Attachment 3 - Additional Resources and References
For Consideration in Revision to "Solar Electricity and Battery Storage Systems Safety Handbook for Firefighters"

CTIF – International Association of Fire and Rescue Services website:

- https://ctif.org/news/large-lithium-battery-fires-created-toxic-smoke-and-evacuations-jacksonville-and-gothenburg
- https://ctif.org/news/accident-analysis-beijing-lithium-battery-explosion-which-killed-two-firefighters
- https://ctif.org/news/large-explosion-and-fire-french-lithium-battery-warehouse
- https://ctif.org/news/900-tonnes-lithium-batteries-fire-french-recycling-plant-north-toulouse
- https://ctif.org/news/california-creates-new-emergency-response-legislation-large-lithium-based-battery-energy
- https://ctif.org/news/norwegian-shipping-company-bans-electric-cars-board-classic-ferry-route
- https://ctif.org/news/lihium-ion-battery-bank-started-offgassing-hospital-80-people-evacuated-due-toxic-fumes
- https://ctif.org/news/despite-fire-hazards-lithium-ion-battery-energy-storage-systems-are-getting-larger-and-larger
- https://ctif.org/news/ev-may-have-started-fire-onboard-cargo-ship-3000-cars-crew-had-jump-water-one-dead
- https://ctif.org/news/150-000-liters-water-needed-put-out-fire-electric-car
- https://ctif.org/news/summary-some-more-severe-lithium-battery-fires-during-last-12-months
- https://ctif.org/news/11-electric-cars-and-48-lithium-batteries-caught-fire-after-exposure-salty-flood-water

Selected relevant scientific papers: (with doi.org links to allow convenient access)

Larsson, F., Andersson, P., Blomqvist, P. et al. Toxic fluoride gas emissions from lithium-ion battery fires. Sci Rep 7, 10018 (2017). https://doi.org/10.1038/s41598-017-09784-z

> Conclusions: This study covered a broad range of commercial Li-ion battery cells with different cell chemistry, cell design and size and included large-sized automotive-classed cells, undergoing fire tests. The method was successful in evaluating fluoride gas emissions for a large variety of battery types and for various test setups.
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> Significant amounts of HF ranging between 20 and 200 mg/Wh of nominal battery energy capacity were detected from the burning Li-ion batteries. The measured HF levels, verified using two independent measurement methods, indicate that HF can pose a serious toxic threat, especially for large Li-ion batteries and in confined environments. The amounts of HF released from burning Li-ion batteries are presented as mg/Wh. If extrapolated for large battery packs the amounts would be 2-20 kg for a 100 kWh battery system, e.g. an electric vehicle, and 20-200 kg for a 1000 kWh battery system, e.g. a small stationary engine storage. The immediate dangerous to life of health (IDLH) level for HF is 0.025 g/m^3 (30 ppm) and the lethal 10 minute toxicity value (AEGL-3) is 0.0139 g/m^3 (170 ppm). The release of hydrogen fluoride from a Li-ion battery fire can therefore be a severe risk and an even greater risk in confined or semi-confined space.

Bordes, A., Papin, A., Mariar, G. et al. Assessment of Run-Off Waters Resulting from Lithium-Ion Battery Fire-Fighting Operations, Batteries (2024), 10 (4), 118; https://doi.org/10.3390/batteries10040118

> Conclusions: In the present work, the two battery modules were triggered in thermal runaway and subsequent degassing and fire. Water was applied to mock-up firefighting operations in order to analyze the composition of the extinguishing water.
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> The tests presented in this paper highlight that waters used for firefighting on NMC Li-ion batteries are susceptible to containing many metals, including Ni, Mn, Co, Li and Al. Those metals are mixed with other carbonaceous species (soots, tarballs). It is also important to note that particles present in the water can be nanometric or in the form of nanostructured clusters. In addition to the solid contaminants, liquid compounds can be present, especially organic carbonates coming from the electrolyte (EC and EMC in this case) and also gaseous species such as PAH. A comparison with PNEC values showed that this water could be potentially hazardous to the environment, depending on the actual situation encountered in the case of thermal runaway propagation with a Li-ion battery-based system.
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> As large Li-ion batteries are fast spreading (in so-called Battery Energy Storage Systems, BESS, for example), and only few data on the environmental impact of fires in those

systems are available, it is crucial to further develop consolidated knowledge in this field.

