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William J. Hughes Technical Center
Aviation Research Division
Atlantic City International Airport
New Jersey 08405

Extinguishment of Lithium-Ion and Lithium-Metal Battery Fires

January 2014

Final Report

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16. Abstract

Lithium-metal and lithium-ion batteries power many consumer electronic devices. There have been incidents in which lithium batteries have overheated, creating either a fire, an explosion, or both. Federal Aviation Administration tests have shown that when a single cell in a battery pack undergoes thermal runaway, its heat causes adjacent cells to do likewise. The propagation of thermal runaway can be prevented and the resultant fire extinguished if the correct extinguishing agent is used.

The objective of this study was to compare the effectiveness of fire extinguishing agents for suppressing lithium-metal and lithium-ion battery fires and preventing thermal runaway propagation.

Tests were performed in a 64-cubic-foot test chamber with a sealable door. First, quantitative tests were done to compare the capacity of extinguishing agents to cool a hot plate; water and other aqueous extinguishing agents were the most effective coolants and nonaqueous agents were the least effective. Next, qualitative demonstration tests were performed with lithium batteries to verify the hot plate results. These tests also showed that aqueous extinguishing agents were most effective.

The lithium-metal cells showed various behaviors while in thermal runaway, such as the creation of alternate vent holes and the ejection of internal contents. The hazards of lithium-metal cells in thermal runaway varied significantly during replicate tests.

Extinguishing agents that contained water were the most effective and their effectiveness increased with greater volumes. The gaseous streaming agents were less effective and exhibited a relatively small increase in effectiveness with increased volume.

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mAh	Milliamp hour
kJ	Kilojoules
T	Temperature
FAA	Federal Aviation Administration

EXECUTIVE SUMMARY

Lithium-metal and lithium-ion batteries power many consumer electronic devices. There have been incidents in which lithium batteries have overheated, creating either a fire, an explosion, or both. Federal Aviation Administration tests have shown that when a single cell in a battery pack undergoes thermal runaway, its heat causes adjacent cells to do likewise. The propagation of thermal runaway can be prevented and the resultant fire extinguished if the correct extinguishing agent is used.

The objective of this study was to compare the effectiveness of fire extinguishing agents for suppressing lithium-metal and lithium-ion battery fires and preventing thermal runaway propagation.

Tests were performed in a 64-cubic-foot test chamber with a sealable door. First, quantitative tests were done to compare the capacities of extinguishing agents to cool a hot plate. The effectiveness of the agent's ability to cool was quantified by calculating the average temperature drop. Water and other aqueous extinguishing agents were the most effective and nonaqueous agents were the least effective. Next, qualitative demonstration tests were performed with lithium batteries to verify the hot plate results. These tests also showed that aqueous extinguishing agents were most effective.

There was a significant variation in the behavior of thermal runaway among various lithium-metal cells. The cells would usually do one of the following: vent from melted holes in the cell, leak plastic and lithium, or eject their contents. The hazards of lithium-metal cells in thermal runaway varied significantly during replicate tests.

The tests showed that the extinguishing agents that contained water were the most effective and their effectiveness increased with greater volumes. The streamed agents were less effective and exhibited a smaller increase in effectiveness with increased volume.

1. INTRODUCTION.

1.1 OBJECTIVE.

The objective of this study was to quantify the cooling effectiveness of various fire extinguishing agents and to verify the effectiveness with lithium-metal and lithium-ion battery fires.

1.2 BACKGROUND.

Today, many electronic devices are powered by lithium-metal and lithium-ion batteries. Occasionally, the batteries undergo thermal runaway and cause fire, explosion, and other hazards. If a lithium battery fire should occur in an electronic device in an aircraft cabin, it is important to quickly extinguish the fire and cool the batteries to minimize safety risks. Attempts to minimize these risks have been carried out by the Federal Aviation Administration (FAA) and other organizations.

In 2009, the FAA issued a Safety Alert for Operators based on experiments conducted to determine effective means of extinguishing a lithium battery fire in a portable electronic device. It was determined that two critical steps are required to extinguish a lithium battery fire in a portable electronic device and to prevent reignition. They are:

1. Use a Halon, Halon replacement, or water extinguisher to extinguish the fire and prevent its spread to additional flammable materials.

2. After extinguishing the fire, douse the device with water or other nonalcoholic liquids available in the cabin to cool the device and prevent additional battery cells from reaching thermal runaway.

The FAA also warned against handling the device and smothering it with an insulative material. More information, including a training video, can be found at www.fire.tc.faa.gov [1].

1.3 LITHIUM BATTERIES.

There are three common types of lithium batteries or cells: lithium-metal, lithium-ion, and lithium-ion-polymer. Lithium-metal cells are discharged once, then must be disposed of; they can be found in such items as cameras, watches, and cardiac pacemakers. Lithium-ion cells are rechargeable and are typically found in laptop computers or electronic devices. Finally, rechargeable lithium-ion-polymer cells are typically found in computer tablets and smart phones and differ from lithium-ion cells only in their geometry and outer-case material. For extinguishment purposes, lithium-ion and lithium-ion-polymer cells may be considered identical because they have similar heat-release characteristics.

Thermal runaway in a lithium cell occurs when internal heating is greater than the rate at which heat leaves, resulting in the runaway of internal temperature rise. When a cell undergoes thermal runaway, the increased temperature of the cell causes an internal pressure rise. The continuous pressure rise may eventually cause the cell to expel its contents rapidly and, sometimes, explode.

