# Testing of Aerosol Fire Extinguishing Agent for Li-ion Battery Fires

**Fireaway Inc.**

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## List of abbreviations

| Abbreviation | Meaning |
|---|---|
| Ah | Amp-hours |
| BESS | Battery Energy Storage Safety |
| CO | Carbon Monoxide |
| FTIR | Fourier Transform Infrared Spectroscopy |
| HF | Hydrofluoric Acid |
| HCl | Hydrochloric Acid |
| HCN | Hydrogen cyanide |
| $O_2$ | Oxygen |
| DNV GL | DNV GL Entity |
| NYSERDA | New York State Energy Research & Development Authority |
| NO | Nitric oxide |
| $NO_2$ | Nitrogen dioxide |
| MSDS | Materials Safety Data Sheet |
| ppm | Parts per million |
| SOC | State of Charge |

# EXECUTIVE SUMMARY

The Fireaway Inc. aerosol extinguishing product, Stat-X, was tested for efficacy in putting out Li-ion battery fires. It was found that the product successfully extinguished single and double cell battery fires. This testing was conducted in parallel with a large battery fire testing program on behalf of Consolidated Edison. Fireaway Inc., contracted with DNV GL for testing to be included with that program.

The following conclusions can be made from testing of Fireaway Inc's Stat-X product:

- Stat-X can put out a Li-ion battery fire.
- Stat-X can reduce oxygen in an enclosed environment during a battery fire.
- Due to the deep seated nature of a stacked battery fire, the Stat-X extinguisher removed heat from the interior of the cells more slowly than the exterior.
- The residence time of gases and aerosols during Stat-X deployment is a function of when the atmosphere is ventilated.
- CO, HF, and HCl are present during Stat-X extinguishing and testing did not demonstrate that the concentration of any of these gases is increased by the use of Stat-X.

DNV GL's findings in the Con Ed / NYSERDA scope are overall challenged to resolve technical issues concerning the following:

- Battery fires are emitting both flammable and toxic gases simultaneously, and therefore ventilation is a key control metric that should be controlled throughout the battery burn
- The deep seated nature of battery fires creates extinguishing challenges for all extinguisher types

The Stat-X aerosol extinguisher may have a role in extinguishing battery fires in a staged extinguishing approach, such that a single cell fire may be handled by the aerosol, active ventilation controls may be triggered by BMS outputs and sensors, and water extinguishing can be deployed as a last resort during a full system fire if rapid cooling becomes a priority.

Stat-X may wish to examine the possibility of further testing under variable ventilation conditions. There may also be opportunities to test at larger scales to demonstrate the efficacy of using Stat-X to reduce $O_2$ concentration in full fire environments during module fires.

# 1 BACKGROUND

As part of the Consolidated Edison and NYSERDA[1] funded Battery Energy Storage Safety (BESS) program, DNV GL included the Fireaway Inc. Stat-X aerosol fire suppression extinguishing agent during cell testing.

The Stat-X product is an aerosol designed to chemically interfere with fire propagation radicals such as $OH^-$, $H^+$, and $O^-$. The extinguishing agent is a potassium based aerosol with fine particulates that is claimed to disrupt reactions with oxygen and fuel in the fire tetrahedron (Figure 1).

The MSDS for Stat-X describes the agent as potassium nitrate with the potential to generate $NO_2$, NO, and CO during combustion.

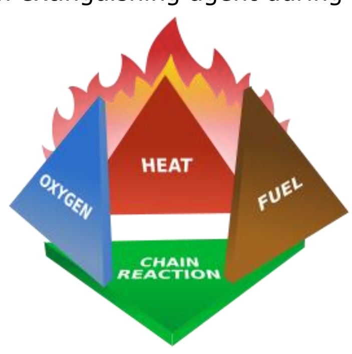


**Figure 1** The fire tetrahedron.

[1] New York State Energy Research & Development Authority

In the context of Li-ion battery fires, there are several unique fire issues that complicate the component interactions in the fire tetrahedron.

