handling of product.
Eyes:	The bulk solid has no effect on the eye.
Inhalation:	Not applicable.
Ingestion:	Ingestion is not likely, given the physical size and state of the cell.

Chronic Exposure

Skin:	Not anticipated.
Eyes:	Not applicable.
Inhalation:	Not applicable.
Ingestion:	Ingestion is not a likely exposure route.

Exposure Limits: None listed	Irritancy: None	Sensitization: Not anticipated	Carcinogenicity: Not anticipated
Teratogenicity: Not anticipated	Mutagenicity: Not anticipated	Reproductive toxicity: Not anticipated	Synergistic Products: None expected

SECTION 12 – ECOLOGICAL INFORMATION

In case of the worn-out cell was disposed in land, the read tabs or the laminate film may be corroded, and leak electrolyte. But, we have no ecological information.

SECTION 13 – DISPOSAL CONSIDERATIONS

Do not disassemble or modify the cell. When the battery is throws away, be sure it is non-conducting by applying vinyl type to (+) and (-) terminals, and thrown away it in the method following the law of each countries. Always consult and obey all international, federal, provincial/state and local hazardous waste disposal laws. Some jurisdictions require recycling of this spent product.

SECTION 14 – TRANSPORT INFORMATION

UN No.:	UN Dangerous goods name:	UN Class:	
3480	LITHIUM ION BATTERIES	9	

There are some laws and regulations for transportation.
Please follow the law or regulation of each country.

Figur 17: Safety data sheet for battery pack N°1

A.iv Aerosols

Safety Data Sheet (SDS)

Date Prepared/Revised: 8/11/2015 Version no.: 01 Supersedes: (10/9/2014)

Mobility in soil: **No Data Available**
Results of PBT and vPvB assessment: **No Data Available**
Other adverse effects: **No Data Available**

13. Disposal Considerations

Waste Disposal: Dispose of material in accordance with EU, national and local requirements. For proper disposal of used material, an assessment must be completed to determine the proper and permissible waste management options permitted under applicable rules, regulations and/or laws governing your location.
Product / Packaging disposal: Dispose of packaging in accordance with federal, state and local requirements, regulations and/or laws governing your location.

14. Transportation Information

US DOT

UN Number	Proper Shipping Name	Hazard Class	Packing Group	Marine Pollutant	Special Provisions
UN1950	Aerosols	2.1	Not Applicable	Not Applicable	Reference 49 CFR 172.101

IMDG

UN Number	Proper Shipping Name	Hazard Class	Packing Group	Marine Pollutant	Special Provisions
UN1950	Aerosols	2.1	Not Applicable	Not Applicable	Reference IMDG code part 3

IATA:

UN Number	Proper Shipping Name	Hazard Class	Packing Group	Marine Pollutant	Special Provisions
UN1950	Aerosols, Flammable	2.1	Not Applicable	Not Applicable	Reference IATA Dangerous Goods Regulation

15. Regulatory Information

Workplace classification:
This product is considered hazardous under the OSHA Hazard Communication Standard (29 CFR 1910.1200). The Occupational Safety and Health Administration's interpretation of the product's hazard to workers.
SARA Title 3:
Section 311/312 Categorizations (40 CFR 372): This product is a hazardous chemical under 29 CFR 1910.1200, and is categorized as an immediate and delayed health, and flammability physical hazard.

Figure 18: Safety data sheet for aerosols

A.V PHYTOSANITARY PRODUCTS

Safety Data Sheet

DuPont™ Glean® XP Herbicide

Version 2.1

Revision Date 06/30/2015 Ref. 130000033378

Contaminated packaging : No applicable data available.

SECTION 14. TRANSPORT INFORMATION

IATA_C	UN number	:	3077
	Proper shipping name	:	Environmentally hazardous substance, solid, n.o.s. (Chlorsulfuron)
	Class	:	9
	Packing group	:	III
	Labelling No.	:	9MI
IMDG	UN number	:	3077
	Proper shipping name	:	ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S. (Chlorsulfuron)
	Class	:	9
	Packing group	:	III
	Labelling No.	:	9

Not regulated as a hazardous material by DOT.

SECTION 15. REGULATORY INFORMATION

Other regulations : This Safety Data Sheet is for a pesticide product registered by the US Environmental Protection Agency (USEPA) and is therefore also subject to certain labeling requirements under US pesticide law (FIFRA). These requirements differ from the classification criteria and hazard information required by OSHA for safety data sheets, and for workplace labels of non-pesticide chemicals. The following is the mandatory hazard information required by USEPA on the pesticide label:

CAUTION!