When lithium-metal and lithium-ion cells go into thermal runaway, the high temperature of the cells and the combustion of the ejected electrolyte and lithium (in the case of lithium-metal cells) may cause burns to people, property, or both.

The most important characteristic of a fire extinguishing agent when extinguishing a lithium battery fire is its ability to cool—in part, because cooling the cell helps to prevent the internal flammable contents from igniting. However, in a realistic lithium battery fire, there are flames present that also need to be extinguished.

Adequate cooling is also required to prevent cell-to-cell propagation of thermal runaway. Propagation of thermal runaway occurs when a cell in thermal runaway heats an adjacent cell and causes it to react and experience thermal runaway as well. The chain reaction could make a series of cells become progressively hotter and more difficult to extinguish.

Further difficulties may be experienced when attempting to control a lithium battery fire in a portable electronic device. When a battery goes into thermal runaway, it is more often the battery casing of an electronic device that gets doused with the extinguishing agent rather than the individual cells. Additionally, the electronic device may be in an inconvenient location or position for direct application of the agent. These challenges may create a need to use more agent than would have been necessary under different conditions.

1.4 EXTINGUISHING AGENTS.

There are many fire extinguishing agents, each with unique characteristics, available for use. Each agent interferes with at least one of the three main requirements for the sustainability of a typical fire: heat, oxygen, and fuel.

Water is the simplest agent and is effective because of its ability to remove heat. Some agents, such as NFS LLC's Hartindo AF-21, AF-31, and Aqueous A-B-D, are water-based and incorporate an additive to cause the water solution to behave differently than water alone.

A class of gaseous fire extinguishing agents called "clean agents" evaporate completely and, therefore, leave a clean dispersion area without any residue. However, gaseous agents have only a limited capacity to cool compared to aqueous agents. Nonconducting clean agents are generally preferable for electrical fires, for which it is necessary to prevent a short circuit or other electrical malfunctions.

Lithium-ion cells do not contain metallic lithium, but lithium-metal cells do. Because water reacts with lithium and many extinguishing agents are aqueous, it is important to know the severity of the reaction. Lithium reacts with water, according to equation 1. The total potential energy release that would result from the reaction of all the lithium in a 1500 milliamp hour (mAh) cell with water is approximately 14.39 kilojoules (kJ), assuming there are .3 grams of lithium per amp hour [2]. This may be considered low when compared to the heat capacity of water (4.1855 kJ/(liter °C)). Additionally, much of the lithium is not exposed to the water because it remains within the steel battery shell.

$$Li + H_2O \rightarrow LiOH + .5H_2 \qquad H(rxn) = 31.98 \text{ kJ/gram [3]} \qquad (1)$$

where H(*rxn*) is the heat of the reaction.

Lithium is known to react relatively slowly with water when compared to other group 1 elements [4]. Figure 1 shows the amount of time necessary for the lithium in a 1500mAh cell to react with water at atmospheric pressure. The original equation for the reaction rate of lithium and water [4] was modified to account for the available surface area of the lithium coil (.0116 m^2) within a 123a lithium-metal cell. The result is given in equation 2, which also assumes that the mass of lithium is .45g and that atmospheric pressure is 760 torr. The reaction (*rate*) is measured in grams/sec and temperature (*T*) is measured in Celsius. The plot shows that, at a temperature of 100°C, the shortest reaction time would be 17 seconds if all contents were instantly exposed to water.

$$rate = .001342 * exp\left(\frac{1.8951 - 1011.4}{T + 273} + 2.092 \cdot \left(log \frac{P}{50}\right)\right) \qquad (2)$$