- **Chain Reaction:** the "thermal runaway" phenomenon in Li-ion batteries is self-perpetuating when cathode materials are in close proximity to one another and heat is permitted to cascade from cell to cell.
- **Oxygen:** during thermal runaway, oxygen is believed to be self generated during cathode consumption, which may defeat oxygen-depriving extinguishers
- **Heat:** because the thermal runaway reaction is exothermic, removal of heat becomes a challenge because the fire has an internal heat source.
- **Fuel:** A Li-ion battery fire has multiple sources of fuel.
    - The cathode consumed during thermal runaway is the fire ignition source and is consuming metals, and is momentarily a Class D fire.
    - The electrolyte and its solvents are typically ethylene carbonates, and are therefore highly flammable Class B[2] materials (flammable gases and liquids) and potentially Class C (electrical) if voltage remains on unburned batteries.
    - Lastly, the separator and external pouch and casing of the battery may be polymers and are therefore Class A materials. The duration of the fire can be seconds or minutes, and the majority of consumed mass is likely Class A and B materials (Figure 2).

To compound the complexity of the Li-ion battery fire, the materials involved in the ignition and propagation of the fire are tightly integrated into a pouch, cylindrical cell, or prismatic cell, and therefore the fire is a **"deep seated"** fire. Deep seated fires present extinguishing challenges for all extinguisher types.

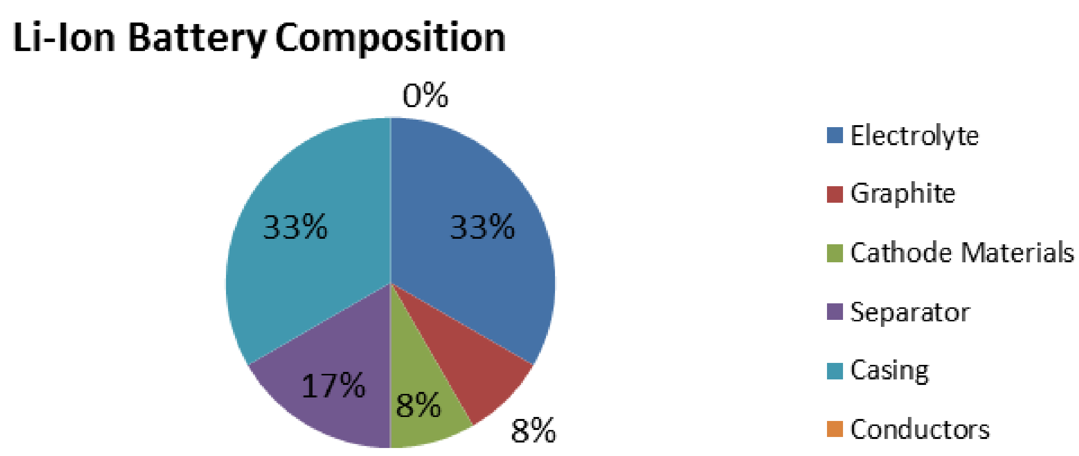


**Figure 2** Approximate composition by mass percentage for Li-ion batteries.

As shown in Figure 3, a Li-ion battery fire can be activated by heat or electrical energy. Li-ion batteries are also subject to ignition by mechanical abuse (such as crush or puncture) which cause electrical shorts in the battery that activate a fire scenario. Once the activation source has been triggered, a rapid chain reaction occurs where the cathode is violently consumed while generating heat and oxygen, and the electrolyte and polymers in the battery are fire fuels that escalate the fire. Because these reactions are taking place within a closely packed, tightly integrated functional device, the fire is deep seated. Disruption of the fire requires either removal of heat, oxidizer, fuel, or disruption of the chain reactions.

