Safety message, Firefighting when large lithium ion batteries are involved

This safety message is to alert Fire and Rescue personnel to a risk associated with fires where large lithium-ion batteries have a thermal rush, more specifically energy storage for solar systems, electric vehicle batteries parked indoors or similar battery solutions. There are still bits of information missing to know exactly how bad this is, but in my opinion the facts known so far is enough to give a heads up that this probably is a new hazard that requires attention. In the text below I will link to facts in order for you to make your own assessment of this safety message. If you find errors or more information please let me know. And if this was not new to you and you have more knowledge, please also let me know.

The problem

The problem is that burning lithium-ion batteries emits large amounts of the very toxic substance hydrogen fluoride (hydrofluoric acid) when it burns or vents. Hydrogen fluoride is toxic both by penetration through the skin and inhaling. It requires a special antidote for the affected person and water alone is not enough for decontamination. Tests show that regular fire PPE turnout gear are not resistant to hydrogen fluoride for more than a minute. Also note that hydrogen fluoride may be toxic in levels below levels that is noticeable to the affected person. It is therefore important at all fires, especially indoors, to consider whether there have been large lithium ion batteries burning or venting to the extent that hydrogen fluoride could be formed, and to assess whether firefighters have been exposed to the gas on skin or through breathing. Also, hydrogen fluoride is easily soluble in water and forms hydrofluoric acid. Extinguishing water and moist surfaces after a fire might need extra precaution.

Author: PerOla Malmquist
Fire Protection Engineer
Fire and Rescue Intelligence Engineer
Former Battalion Chief
From Sweden

Request for information: I collect information about good routines, inventions and ideas for Swedish Fire Departments. If your organization have had some use for this paper, please consider sharing something interesting from your organization with Sweden, please email it to po@utkiken.net. It could be anything from the most dull, but effective routines and SOPs to training material or smart solutions on apparatus or PPE.

The amount of hydrogen fluoride that is formed is huge

Research made by Chalmers institute of Technology and RISE shows that there will form between 280 g (10 oz) and 2.8 kg (100 oz) of hydrogen fluoride when a 14 kWh lithium-ion energy storage burns. Car batteries can be 7 times larger and therefore emit seven times the example below. A calculation example of a 120 square meter (1300 sq ft) house with 2.4 meter (8 ft) ceiling height gives a volume of about 280 cubic meters (10 000 cu ft). If we assume that the smoke is distributed evenly, which it is not, there will be levels of between 1 gram per cubic meter (1170 ppm which is 500 times more than ERPG 1 and 20 times the ERPG-3 level) and 10 grams per cubic meter (11 700 ppm which is 5000 times ERPG-1 and 230 times ERPG-3). A more realistic calculation probably provides significantly higher levels near the fire and lower levels further away. The research article in English >>>

Turnout gear resists hydrogen fluoride for one minute only

The Swedish Civil Contingencies Agency had the Swedish Defence Research Agency to investigate how regular turnout gear resist penetration from gaseous hydrogen fluoride and finds that the gear cannot resist more than one minute. They point out that high hazard environments, like indoor lithium ion battery fires, should be handled with a hazmat suit (which is obviously problematic in fire conditions). Report in swedish >>>

Acceptable levels

In the United States the ERPG Emergency Response Planning Guidelines have levels 1, 2 and 3. ERPG-3 is the concentration most people can stand for an hour without dying. For hydrogen fluoride this ERPG-3 is

equal to 50 ppm. Relating to fire extinguishing where there were Halons (which can also generate hydrogen fluoride), DuPont recalculated the value of ERPG-3 if exposure time was 10 minutes instead of 60 minutes. They decided to use a short time ERPG-3 of 170 ppm instead.
However most of the above levels are based on inhalation and exposure to eyes and do not consider skin penetration. Since SCBA protects lungs and eyes the most interesting values for fire fighters in the acute indoor firefighting operation would be the skin penetration levels. NIOSH have made a paper on skin exposure levels and to me, not being a toxicologist, it seems like the dangerous levels are still very low. They are mentioning levels as low as 0.01% as dangerous to sensitive parts of human skin.
Read about ERPG here >>>
And the NIST recalculated short-term exposure here >>>
NIOSH on skin penetration >>>

Decontamination and antidotes

If affected by hydrogen fluoride it is not enough to just rinse with water. There is also a need for antidotes. You could compare it with the toxic twins, carbon monoxide and hydrogen cyanide that requires special countermeasures when people are affected. Now we can add the toxic triplet hydrogen fluoride as one more toxic that needs special precaution and treatment when fighting fires.
Read more about antidotes and decontamination here >>>

Gaseous hydrogen fluoride and skin penetration

When reading about hydrogen fluoride (gas) and hydrofluoric acid (liquid) it is often mentioned that the gas is inhaled and that the aqueous solution is penetrating the skin. It is important to know that the gas is easily soluble in water and therefore will be a problem when coming in contact with the sweat on a firefighter's skin. I have not been able to find any research that looks more closely to this phenomenon. I also haven't figured out the amount of hydrogen fluoride, if any, that penetrates the skin as a gas without liquifying first. That is a weakness in my above reasoning about levels.
However, at my Fire Department in the 1990s we made a lot of drills sealing leaks on Sulphur dioxide train tanks in regular fire PPE. It made us speed up the life saving part of that kind of HazMat operations. However, the Sulphur dioxide gas was solved in our sweat, and myself and many colleagues had to visit the hospital with skin problems due to sulphuric acidity formed by sweat and the gas. I assume hydrogen fluoride will behave the same way, but have no data on the speed and amount of the solubility. If there is someone with more knowledge in this field, please let me know.

Other uncertainties in above text

Hydrogen fluoride will be formed over a period of time depending on how fast the thermal runaway in the battery proceeds. If it is a thermal runaway cell by cell then it might be a slower process than if the thermal runaway is caused by external heating of the entire battery thus causing a simultaneous thermal runaway.

What to do

Unfortunately, the above is only focusing on the problem at firefighting and not the solution. This is rather new news to me as well and I haven't had time to work the solution side of the problem. Your department or agency first needs to consider if you think there is any substance in the text above with its references and if it is or will be a problem in your area.
If you find this not relevant, please let me know. Tell me what you base the irrelevancy on. Because no one is happier than me if I am wrong.

If you are uncertain about all this chemistry stuff, speak to your HazMat experts and ask them about their opinion on a HazMat call where you had a leaking canister of hydrogen fluoride with the above weight and concentrations in a building.

If you find one or more solutions to handling the problem or research about it, please let me know. Email me at po@utkiken.net

More to consider

The above is only focused on firefighter safety. Of course, the introduction of hydrogen fluoride in the fire environment creates a need for considerations about fire prevention and evacuation of people, EMS training and antidotes, how to pass information on to hospitals that the patients might have been exposed to hydrogen fluoride and much more.

PerOla Malmquist
Fire Protection Engineer