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Case Report

Suppression capacity and environmental impact of three extinguishing agents for lithium-ion battery fires

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ABSTRACT

Fire suppression and rapid cooling methods are required to reduce the risk of battery fires. However, the liquid and solid residues generated during fire extinguishing pose a risk to the environment and human health. With the aim of correlating the extinguishing efficiency and environmental impact of the residues, fire tests were carried out on NMC lithium-ion pouch cells using different agents, namely water mist, F-500 water additive 2 % (v/v) and CO_2. The combination of cell temperature measurements and videos allowed the efficiency of the extinguishing agents to be assessed. It was found that the efficiency of the water-based agents was higher than that of the gaseous agents (cooling rate of 30.5 ± 4.9 °C/s for water mist, 36.5 ± 6.4 °C/s for F-500 and 20.0 ± 1.4 °C/s for CO_2). Analysis of solid and liquid residues using gas chromatography and induced coupled plasma showed that the use of F-500 resulted in a higher (one order of magnitude) concentration of VOCs in solid residues compared to the other extinguishing agents. The comparison of these concentrations of VOCs with the limits established for waste (EU Regulation N. 1357/2014) showed that the solid residues did not exceed the concentration limit for classification as hazardous waste. Regarding the concentration of metals, the highest values in the solid and liquid residues are due to Li, Ni and Cu. Based on these values, all solid samples can be classified as carcinogenic and toxic for reproduction. While the concentration of metals in the liquid residues was higher than the limit value that poses a risk to aquatic organisms. The overall results showed the need for site remediation and waste management procedures in the event of a major accident.

1. Introduction

Lithium-ion batteries (LIBs) generate electrical energy through the conversion of chemical energy [1]. Applications can range from portable devices to vehicles, i.e., electric vehicles (EVs), plug-in hybrid electric vehicles (PHEVs), to an accumulation system, i.e., an energy storage system (ESS) [2]. LIBs provide higher energy and power densities than conventional batteries, but recurrent fires highlight the risks of LIBs [3]. In fact, the LIBs must operate within the so-called *safety window*, which is defined by the cell temperature (0–80 °C) and voltage (2–4 V) [4]: operation outside this window results in a rapid degradation of the battery performance, leading to safety issues, such as venting of gases and vapours and the thermal runaway (TR) [5,6]. During TR an undesirable chain of exothermic reactions occurs violently inside the battery, with a high rate of generation of heat and low molecular weight products, which can lead to fire and/or explosion, projection of fragments and emission of toxic gases and vapours [7,8]. Several previous studies have investigated the thermal stability and fire hazards of battery materials [9]. The tests are usually carried out on cells or small-scale LIBs with the aim of investigating the influence of parameters, such as chemical composition, state of charge (SoC) on the fire hazards of LIBs [10,11].

Considerable effort has also been devoted to research efficient fire extinguishing agents for LIBs, but a comprehensive review is still lacking. The basic properties required for an extinguishing agent are: high heat capacity, high wettability, low viscosity, low electrical conductivity, and a positive environmental impact [12]. Extinguishing agents are classified according to their physical state, such as gaseous, water-based,

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dry powder foam and aerosol [12]. The main problems with LIB fires are the high heat release rate (HRR), the rate of reaction, and the complexity of the composition. Therefore, an extinguishing agent applied to a LIB fire must be able to prevent heat propagation between the cells within a module and between modules, such as a coolant, and to inhibit the chemical reactions taking place within the cell, such as an inhibitor [13]. The main agents studied for this scenario are water, microencapsulation technology called F-500, dry powders, Novec and CO_2 [14–16]. Water is the most commonly used extinguishing agent because of its high thermal capacity and latent heat of vaporization. The most commonly used is water mist, with droplet sizes less than 1000 μm and, hence, high surface/volume ratio which determines a high heat absorption due to good penetration into the fire plume and burning material [13]. On the other hand, water can react with the Li salt, (i.e., lithium hexafluorophosphate, $LiPF_6$ used as an electrolyte) to form toxic (i.e., hydrofluoric acid, HF) and flammable (i.e., hydrogen, H_2) substances, and can conduct current, causing an external short circuit in a cell. The encapsulating agent F-500 is a water-based extinguishing agent, is a surfactant and consists of molecules with a hydrophilic and a hydrophobic part, which lead to the formation of micelles capable of encapsulating a variety of liquid, gaseous and solid substances by intensive mixing, which are not flammable in the long term [16]. F-500 forms a protective film on the surface of the water, forming spherical microcapsules that allow rapid cooling, inhibit reactions and prevent the re-ignition [14]. The composition of the liquid phase after extinguishing must be considered from an environmental point of view, as the fuel molecules are absorbed and enveloped by the solution. Dry powders are divided into ABC powder, D powder and BC powders according to the class of fire and have a different composition. The extinguishing mechanism is based on the chemical interruption of the reactions and, due to the small particle size, the powders have a total flood extinguishing capacity, filling the entire space, but only under certain conditions. However, powder agents do not provide cooling, with a high risk of re-ignition [13]. Novec is an environmentally friendly agent that, due to its low boiling point of 49.2 °C, can be effectively evaporated over a wide range of temperatures reducing the CO emissions [15]. However, its cooling efficiency is limited compared to other extinguishing agents. CO_2 as an extinguishing agent replaces the oxygen in the combustion zone with CO_2. It is suitable for electrical fires and leaves no residue. However, the extinguishing effect is limited because CO_2 reduces the surface temperature but not the internal temperature, causing the temperature to rise again in a short time. From the results reported in the literature, it appears that the best class of extinguishing agents currently available for extinguishing LIB fires are water-based agents. The extinguishing efficiency is evaluated taking into account the cooling rate, the re-ignition capacity, the temperatures reached and the amount of extinguishing agent used.