[2] By US Fire Class designations

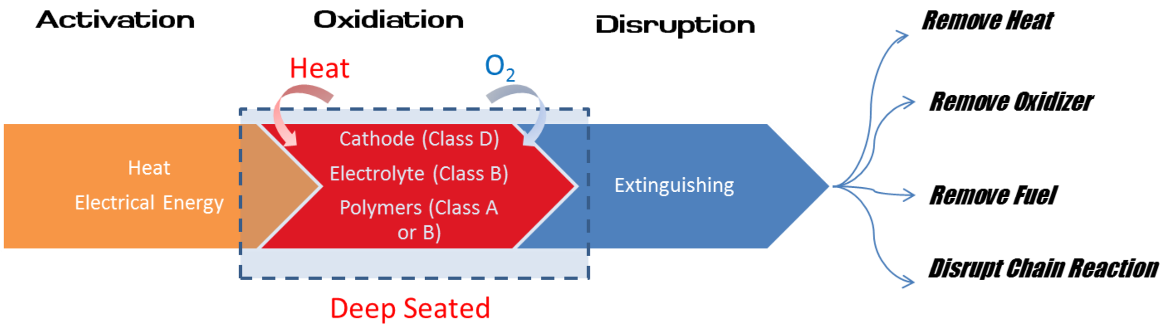


**Figure 3** Stages of a Li-ion battery fire and mechanisms for its propagation and extinguishment.

# 2 RESULTS

The findings from the testing of the Stat-X extinguisher are shown below. These findings can be categorized by extinguishing efficacy, heat removal, and gas analysis. The testing configuration for batteries is shown in Figure 4 and Figure 5. In these cell tests, the batteries were charged to 75-90% state of charge[3] (SOC) and then heated until failure by heat lamps. The thermal abuse mechanism is designed to simulate radiant or convective heating that may occur during a building fire. For water or water-carried extinguishers, the extinguishing nozzle was arranged above the batteries. For the Stat-X test, a suppression canister was deployed in the lower corner of the chamber.

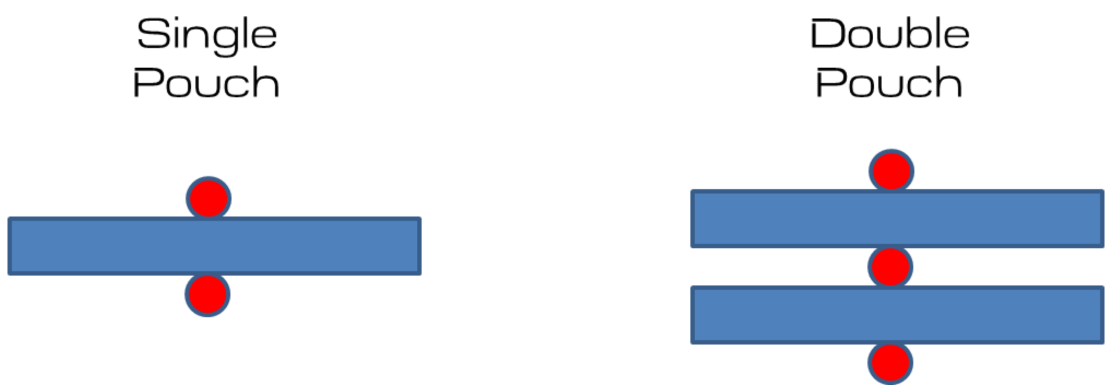


**Figure 4** Cell tests were conducted with thermocouples (red) monitoring the upper and lower surfaces of a single pouch (left), as well as scenarios simulated packed pouches in a battery module with thermocouples monitoring the upper and lower surfaces as well as the interior (right).

[3] State of Charge (SOC) is an indication of how much capacity is available in a battery, expressed as a percentage of the total available.

**Figure 5** DNV GL's large battery abuse chamber is designed to hold battery cells on a rack with radiant heating from above, while temperature are monitored at multiple locations and the FTIR gas monitoring probe extends from above.

## 2.1 Extinguishing the Fire

During DNV GL testing, the StatX product successfully extinguished the battery fire in both the single cell and multi-cell cases. This was a consistent occurrence. The timing of the extinguishing event was triggered when cell temperatures exceeded 350ºC. This was the same triggering mechanism for all extinguishers. No flames were present after extinguishing. Flashover after extinguishing was a function of the reactivation of ventilation.

Events:

1. At time zero, the battery vents and causes a flashover in the battery test chamber (Figure 6).
2. Within 5 seconds of the thermal spiking event, Stat-X is deployed (Figure 7)
3. By 10 seconds, flames are fully suppressed (Figure 8)
4. The battery continues to smolder without flashover (Figure 9)
5. A flashover occurs. It is assumed oxygen is re-entering the environment (Figure 10)
6. The battery is fully consumed and the fire remains out, and heat decays. (Figure 11)

**Figure 6** Time 0: Flashover immediately following battery venting events.

**Figure 7** Time 5: Deployment of Stat-X

**Figure 8** Time 10: Flames fully suppressed as Stat-X is deployed.

**Figure 9** Time 20: Battery continues to smolder.

**Figure 10** Time 80: Flashover as oxygen is introduced

**Figure 11** Time 120: Battery fully consumed, fire out. The battery remained hot for ~20 minutes.

## 2.2 Heat Removal

A decrease in temperature was observed once the Stat-X product was deployed. Refer to single pouch cell test configuration in Figure 4. In Figure 12 it is shown that the top thermocouple and the bottom thermocouple showed differences in behavior due to the shielding effect created by the battery on the bottom thermocouple. On the exterior surfaces of the battery, Stat-X cooled the fire to below 200ºC by 400s. However the Stat-X case continued to have temperatures > 200ºC for ~200s after extinguishing.