Quant, M., Willstrand, O., Mallin, T., Hynynen, J., Ecotoxicity Evaluation of Fire-Extinguishing Water from Large Scale Battery and Battery Electric Vehicle Tests, ACS Publications, Environmental Science & Technology, Vol 57 (12) https://pubs.acs.org/doi/10.1021/acs.est.2c08581

Conclusions: Electrified transport has multiple benefits but has also raised some concerns, for example, the flammable formulations used in lithium-ion batteries. Fires in traction batteries can be difficult to extinguish because the battery cells are well protected and hard to reach. To control the fire, firefighters must prolong the application of extinguishing media.

In this work, extinguishing water from three vehicles and one battery pack fire test were analyzed for inorganic and organic pollutants, including particle-bound polycyclic aromatic hydrocarbons and soot content. Additionally, the acute toxicity of the collected extinguishing water on three aquatic species was determined. The vehicles used in the fire tests were both conventional petrol-fueled and battery electric.

For all of the tests, the analysis of the extinguishing water showed high toxicity toward the tested aquatic species. Several metals and ions were found in concentrations above the corresponding surface water guideline values. Per- and polyfluoroalkyl substances were detected in concentrations ranging between 200 and 1400 ng L^{-1}. Flushing the battery increased the concentration of per- and polyfluoroalkyl substances to 4700 ng L^{-1}. Extinguishing water from the battery electric vehicle and the battery pack contained a higher concentration of nickel, cobalt, lithium, manganese, and fluoride compared with the water samples analyzed from the conventional vehicle.

Jeevarajan, J.A., Joshi, T., Parhizi, M., Rauhala, T., Juarez-Robles, D., Battery Hazards for Large Energy Storage Systems, ACS Energy Letters, Vol 7 (8), https://pubs.acs.org/doi/10.1021/acsenergylett.2c01400?ref=recommended

Highlights: Hazards for Li-ion batteries can vary with the size and volume of the battery, since the tolerance of a single cell to a set of off-nominal conditions does not translate to a tolerance of the larger battery system to the same conditions. Li-ion batteries are prone to overheating, swelling, electrolyte leakage venting, fires, smoke, and explosions in worst-case scenarios involving thermal runaway. Failures associated with Li-ion batteries are described to be deflagration in nature. However, the gases produced as a result of a fire, smoke, and/or thermal runaway can accumulate to a combustible level in the installation location and cause an explosion (detonation). In general, the off-nominal conditions that can cause the occurrence of catastrophic events with Li-ion batteries can be categorized into electrical, mechanical, and environmental types. The most common electrical hazards are over-charge, over-discharge, and external and internal short circuits. Of the environmental hazards, off-nominal conditions such as temperatures beyond the manufacturer's recommended range are those that are well understood. The influence of other environmental hazard causes, such as changes in altitudes, pressures, salt fog, floods, rain, etc., are not as well understood. Mechanical hazards such as those caused by vibration, shock, and impact are understood to a certain level, especially those encountered under transportation conditions.

High and low temperatures can lead to different unsafe conditions in Li-ion cells and batteries. High temperatures can lead to decomposition of the electrolyte and the solid-electrolyte interface (SEI) layer, destabilization of the cathode and anode that eventually lead to a violent venting, fire, and thermal runaway. Low temperatures increase the viscosity of the electrolyte in a Li-ion cell, reducing the mobility of the lithium ions in the electrolyte. The reduction in ionic conductivity causes the deposition of the ions as dendritic lithium metal due to the reduced ease of intercalation into the anode. This subsequently leads to increased internal cell temperatures, and in the presence of high temperatures due to increased internal resistance, growth of lithium metal dendrites, and the organic flammable electrolytes, the inevitable thermal runaway and fire occurs. Hazardous conditions due to low-temperature charging or operation can be mitigated in large ESS battery designs by including a sensing logic that determines the temperature of the battery and provides heat to the battery and cells until it reaches a value that would be safe for charge as recommended by the battery manufacturer. When heaters are used, the power to the heaters should be controlled to prevent uncontrolled heating due to heater failures.