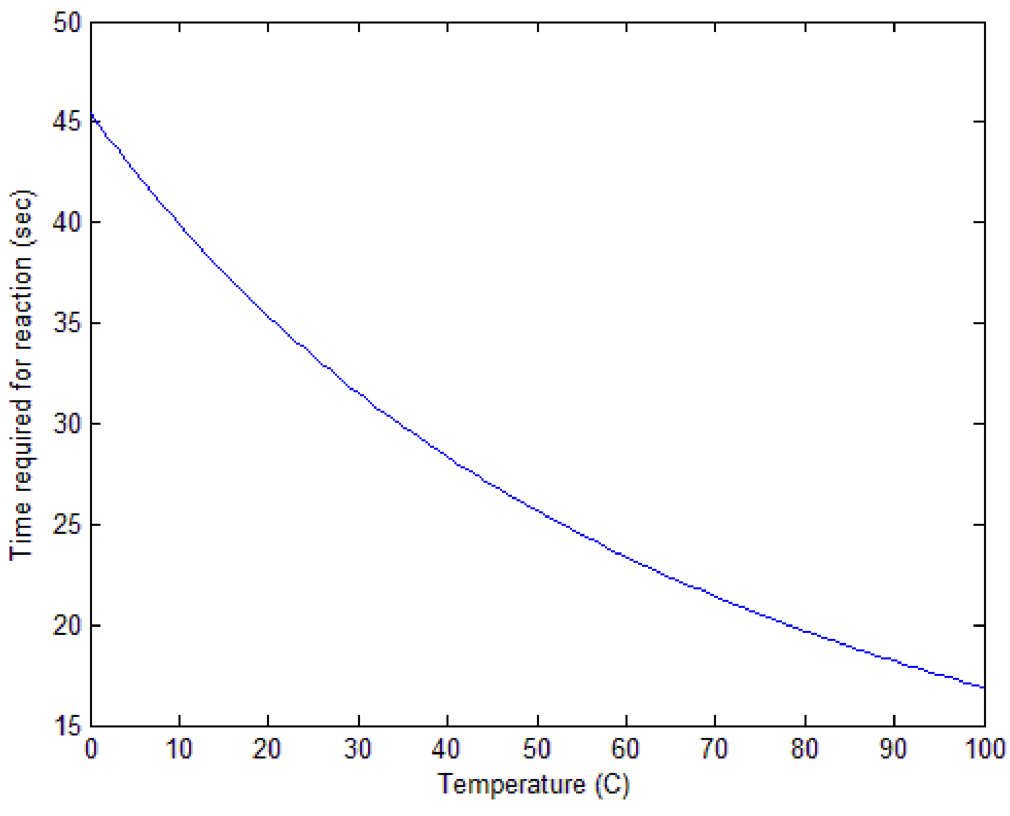

Figure 1. Approximate Time for Lithium in a 123a 1500mAh Cell to React With Water

<u>2. SETUP</u>.

All tests were conducted within a 4 ft x 4 ft x 4 ft steel test chamber with a clear plastic sealable door for viewing (figure 2).

Figure 2. Test Chamber

2.1 HOT PLATE TESTS.

The hot plate test setup consisted of five type-K thermocouples embedded within a quarter-inch aluminum plate. The plate had dimensions of 7 1/2 in. x 7 1/2 in. and rested on a 750-watt hot plate (figure 3). The agent was introduced to the aluminum plate from above through a 1/4-in. copper tube that was connected to a glass funnel. There was an additional section of 1/4-in. tube that was reduced to 1/8 in. and then converted back to 1/4 in. to reduce the flow rate for less viscous liquid agents. The plate configuration was placed within the steel test box and remained fixed for the duration of the tests. The extinguishing agents that were tested with the hot plate were water, AF-31, NFS LLC's Hartindo AF-21, A-B-D agent, Novec™ 1230, Halon 1211, Dupont™ FM-200®, Halotron I, Dupont™ FE-36™, and Purple-K.

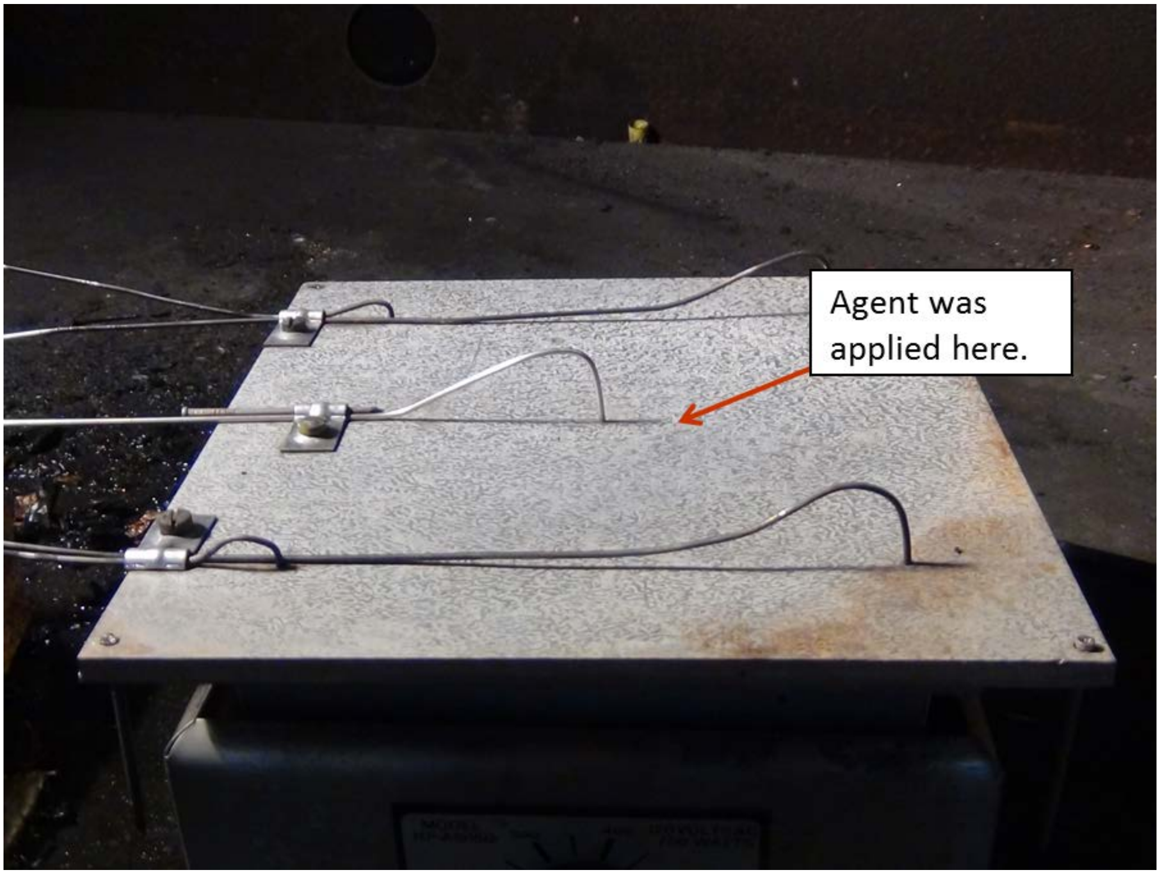

Figure 3. Hot Plate With Embedded Thermocouples

2.2 BATTERY TESTS.

Five 2600mAh 18650 lithium-ion cells that were charged to 50% capacity (1300mAh) were used for the verification/demonstration tests. Five 1500mAh 123a lithium-metal cells at full capacity were also used.