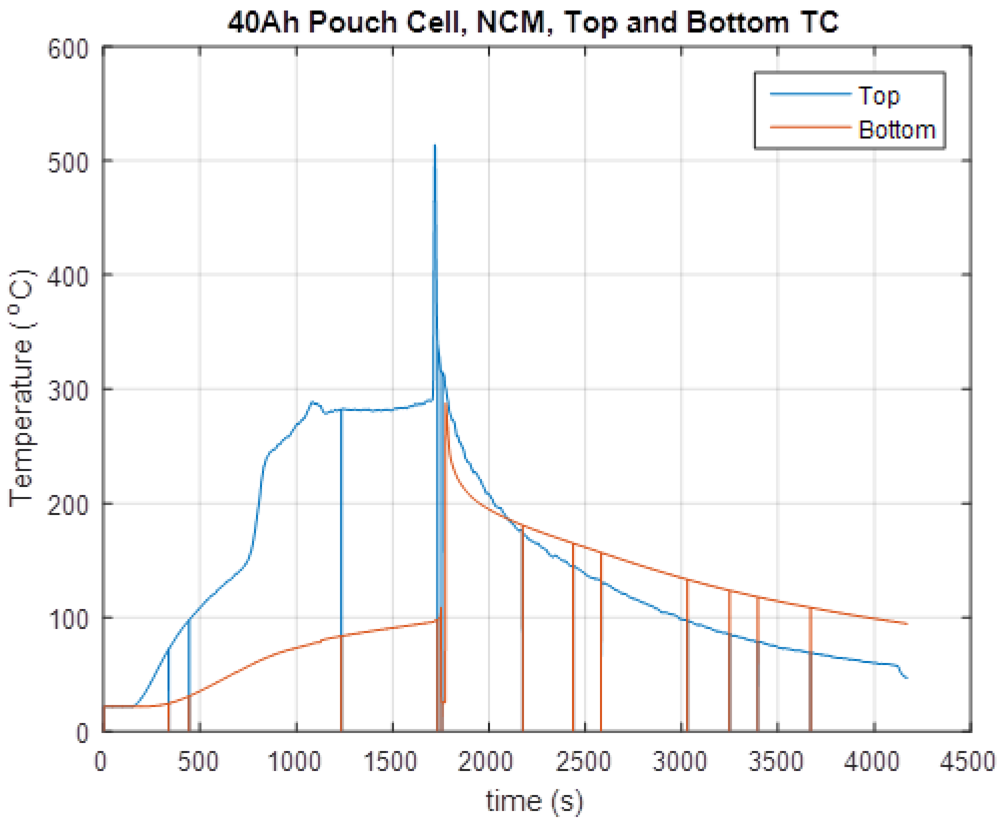


**Figure 12** Battery cell temperatures above and below the cell during Stat-X extinguishing.

The greater thermal mass of the 75 Ah NCM Li-ion cell exhibited similar behaviors with larger numbers overall. The testing in Figure 13 shows that the battery failure peaked at 400-450ºC. The deployment of Stat-X demonstrated about 50-75ºC of cooling on the upper surface and the battery did not drop below 150ºC until ~950s (15-16 minutes) after extinguishing. Similarly on the shielded side of the battery, Stat-X extinguishing demonstrated that temperatures remained > 150ºC for 1000s or more.

