Safety of Li batteries in transportation: is a protection in case of thermal runaway affordable?

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Recharge membership in all the Value Chain.

The European Association for Advanced Rechargeable Batteries
1-Li batteries transport: legislative framework

Li batteries are classified as dangerous good for transport under UN transport regulation=

No. 3480 and 3090
Lithium ion and Lithium metal batteries
Risk UN class: 9, Packing Group: II
Special Provisions : 188,230,310
Packing Instruction : P903

No. 3481 and 3091
lithium ion and Lithium metal batteries, contained in equipment, or packed with equipment,
Risk UN class: 9, Packing Group: II
Special Provisions : 188,230,310, 360
Packing Instruction : P903
1- UN Dangerous goods transport regulation

Part 1. GENERAL PROVISIONS, DEFINITIONS, TRAINING AND SECURITY

Chapter 1.1 - General provisions

1.1.1 Scope and application

1.1.1.1 These Regulations prescribe detailed requirements applicable to the transport of dangerous goods. Except as otherwise provided in these Regulations, no person may offer or accept dangerous goods for transport unless those goods are properly classified, packaged, marked, labelled, placarded, described and certified on a transport document, and otherwise in a condition for transport as required by these Regulations.

General Requirements:
- identified products (classification, labelling, declaration,..)
- tested products (safety test according UN Manual of Tests and Criteria, Part III, sub-section 38.3)
- qualified packagings (UN class II)
- trained operators
A booklet can be used to identify the applicable packaging (Recharge and Hyper) on line demo:
http://www.rechargebatteries.org/knowledge-base/transport/

- Information describing all modes of transport
  - White: all modes of transport
  - Orange: specific to Road
  - Violet: specific to Maritime
  - Blue: specific to Air

- Pictures for packaging and labelling
LIQUID METAL CELLS (including lithium alloy cells)
Fully regulated cells

UN 3090

On line preview: http://www.rechargebatteries.org/knowledge-base/transport/

Li battery transport, M. Ottaviani: New edition 2014
1-Li batteries transport: cushioning requirement

• The packaging instructions P908, applicable for damaged and defective cells and batteries, requires the use of cushioning material:

  “2. Each inner packaging shall be surrounded by sufficient non-combustible and non-conductive thermal insulation material to protect against a dangerous evolution of heat.”

• It is the responsibility of the shipper to define the sufficient amount of cushioning material, but no more information is provided.

There is a need of practical tests and models to provide valid information to the professionnels shipping batteries.
2- ACCUREC Experimental study: materials

ACCUREC has tested several cushioning materials to compare their effectiveness in protecting in case of Li-ion battery thermal runaway (ref. 1).

• At first, the thermal properties of the selected materials were measured

- Electrical insulation:

- Density:

- Volumetric heat capacity:

- Thermal insulation:

Ref 1. : ACCUREC, Investigation on packaging materials for safe transport of spent Li-ion batteries, March 4-2014.
2- ACCUREC Experimental study: testing configuration

• One Li-ion single cell (18650) was placed in a drum filled with cushioning material. A heater was placed at 15 mm to cause a run-away.

• Thermocouples were placed on the heater, the cell, and in the cushioning material at 15 mm distance to measure the thermal propagation.
2- ACCUREC Experimental study: testing results

• Similar behavior was observed in all materials: after the heating phase up to about 200°C (phase A), the cell temperature increases abruptly due to the runaway (phase B), then the system cools down progressively (phase C).

• Significant differences: the higher the material heat capacity, the longer the heating phase A, and the lower the runaway max. temperature during phase B.
2-ACCUREC experimental study: thermal diffusion

- The temperature increase of the cushioning material depends on its thermal properties.

![Graphs showing temperature vs. time for different materials: Vermiculite, PyroBubbles, Sorbix, Absorbent, and Sand.](image)

- **Vermiculite**: \(\Delta T = 174^\circ C\)
- **PyroBubbles**: \(\Delta T = 21^\circ C\)
- **Sorbix**: \(\Delta T = 21^\circ C\)
- **Absorbent**: \(\Delta T = 21^\circ C\)
- **Sand**: \(\Delta T = 21^\circ C\)
3- Modeling: model description

Objective:
- A simple static thermal model was not sufficient to analyze the results of the testing.
- The testing was limited to one type and size of battery: there is a need of a model allowing a good prediction of the thermal behavior in case of different battery and packaging sizes or other cushioning materials.

Model description:
- A dynamic model has been created: simplified finite elements calculation under Excel, using heat propagation in isotropic spherical conditions through 4 layers of material.
- Boundary conditions can be adjusted.
- Heat source size and layer thickness can be adjusted.
3- Modeling: calibration

- The heating phase (phase A) with stable parameters (heater at 150 W), was used for the calibration of the thermal parameters, based on the data for thermal properties of 5 cushioning materials.
- Comparison of experimental data with simulated data shows an acceptable fit: example for sand and pyrobubbles, temperature T1 of the material at 30 mm from the heater.

![Pyrobubbles](image1)

![Sand](image2)
3- Modeling: cooling simulation

- Using the same parameters defined in the calibrating phase, the runaway phase and the cooling phase were calculated.
- The initial temperature was set at the level of the material surrounding the cell at the runaway phase start.
- The simulation is showing acceptable results for the different layers of the cushioning materials during the cooling phase.