In the test setup, the cells were each secured with nichrome wire to an ungrounded type-K thermocouple. The five cells were placed side-by-side with a 100-watt cartridge heater on the end and wired together. The configuration was then placed in a steel holder lined with 1/2-inch thick Kaowool® insulation (figure 4).

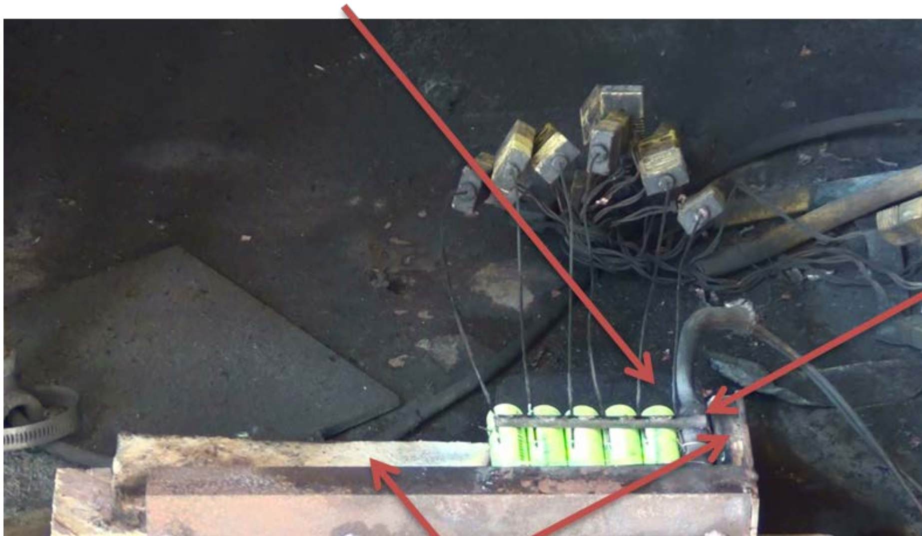

Figure 4. Setup for Propagation Tests

The test setup had a 1-in.-National Pipe Thread pipe cap filled with hexane in front of the first cell. The hexane was ignited before the first cell vented and created an ignition source for the materials ejected from the cells.

The following agents were liquid at room temperature and pressure: water, Novec 1230, AF-21, AF-31, and A-B-D agent. Each agent was poured by hand from a 500 mL water bottle. Other agents that were discharged from a portable fire extinguisher from the distance specified on the extinguisher included Halon 1211, Halotron I, FE-36, FM-200 CO_2, and Purple-K. The target quantity of the streaming agents was predetermined and was calculated from the capacity and discharge time of the extinguisher for which it contained. For example, if 500 mL of agent were required for a test and the extinguisher was designed to discharge 1000 mL in 10 seconds, then the required discharge time for the test was 5 seconds.

2.3 DATA PROCESSING.

Data were collected with Iotech™ PDaq 56 hardware and software created on site. The data were processed in MATLAB®.

2.3.1 Hot Plate Tests.

A calculated average temperature decrease, T_d, was the main parameter used to quantify the cooling effectiveness of the agents. The T_d was the average initial temperature of the five thermocouples minus the average temperature of the five thermocouples over the next 100 seconds. This was represented by equation 2, where T_i was the temperature of the i^{th} cell and $T_{i,j}$ was the temperature of the i^{th} cell at the j^{th} time interval after dispersion of the agent. The calculation of T_d is shown in figure 5; the test results are shown in figure 6 with T_d on the *y*-axis and the volume of agent on the *x*-axis.

$$T_d = \frac{\sum_{i=1}^{5} T_{i,time=0}}{5} - \frac{\sum_{j=1}^{100}\sum_{i=1}^{5} T_{i,j}}{500} \qquad (2)$$

When more than one test was performed with a specific agent and volume, the average value of T_d was plotted with error bars of 5% uncertainty.