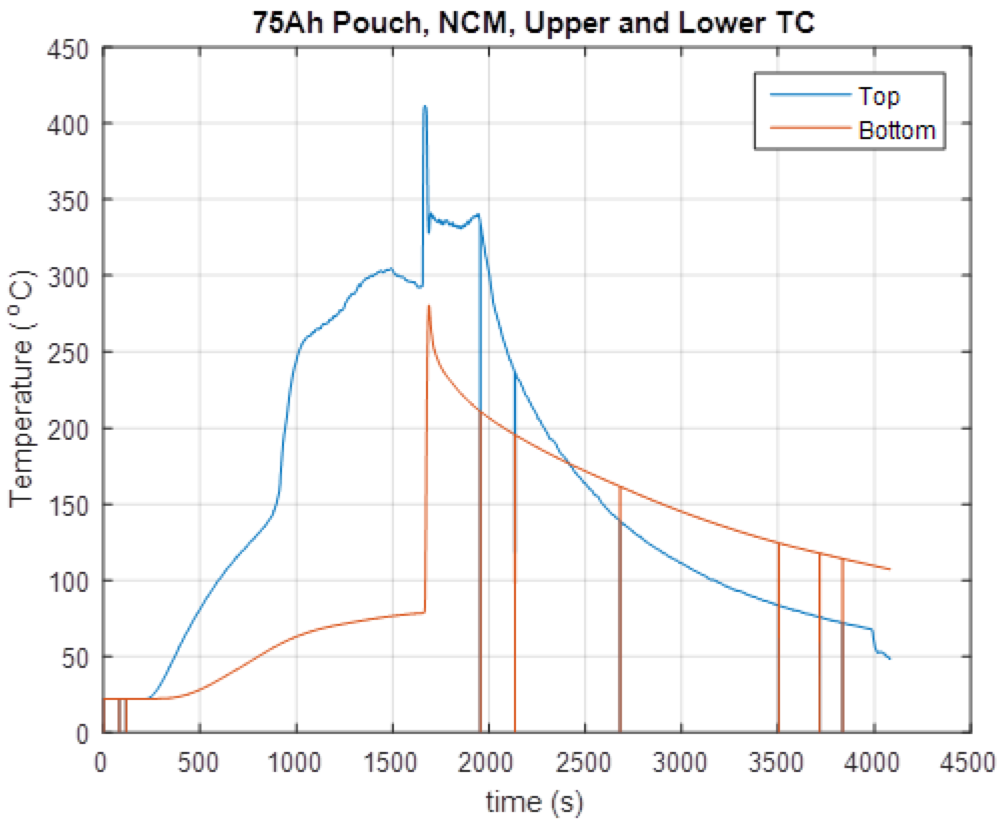


**Figure 13** Stat-X temperature performance for a single 75 Ah NCM Li-ion pouch cell.

In Figure 14 it is shown that during a "stacked" cell test, which is a configuration similar to how cells are integrated into modules in energy storage systems, Stat-X extinguishes the fire and exterior temperatures begin to cool from ~400ºC at a rate of 0.25ºC/min (bottom) to 0.16 ºC/min (top). Also note that the temperature continued to rise on the top surface of the battery after Stat-X deployment, until finally peaking and beginning reduction within 100-200s. The most significant feature of Figure 14, however, is the middle thermocouple behaviour. Even after Stat-X was deployed, temperatures between the cells remained >300ºC for nearly 2000s (33 minutes).

This behaviour is consistent with other findings that DNV GL has made in the Consolidated Edison / NYSERDA BESS program. Even with water extinguishing during full scale module testing, DNV GL observed that the thermal hazard remained between cells, causing un-burned cells to ignite in a delayed cascading phenomenon. This behaviour highlights the challenge of the deep-seated nature of Li-ion battery fires. The cooling behaviour Stat-X vs. water is again demonstrated in Figure 15. However it is also important to point out that the oxygen in the environment is reduced and held below 15% for 600s in the Stat-X case, demonstrating its ability to reduce oxygen to Class A and B fires in a stagnant environment. It should be pointed out that the water extinguishing case was performed in an actively ventilated environment.