Sorbix

Absorbant
Due to the large difference observed in the max. runaway temperature, it is necessary to adjust the Li-ion battery energy release in order to fit the observed temperatures.

Simulation of the vermiculite and sand is showing acceptable results, even in this case of large heat release difference.
3- Modeling: thermal runaway energy calculation

- The simulation allows to recalculate the total heat emitted during the runaway: the results are reported in the table.
- They are compared to a reference energy release for Li-ion cell runaway without flames of 870 kJ/cell kg (ref. 2).

<table>
<thead>
<tr>
<th>Material</th>
<th>Calculated heat release (kJ/cell kg)</th>
<th>% theoretical heat release</th>
</tr>
</thead>
<tbody>
<tr>
<td>sand</td>
<td>500</td>
<td>58%</td>
</tr>
<tr>
<td>absorbent</td>
<td>700</td>
<td>81%</td>
</tr>
<tr>
<td>Pyrobubbles</td>
<td>800</td>
<td>93%</td>
</tr>
<tr>
<td>sorbix</td>
<td>800</td>
<td>93%</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>800</td>
<td>93%</td>
</tr>
</tbody>
</table>

- It is clear that the heat absorbing properties of the sand contributes in reducing the total energy release (this effect of slowing the runaway reaction by external cooling was already identified, particularly for small cells).

Ref 2: RECHARGE, Li-ion safety, July 2013, [http://www.rechargebatteries.org/communication/recharge-positions/](http://www.rechargebatteries.org/communication/recharge-positions/)
4- Cushioning calculation: Minimum Safe Distance (MSD)

- The « Minimum safe distance » MSD, is the thickness of the cushioning material layer allowing to stop the propagation to the next battery in case of one battery runaway.
- It has been shown that Li-ion batteries do not release significant amounts of heat up to 100°C (ref 1). It is then considered that the distance where the cushioning material is heated at 100°C maximum is the MSD.

- ACCUREC has conducted experiments (ref 1) to measure this MSD with different cushioning materials.
- Results obtained with the model are quite comparable to the experiments, except for pyrobubbles: the test result is not in relation to the thermal properties measured in this case.
Using the same model, the Minimum Safe Distance has been calculated according to the battery size and weight.

For this study, a maximum runaway energy has been used, whatever the cushioning material type, the type of li-ion chemistry or the battery size: 870 kJ/kg.

**MSD according battery weight**

- Materials with high volumetric heat capacity require less thickness for the MSD.
4- Cushioning calculation: material weight vs battery weight

- The weight of a layer of MSD thickness, surrounding the battery has been calculated, and compared to the battery weight.

![Graph showing material weight vs battery weight for different materials.](image)

- The % in weight of cushioning material is about constant over the batteries size range, for all cushioning materials.
- For this reason, an homogenous mix of batteries and cushioning material can be safe in case of one battery runaway, what ever the size of the battery, if the total ratio of cushioning material is respected.
4- cushioning calculation: simple rules

- Proposed quantities: based on the model MSD calculation, a simple geometrical calculation allows to propose the following quantities of cushioning material, respecting the MSD between batteries in an homogeneous mix of batteries and cushioning material:

<table>
<thead>
<tr>
<th></th>
<th>vermiculite</th>
<th>sorbix</th>
<th>Pyrobub.</th>
<th>Absorbant</th>
<th>sand</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>weight ratio</strong> vs battery</td>
<td>0,4</td>
<td>0,4</td>
<td>0,6</td>
<td>0,2</td>
<td>1</td>
</tr>
<tr>
<td><strong>volume ratio</strong> vs battery</td>
<td>10</td>
<td>5,5</td>
<td>5</td>
<td>1,7</td>
<td>1,6</td>
</tr>
</tbody>
</table>

- Many other materials are available. Some have specific properties (i.e. phase transition materials) and may not have the behavior described in this model.
- Decision on the best material can be made based on the product cost, the transport cost, or other constraints (max weight, max volume, process constraints, etc.).
4- cushioning calculation: other cases

- **Case of Li metal battery:**
  - the model can calculate a minimum value: based on a typical runaway energy of 1300 kJ/kg, the required weight of cushioning material is about the double, compared to the Li-ion.

- Nevertheless, this would require some test for validation, particularly for small cells, where the cooling effect of the cushioning material can reduce significantly the thermal runaway energy.
4- cushioning calculation: other cases

- **Case of large batteries in packaging with limited cushioning:**
  - boundaries conditions of the model adapted: the key parameter is the cooling efficiency of the packaging.
  - Example of a 100 kg battery surrounded by 7 cm vermiculite thickness in a metallic drum, in conditions allowing the natural convection cooling (i.e. single drum on a pallet).

- the max. external temperature is 100°C, and decreases after 5h.
Conclusion

- the UN regulation on the transport of dangerous goods requires cushioning materials usage to protect for dangerous evolution of heat in case of battery runaway during transport.

- The thermal behavior of different cushioning has been modeled, and compared with the experimental results, showing an acceptable representation.

- It is shown that the key criteria to control the temperature increase in case of runaway of the battery is the % by weight of cushioning material versus the battery weight.

- Several ratios of cushioning materials versus battery are proposed as a result of this study.

- The amount of material is significant, involving some packaging costs. Nevertheless, a cost optimization is possible, based on the presented results.

Keep Li batteries transport safe !