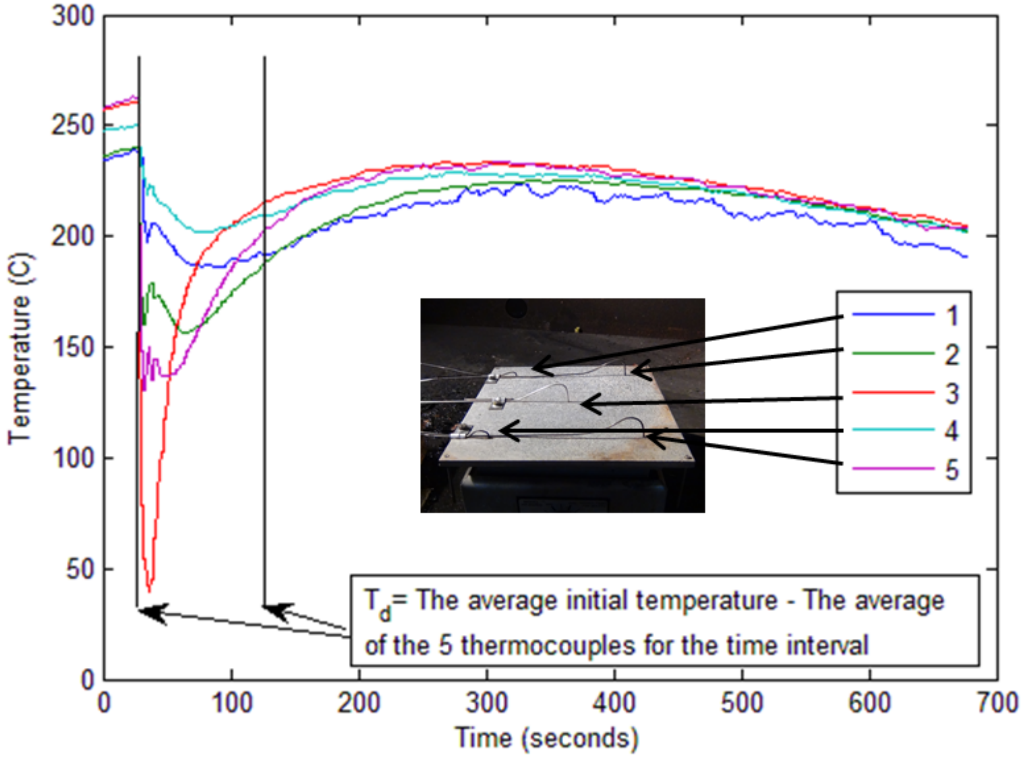

Figure 5. Illustration of T_d Calculation

3. EXPERIMENTS.

Tests were conducted to study the effect of various extinguishing agents on the thermal runaway of lithium-metal and lithium-ion batteries. First, tests were conducted to study and compare the cooling effectiveness of various agents on a hot plate. Five agents were poured onto the plate and five were discharged from an extinguisher. Next, fixed amounts of the same agents were applied to lithium-metal and lithium-ion cells induced into thermal runaway to further demonstrate effectiveness. Table 1 shows the tests performed.

Table 1. Tests Performed

	Hot Plate	Lithium-Ion	Lithium-Metal
Baseline (no agent)	X4	X4	X7
100 mL water	X5		
100 mL Aqueous A-B-D agent	X2		
100 mL AF-21	X1		
100 mL AF-31	X2		
100 mL Novec 1230	X3		
175 mL water	X3		
175 mL Aqueous A-B-D agent	X1		
250 mL water	X6		
250 mL Aqueous A-B-D agent	X2		
250 mL AF-21	X1		
250 mL AF-31	X2		
250 mL Novec 1230	X3		
500 mL water		X3	X1
500 mL Aqueous A-B-D agent		X3	X1
500 mL AF-21		X3	X1
500 mL AF-31		X2	X1
500 mL Novec 1230		X3	X1
Halon 1211 with various volumes	X4	X2	X1
FM-200 with various volumes	X2	X2	X2
Halotron I with various volumes	X3	X2	X2
FE-36 with various volumes	X2	X1	X2
Purple-K with various volumes	X1	X2	X1
CO2 with various volumes		X2	

3.1 HOT PLATE TESTS.

First, hot plate tests were performed to rank the cooling effectiveness of various agents when applied to a hot plate. The hot plate was representative of an overheated tablet or laptop and was also chosen for its simplicity and its capacity to easily perform repeatable tests.

3.1.1 Experimental Procedure.

The predetermined quantity of extinguishing agent was poured into the funnel apparatus. Next, the hot plate was plugged in and data collection began. When the center thermocouple reached 160°C, the hot plate was turned off and the agent was released. Data collection resumed for a sufficient amount of time (approximately 10 minutes) to further observe the trend of the temperature profile.

3.1.2 Results and Discussion.

Figure 6 is a plot of the resulting calculated average temperature drop for the agents tested. As shown, the aqueous extinguishing agents had a greater cooling effectiveness. As the volume of aqueous agent increased, the temperature drop also increased. For a fixed amount of aqueous agent, the slower flow rates showed greater cooling to the plate. The cooling effectiveness of the nonaqueous agents, which was minimal, increased less with an increase in volume. Figure 7 shows images of the dispersion of each agent.