Yang Peng, Lizhong Yang, Xiaoyu Ju, Baisheng Liao, Kai Ye, Lun Li, Bei Cao, Yong Ni, A comprehensive investigation on the thermal and toxic hazards of large format lithium-ion batteries with LiFePO4 cathode, Journal of Hazardous Materials, Volume 381, 2020, 120916, ISSN 0304-3894, https://doi.org/10.1016/j.jhazmat.2019.120916.

Toxic gases released from lithium-ion battery (LIB) fires pose a very large threat to human health, yet they are poorly studied, and the knowledge of LIB fire toxicity is limited. In this paper, the thermal and toxic hazards resulting from the thermally-induced failure of a 68 Ah pouch LIB are systematically investigated.

The LIBs with higher state of charge (SOC) are found to have greater fire risks in terms of their burning behavior, normalized heat release rate, and fire radiation, as well as the concentration of toxic gases.

The major toxic gases detected from the online analysis are CO, HF, SO_2, NO_2, NO and HCl.

Results show that the effects of irritant gases are much more significant than those of asphyxiant gases. HF and SO_2 have much greater toxicity than the other fire gases. The maximum FEC value is approaching the critical threshold in such fire scenarios.

Larsson, F., Andersson, P., Blomqvist, P. *et al.* Toxic fluoride gas emissions from lithium-ion battery fires. *Sci Rep* **7**, 10018 (2017). https://doi.org/10.1038/s41598-017-09784-z

Lithium-ion battery fires generate intense heat and considerable amounts of gas and smoke. Although the emission of toxic gases can be a larger threat than the heat, the knowledge of such emissions is limited. This paper presents quantitative measurements of heat release and fluoride gas emissions during battery fires for seven different types of commercial lithium-ion batteries. The results have been validated using two independent measurement techniques and show that large amounts of hydrogen fluoride (HF) may be generated, ranging between 20 and 200 mg/Wh of nominal battery energy capacity. In addition, 15–22 mg/Wh of another potentially toxic gas, phosphoryl fluoride (POF_3), was measured in some of the fire tests. Gas emissions when using water mist as extinguishing agent were also investigated. Fluoride gas emission can pose a serious toxic threat and the results are crucial findings for risk assessment and management, especially for large Li-ion battery packs.

Significant amounts of HF, ranging between 20 and 200 mg/Wh of nominal battery energy capacity, were detected from the burning Li-ion batteries. The measured HF levels, verified using two independent measurement methods, indicate that HF can pose a serious toxic threat, especially for large Li-ion batteries and in confined environments. The amounts of HF released from burning Li-ion batteries are presented as mg/Wh. If extrapolated for large battery packs the amounts would be 2–20 kg for a 100 kWh battery system, e.g. an electric vehicle and 20–200 kg for a 1000 kWh battery system, e.g. a small stationary energy storage. The immediate dangerous to life or health (IDLH) level for HF is 0.025 g/m^3 (30 ppm)22 and the lethal 10 minutes HF toxicity value (AEGL-3) is 0.0139 g/m^3 (170 ppm)23. The release of hydrogen fluoride from a Li-ion battery fire can therefore be a severe risk and an even greater risk in confined or semi-confined spaces.

Using water mist resulted in a temporarily increased production rate of HF but the application of water mist had no significant effect on the total amount of released HF.