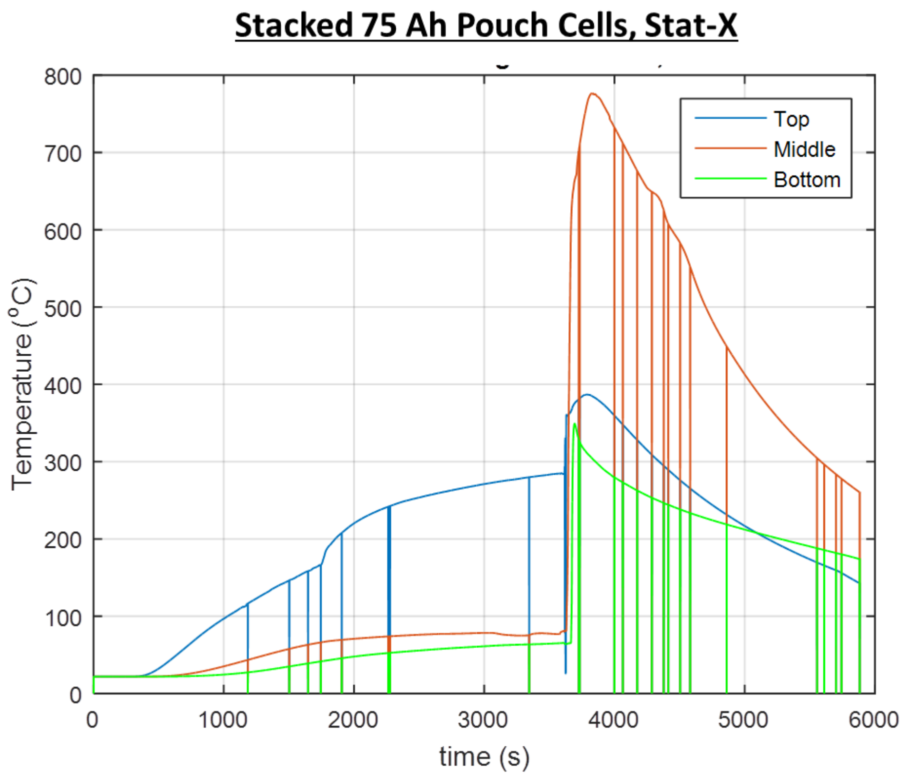


**Figure 14** Results from stacked cell test, 75 Ah NCM Li-ion pouch cells.

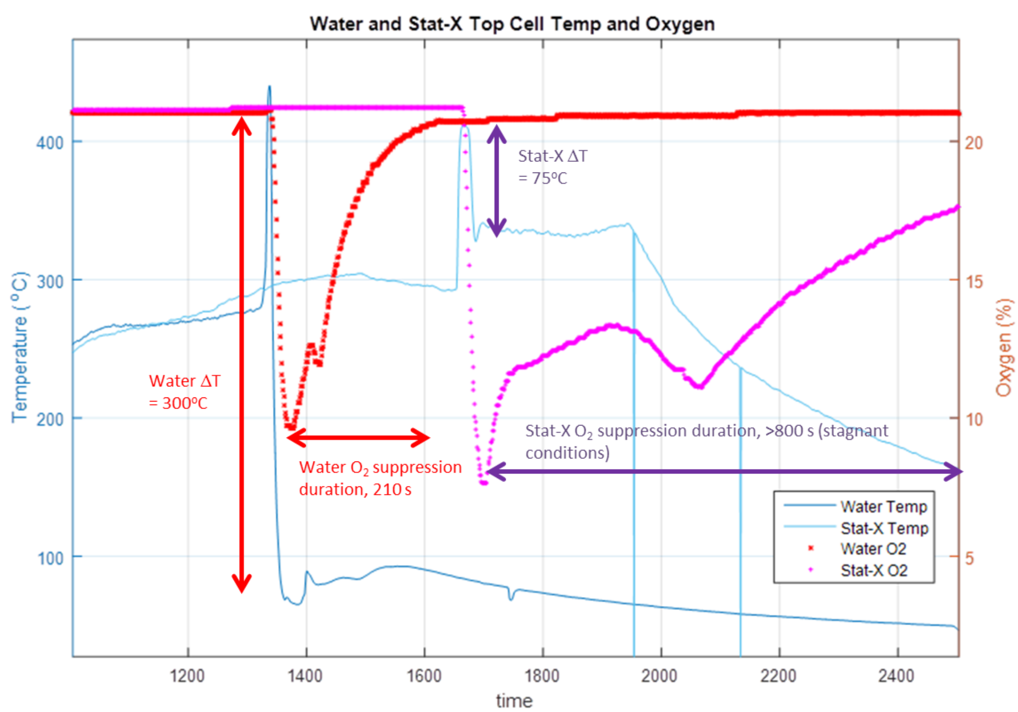


**Figure 15** Water vs. Stat-X in cooling capability and oxygen suppression for the 75 Ah NCM Li-ion cell.

## 2.3 Gas Analysis

In nearly all of the Li-ion battery testing in the Consolidated Edison /NYSERDA BESS program, toxic and flammable gas species were detected. In particular, gases common across chemistries were CO, HCl, HF, and HCN. In the Stat-X testing, DNV GL benchmarked Stat-X against other extinguishers for CO, HF, and HCl. The calibration detection limit for the FTIR unit for the gases were as follows:

- HF = 500 ppm
- HCl = 100 ppm
- CO = 2000 ppm

In the figures below, if the time-series plot of gases reflects concentrations higher than these values, it is highly likely that the gases were present at or near these levels, however the linear calibration grows increasingly non-linear above these values. Therefore it is only possible to say with confidence that the concentration was at or above this value from the testing.

It is important to note that the Stat-X suppression tests had one significant difference in their execution than all other cell tests. The test chamber had active ventilation in all cell tests, yet the Stat-X tests did not. This was intentional, as the Stat-X product is designed to suppress a static environment in order to give the aerosol time to work. Therefore, it is difficult to state whether the use of Stat-X increases or decreases the presence of some gases because the ventilation conditions were different.

In Figure 16 it is shown that the typical residence time of CO in the chamber after destructive testing of the 75 Ah NCM Li-ion cell is about 250s, regardless of SOC or whether or not it was extinguished with water. In the case of Stat-X, CO was observed in the chamber for a period of 1200-1500 seconds. Because Stat-X was intentionally deployed in a stagnant environment, this residence time is likely affected. The minimum recommended saturation time for Stat-X in a stagnant environment was 10 minutes[4] (600s). The duration of CO detection is greater in the two-cell tests and this may be attributed to greater cell mass and therefore reaction mass. No flashovers were observed in the chamber after the deployment of Stat-X.

[4] According to Fireaway Inc.