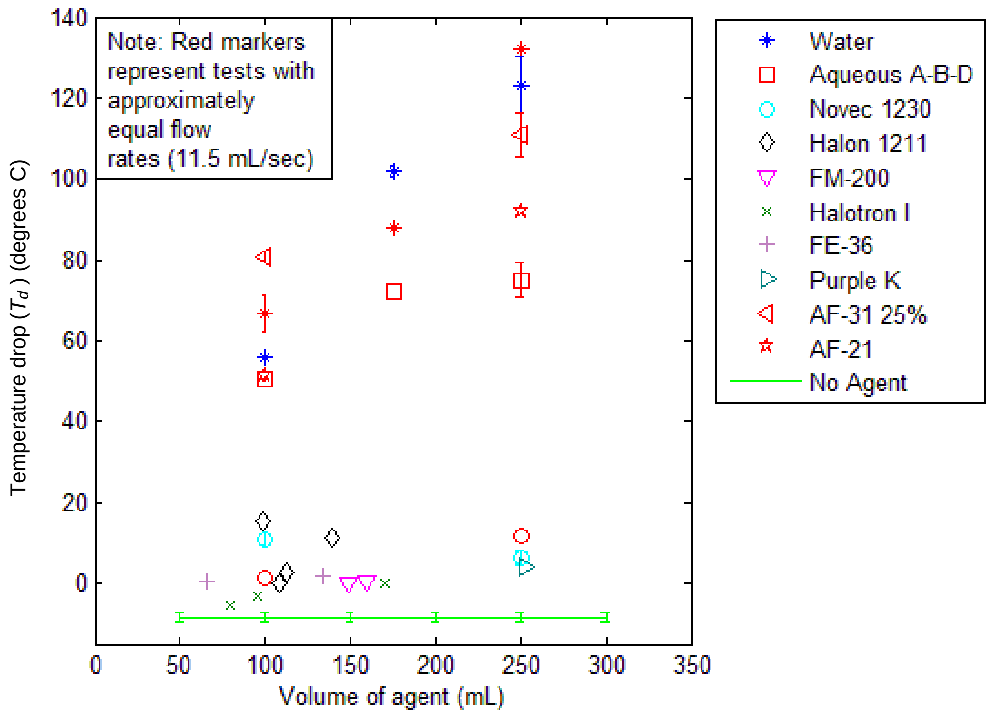

Figure 6. Temperature Drop vs. Volume for Various Agents

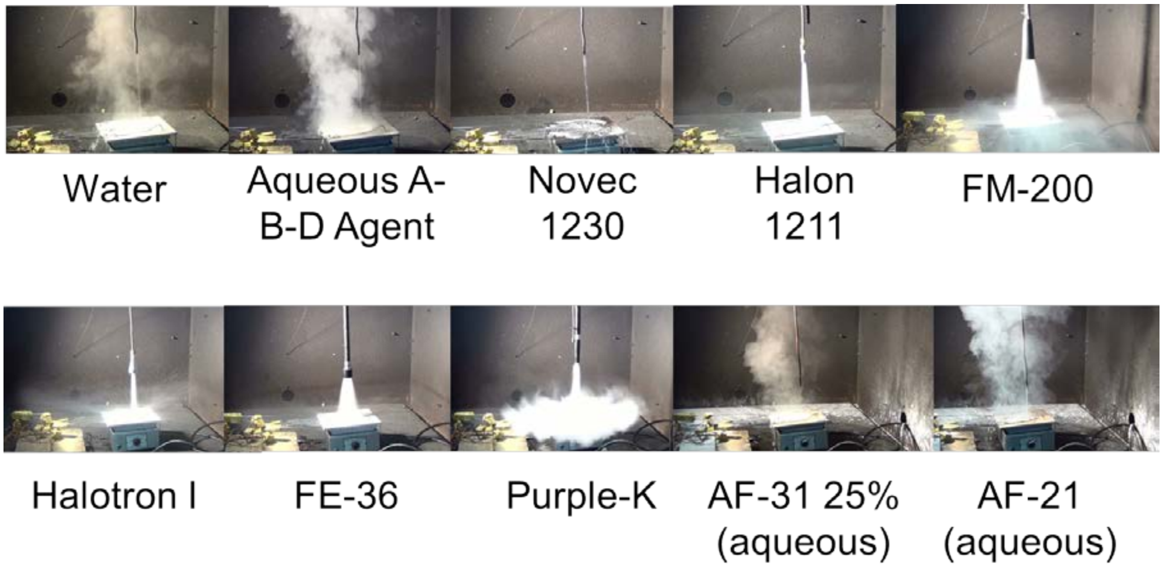

Figure 7. Dispersion of Various Streaming Agents

3.2 BATTERY VERIFICATION TESTS.

Propagation tests were performed initially to ensure that cells would fully propagate without the presence of an extinguishing agent. Tests were then performed to verify and demonstrate the agents' cooling effectiveness, previously found in the hot plate tests, with lithium-metal and lithium-ion cells in thermal runaway. The tests were similar to the extinguishment of a laptop battery or the battery of a small portable device in thermal runaway, although, during the tests, the batteries were directly exposed to the agent instead of being enclosed in a battery case.

3.2.1 Experimental Procedure.

The cartridge heater was turned on and data collection and camera recording began. The hexane was ignited when the first cell reached a temperature of about 100°C. After the first cell underwent thermal runaway, the extinguishing agent was applied by hand from the 500 mL water bottle for the aqueous agents and Novec 1230, and from a fire extinguisher for the streaming agents. The heater was then turned off and data collection continued for approximately 20 minutes.

3.2.2 Results.

Table 2 shows results for the lithium-ion and lithium-metal extinguishment tests. As shown, there were two cases observed: either all of the cells propagated or none of the cells propagated. In these tests, if a cell exploded, the remaining cells were not included as part of the series because the explosion, not the agent, generally stopped the propagation.