Conzen, J., Lakshmipathy, S., Kapahi, A., Kraft, S., DiDomizio, M., Lithium ion battery energy storage systems (BESS) hazards, Journal of Loss Prevention in the Process Industries, Vol 81, Feb. 2023, 104932
https://doi.org/10.1016/j.jlp.2022.104932

Highlights: There has been an increase in the development and deployment of battery energy storage systems (BESS) in recent years. In particular, BESS using lithium-ion batteries have been prevalent, which is mainly due to their power density, performance, and economical aspects. BESS have been increasingly used in residential, commercial, industrial, and utility applications for peak shaving or grid support. As the number of installed systems is increasing, the industry has also been observing more field failures that resulted in fires and explosions. Lithium-ion batteries contain flammable electrolytes, which can create unique hazards when the battery cell becomes compromised and enters thermal runaway. The initiating event is frequently a short circuit which may be a result of overcharging, overheating, or mechanical abuse. During the exothermic reaction process (i.e., thermal runaway), large amounts of flammable and potentially toxic battery gas will be generated. The released gas largely contains hydrogen, which is highly flammable under a wide range of conditions. This may create an explosive atmosphere in the battery room or storage container. As a result, a number of the recent incidents resulted in significant consequences highlighting the difficulties on how to safely deal with the hazard. This paper identifies fire and explosion hazards that exist in commercial/industrial BESS applications and presents mitigation measures.

Other relevant reference considerations:

Hydro One – BESS Fire Protection – Risk & Response Assessment Standard

- prepared by Fire & Risk Alliance, LLC, Rockville, MD for Hydro One, July 19, 2023
    - While this standard is not directly related to protection of firefighters or the public, the approach taken is relevant for reference
- goal is to ensure operation of Hydro One high voltage transmission facilities is not affected by any BESS event
- sets two step approach to achieve this:
    - first step is to design and test BESS equipment based on existing standards and industry experience to minimize the adverse effects from a BESS event, along with adequate protection and control and spatial separation within the BESS facility itself
    - second step is to establish and maintain appropriate spatial separation of BESS facility from the transmission facilities to ensure BESS facility results in minimal or no impact on the present and/or future expansion of Hydro One transmission facilities and in the event of an event is confined to the immediate BESS area.
        - setback of BESS from Hydro One – 500 kV Right of Way to be 150 metres
        - setback of BESS from Hydro One – 230 kV Right of Way to be 100 metres
        - setback of BESS from Hydro One – 115 kV Right of Way to be 60 metres
        - setback from 500 kV substation to be 300 metres, 230 kV substation to be 200 metres, 115 kV substation to be 120 metres
- these setbacks make it clear that BESS events are considered capable of causing an equipment impact at a distance from BESS equipment, and suggest consideration be made when siting BESS facilities impacting the public, which may not be as robust to injury as is transmission towers or substations when considering an impact
- what these setbacks do not consider, that is very relevant to public safety, is the issue of toxicity of vapour emissions, or of liquid emissions to waterways that may impact drinking water

- an additional fact that is not apparent from these Hydro One setbacks when considering public safety, is that a major consideration for setbacks to Hydro One equipment is the impact on the overall system on loss of the particular piece of equipment considering redundancy. Loss of a single 115 kV transmission will impact far fewer customers than loss of a 500 kV circuit. Thus, setbacks to prevent loss of a 500 kV circuit are greater than setbacks to prevent loss of a 115 kV circuit. In contrast, when considering public safety, we consider that loss of “a few lives” is still relevant, and society does not consider that we should take no protective action until considering protection against loss of an entire community. Both individual and population effects are relevant, and we would not want to tell a citizen (as for the Neoen Tara BESS site) who unfortunately lives close to the site where a BESS facility will be located, that their life does not matter.

UL Standard 9540A – Test Method for Evaluating Thermal Runaway Fire Propagation in Battery Energy Storage System

- It is of note that the UL 9540A Test Method permits certification of a battery that passes a test of charge-discharge-charge-discharge without initiating thermal runaway
- In practice, thermal runaway is unlikely to occur in 2-cycles of charge-discharge, but only after repeated cycles, particularly following damage, overcharging, or charging beyond lower or higher temperature limits
- A BESS system may experience charge and discharge cycles on a daily basis over it’s lifetime, far exceeding a 2-cycle test, and BESS batteries may be expected to be charged to their full charge value to be able to supply load for their design period (typically full load for 4-hours)
- This suggests that consideration of the test success criterion of UL 9540A may require reconsideration to assure that certification gives assurance that the BESS will not fail during normally anticipated operation