Harmful if swallowed. Wash hands thoroughly with soap and water after handling and before eating, drinking, chewing gum, using tobacco, or using the toilet.

SARA 313 Regulated : Chlorsulfuron

10 / 12

Figure 19: Safety data sheet for the herbicide chlorsulfuron

APPENDIX D:
EXAMPLE OF A POSSIBLE PROCEDURE FOR BATTERY TRANSPORT CLASSIFICATION

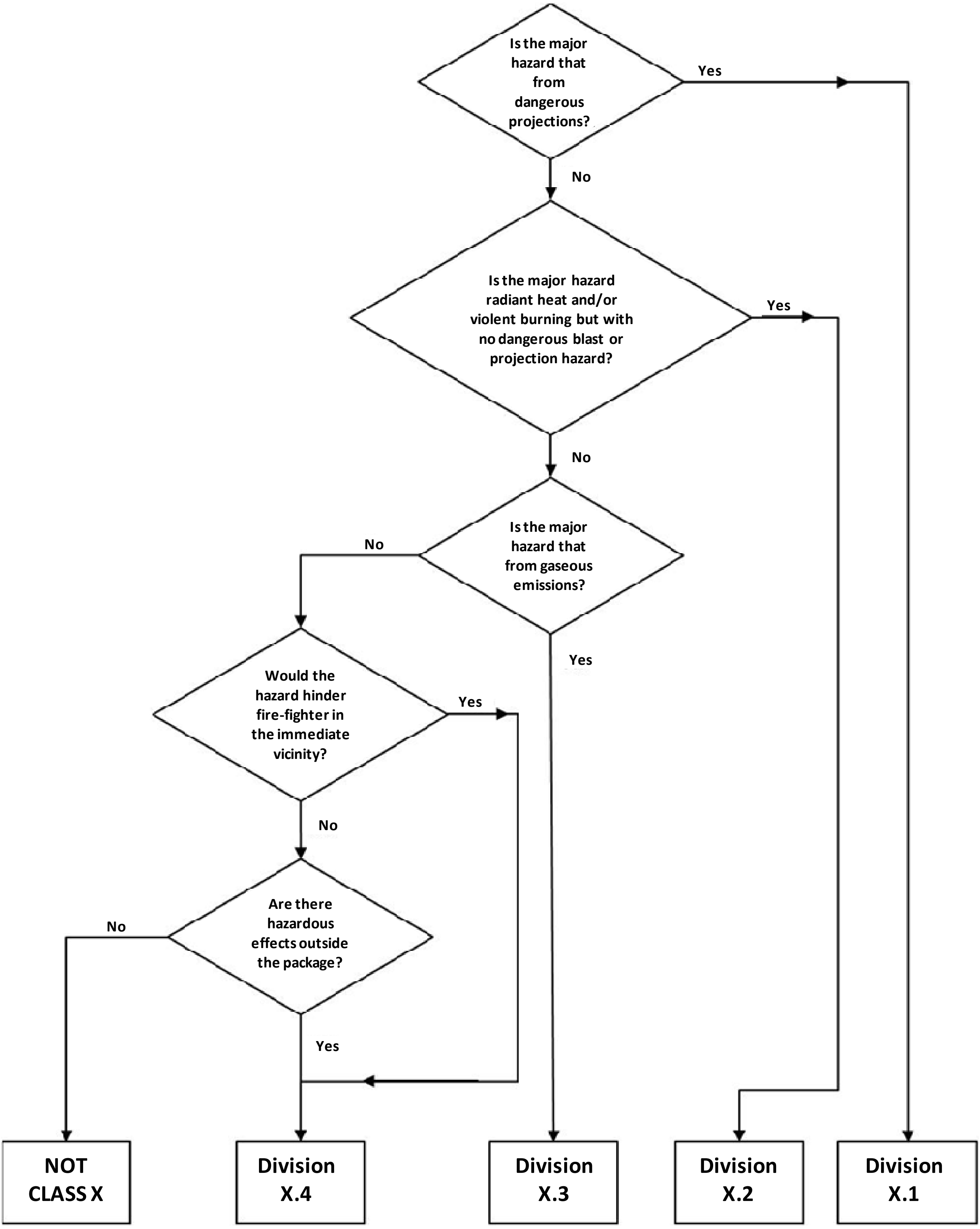

Figure 20: Example for a battery transport classification procedure