Table 2. Lithium and Lithium-Ion Battery Test Results

Test Number	Agent	Cell Chemistry	All of the Cells Propagated	None of the Cells Propagated
1-4	No agent	Lithium-Ion	X	
5	Water	Lithium-Ion		X
6	Water	Lithium-Ion		X
7	Water	Lithium-Ion		X
8	Aqueous A-B-D	Lithium-Ion		X
9	Aqueous A-B-D	Lithium-Ion		X
10	Aqueous A-B-D	Lithium-Ion		X
11	AF-21	Lithium-Ion		X
12	AF-21	Lithium-Ion		X
13	AF-21	Lithium-Ion		X
14	AF-31	Lithium-Ion		X
15	AF-31	Lithium-Ion		X
16	Novec 1230	Lithium-Ion		X
17	Novec 1230	Lithium-Ion		X
18	Novec 1230	Lithium-Ion		X
19	Halon 1211	Lithium-Ion	X	
20	Halon 1211	Lithium-Ion	X	
21	FM-200	Lithium-Ion	X	
22	FM-200	Lithium-Ion	X	
23	Halotron I	Lithium-Ion	X	
24	Halotron I	Lithium-Ion	X	
25	FE-36	Lithium-Ion	X	
26	Purple-K	Lithium-Ion	X	
27	Purple-K	Lithium-Ion	X	
28	CO2	Lithium-Ion	X	
29	CO2	Lithium-Ion	X	
30-36	No agent	Lithium-Metal	X	
37	Water	Lithium-Metal		X
38	Aqueous A-B-D	Lithium-Metal		X
39	AF-21	Lithium-Metal		X
40	AF-31	Lithium-Metal		X
41	Novec 1230	Lithium-Metal		X
42	Halon 1211	Lithium-Metal		X
43	FM-200	Lithium-Metal		X
44	FM-200	Lithium-Metal		X
45	Halotron I	Lithium-Metal		X
46	Halotron I	Lithium-Metal	X	
47	FE-36	Lithium-Metal		X
48	FE-36	Lithium-Metal	X	
49	Purple-K	Lithium-Metal	X	

3.2.3 Lithium-Ion (18650) Results and Discussion.

The initial baseline tests showed that all cells would proceed into thermal runaway without suppression. To stop propagation, 500 mL of each aqueous agent were sufficient. None of the streamed nonaqueous agents stopped propagation. As shown by the dips in temperature in figure 8, a typical aqueous agent cooled far more than a typical nonaqueous agent. Aqueous agents also remained in contact with the cells longer and absorbed into the Kaowool® insulation, which further reduced the temperature of the cells.

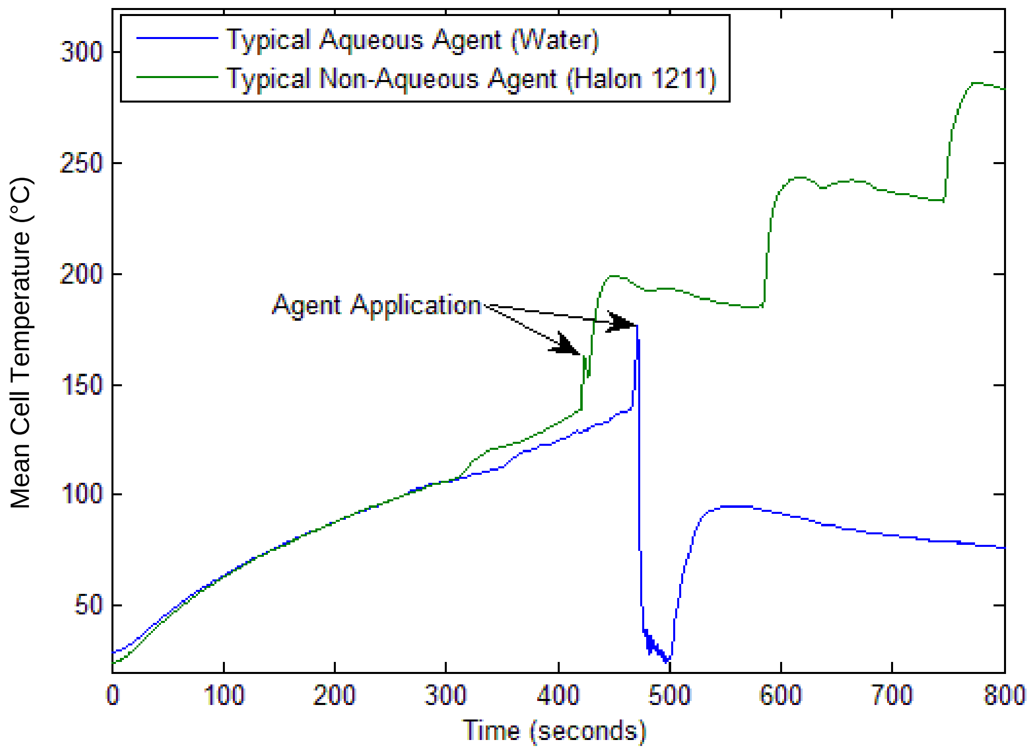

Figure 8. Temperature Plot of a Typical Aqueous Agent and a Typical Nonaqueous Agent

3.2.4 Lithium-Metal (123a) Results and Discussion.

Without suppression, the lithium primary cells completely propagated. This test was repeated and demonstrated seven times, as shown in table 1.