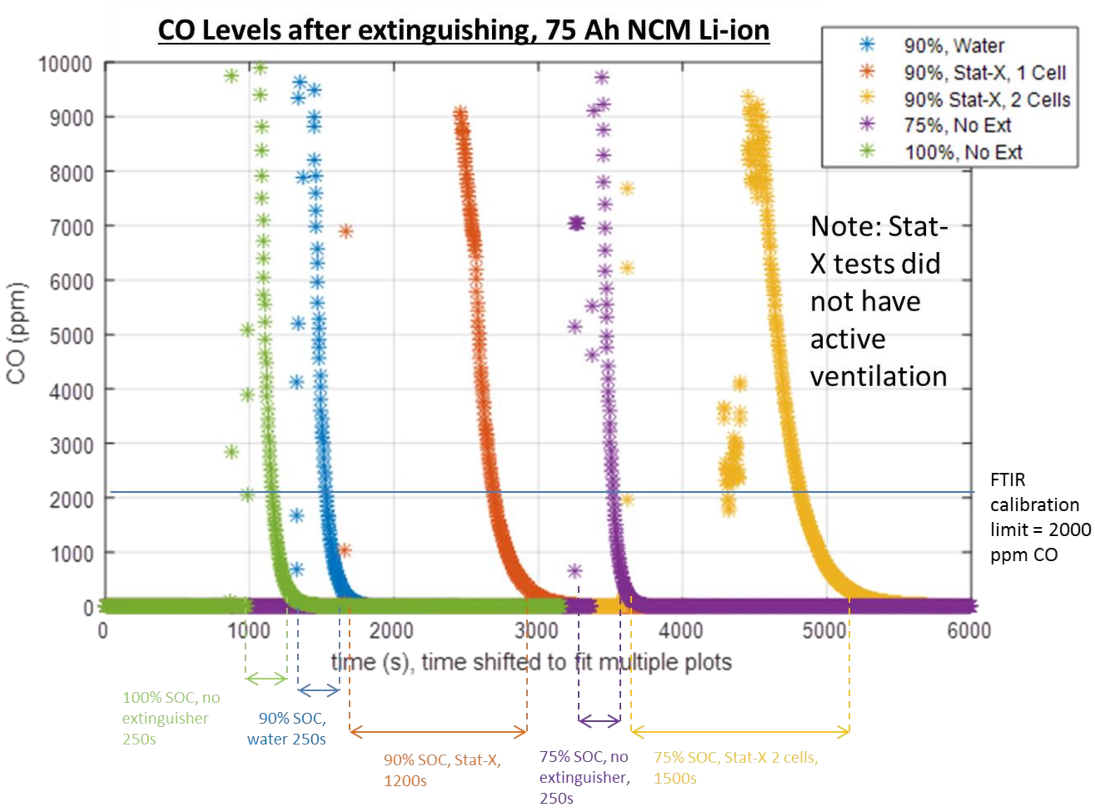


**Figure 16** CO levels after extinguishing for several tests on the 75 Ah NCM Li-ion cell.

In DNV GL's extinguisher tests for the Consolidated Edison testing program, HF was present with and without extinguishing for all of the 75 Ah NCM Li-ion cell tests. The duration of HF residence time in the chamber for Stat-X testing is ~1000s, likely due to reduced ventilation. All cell testing tests demonstrated HF values > 500 ppm. HCl is present in all tests and the duration is 250s or greater for the Stat-X case. In all tests, HCl exceeded the 100 ppm calibration threshold.

# 3 CONCLUSIONS

The following conclusions can be made from testing of the Stat-x product.

- Stat-X can put out a Li-ion battery fire.
- Stat-X can reduce oxygen in an enclosed environment during a battery fire.
- No flashovers were observed in the test chamber after the deployment of Stat-X
- Extinguishers of any type are challenged by the deep-seated nature of Li-ion battery fire and will remove heat from the interior of battery stacks more slowly than the exterior.
- The residence time of gases during Stat-X deployment is a function of when the atmosphere is ventilated.
- CO, HF, and HCl are present during Stat-X extinguishing but their concentrations were not increased as a result of using the aerosol.

Stat-X performed equivalently to other extinguishers in the following ways:

- The fire was extinguished
- CO, HF, and HCl remained in the environment after extinguishing

## 3.1 Relation to the Larger Con Ed / NYSERDA BESS Scope

DNV GL’s findings in the Con Ed / NYSERDA scope are overall challenged to resolve technical issues concerning the following:

- Battery fires are emitting both flammable and toxic gases simultaneously, and therefore ventilation is a key control metric that should be controlled throughout the battery burn
- The deep seated nature of battery fires creates extinguishing challenges for all extinguisher types

DNV GL is tentatively recommending that staged extinguishing be investigated, such that gas-type or aerosol extinguishers are deployed as a line of first defense against a battery failure. The industry has effectively already adopted this solution. However, battery system integrators have confused first responders by claiming that gas-based fixed suppression agents can extinguish and cool the fire; Figure 14 demonstrates that deep seated heat sources will not cool as rapidly as exterior faces.

However, it is also the case that first responders may over-prescribe water extinguishing for battery fires, thereby creating two problems: 1) Excessive system integration costs, 2) potential perpetuation of the battery fire by additional cell shorting, and 3) unnecessary collateral damage to systems when single cell fires could be managed with gas-based or aerosol agents.

Tentatively, a solution which is a hybrid of both aerosol or clean agent + water extinguishing may be required. This strategy may also include sensor-activated ventilation controls which ramp up or ramp down ventilation depending on cell temperatures, whether or not an aerosol or clean agent extinguisher has been deployed, or the composition of the smoke. This may move the industry toward integrated fire suppression solutions that rely on information from the battery management system (BMS). As a line of last defense, a parallel water connection allowing water to deploy inside battery rooms via the existing clean agent or aerosol pipe network may provide first responders a means to deploy water for its cooling efficacy when the battery system is already aflame and likely a total loss.

# 4 RECOMMENDATIONS

To position itself for likely upcoming requirements in the New York market, Fireaway Inc. may consider further testing or analysis to resolve some of the challenges illuminated in this report.

- Test against extinguishers in equivalent ventilation conditions to more equivalently compare the duration of CO, HF, or HCl residence in the enclosed environment, and confirm the oxygen reduction effect of Stat-X.
- Examine the efficacy of Stat-X when used in tandem with water or water-based extinguishers in simulated staged extinguishing approaches.
- Module- or system level testing to demonstrate the efficacy of using Stat-X as a replacement or delay for active ventilation.

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