In each of the tests, 500 mL of the aqueous agents were sufficient to stop propagation. There was no apparent visual indication of a reaction between lithium and water, nor was the flame of the hexane flame ignition source intensified. Surprisingly, all of the nonaqueous streaming agents also stopped propagation, except for one test with Halotron I, one test with FE-36, and one test with Purple-K.

The nonaqueous streamed agents were likely more effective at halting propagation for the lithium-metal cells than for the lithium-ion cells because of the lower mass of the lithium-metal cells.

3.2.5 Characteristics of Thermal Runaway in Lithium-Metal Cells.

Figure 9 shows the range of behavior of lithium-metal cells experiencing thermal runaway and the variability of the process. The images are arranged in an approximate order of most common to least common.

1)

Vent holes were in alternate locations.

2)

Cell vented through pre-existing vent holes at the positive terminal.

3)

Internal components were partially ejected.

4)

Internal components were fully ejected.

Figure 9. Lithium-Metal Cells After Thermal Runaway

Most cells in thermal runaway ejected burning lithium droplets. Because the droplets became detached from the cell, they did not contribute to the cell temperature. The amount of lithium and the location from which it was ejected varied. Without suppression, the reacting lithium usually created a hole in the side of the cell for additional lithium and other burning battery components to exit. This also provided an entrance for oxygen and led to further oxidation. The location, size, and quantity of the holes varied and affected the resultant temperature.

The cells sometimes ejected their internal components. The ejection of the hot internal battery components usually caused the remainder of the cell to cool fast enough to halt propagation. Figure 10 shows an example of a full ejection.

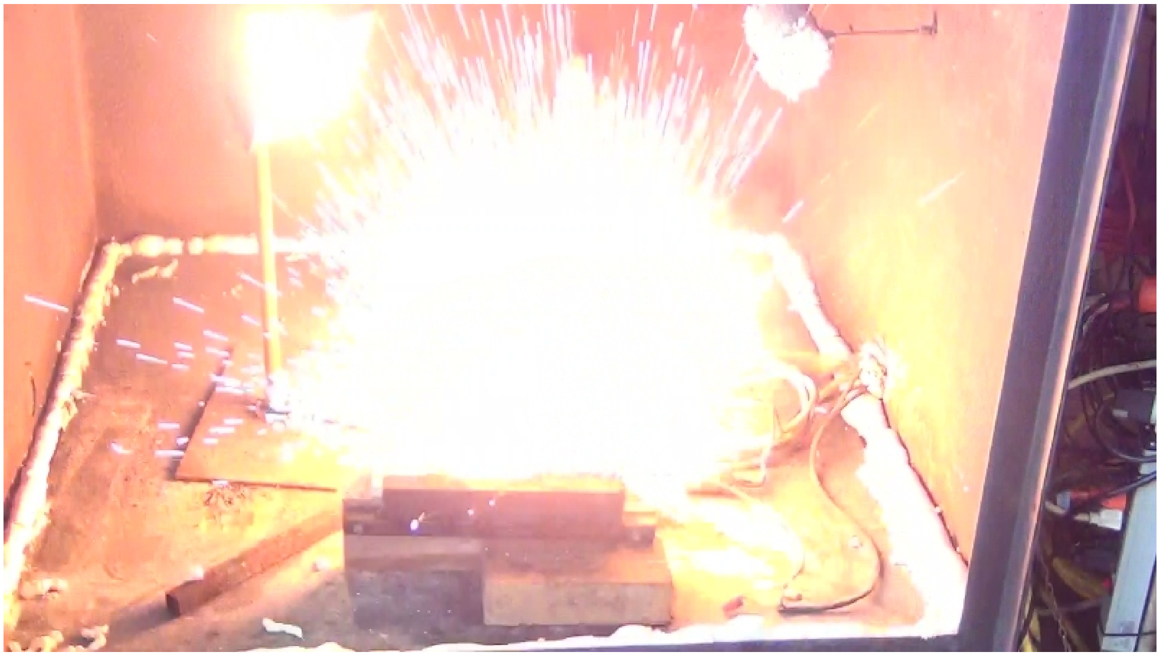

Figure 10. Explosion of a Lithium-Metal 123a Cell

Because the lithium-metal cells displayed a significant variability in thermal runaway events, it was difficult to rank the relative effectiveness of each agent. Therefore, the results are of qualitative effectiveness.

4. CONCLUSIONS.

The hot plate tests and the battery fire tests showed agreement with each other. This showed that the capacity of an extinguishing agent to stop the thermal runaway propagation of lithium batteries may be accurately determined by the cooling effectiveness of the agent.

4.1 HOT PLATE TESTS.

For the hot plate tests with 250 mL of poured agent, the cooling effectiveness from most effective to least effective was as follows: water, AF-31, AF-21, Aqueous A-B-D, Novec 1230.

The streamed agents were far less effective coolants, showed little variability from one to the other, and showed only a small increase in effectiveness with an increase in volume.

4.2 LITHIUM-METAL AND LITHIUM-ION BATTERY TESTS.

The battery verification tests confirmed that aqueous agents were most effective for the prevention of thermal runaway propagation. For the lithium-ion cell chemistries tested, none of the handheld agents at their recommended application distances were able to prevent propagation.

The lithium-metal battery tests revealed that, without suppression, the cells would propagate into thermal runaway. To stop propagation, 500 mL of the aqueous agents were sufficient.

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