Once the fire has been extinguished, the site can be considered safe in terms of fire hazard. However, a new risk must be assessed, as the gaseous, liquid and solid residues emitted remain at the site and can affect the surrounding environment and human health. The residues that remain after extinguishing are not only the burnt LIBs but also the extinguishing agents. In the case of water-based extinguishing agents, this is a liquid; in the case of foam or powder extinguishing agents, it is a solid. In the case of gaseous extinguishing agents, the release of gases must also be taken into account [17]. The liquid residues can have a major impact on the environment by percolating through the soil and reaching underground aquifers or surface watercourses. It is important to note that even if the extinguishing agent is water-based, it must be considered that during the extinguishing phase, the extinguishing agent comes into contact with the cell materials and their combustion products, with which the extinguishing agent itself may react to form other products. Thus, even water, the most environmentally friendly extinguishing agent, may contain various species, such as volatile organic compounds (VOCs), at the end of the extinguishing process.

The composition of the solid residues, namely the burnt LIBs, differs from that of the initial material due to combustion reactions. It is therefore necessary to analyse the composition of both liquid and solid samples after the application of extinguishing agents and to compare the concentration values of hazardous substances (organic and inorganic) with regulatory limits. Environmental information is of great interest, especially for the post-fire soil management and to prevent risks to human health and aquatic organisms. The characterisation analyses that can be carried out on the samples are standardised by the US Environmental Protection Agency (EPA), while for the classification of waste, both solid and liquid, reference is made to the European Regulation N. 2008/98/EC [18], and the subsequent amendment of the EU Regulation 1375/2014 [19], to which the Italian regulation refers, by the Legislative Decree no. 152 [20].

In the existing literature, the composition of the products generated by the emission during the TR of the LIBs is adequately addressed, as are the discussions on the efficiency of the different extinguishers. It is evident that further research is required to gain a deeper insight into the impact of the extinguishing agent on the products remaining after a fire scenario. This aspect is of paramount importance in order to minimise the impact on the environment and human health both during and after fire events involving large quantities of LIBs, such as ESSs and gigafactories. In light of the aforementioned considerations, the development of an operational procedure for extinguishing the fire and subsequent post-fire soil management in the event of major accidents is of significant importance.

To fill this gap, fire tests were carried out on Kokam lithium-ion pouch cells of different capacities (25 Ah and 40 Ah). The cell temperature and key events during the tests were recorded and then the extinguishing efficiency of three different extinguishing agents, i.e., water mist, F-500 and CO_2, was evaluated. In addition, solid and liquid samples were collected at the end of each test for subsequent analysis to identify and quantify the VOCs and metals, i.e., gas chromatography coupled with flame ionization detector (GC-FID) according to the EPA Method 8015D [21], solid phase microextraction with gas chromatography coupled with mass spectrometry (SPME-GC-MS) according to the EPA 8260D Method [22] and the EPA 5012A Method [23], and inductively coupled plasma – optical emission spectroscopy (ICP-OES) according to the EPA 200.8–1 Method [24]. The final aim is to correlate the efficiency, in terms of cooling rate, and the presence of hazardous compounds in the samples collected after the application of the three extinguishing agents studied, in order to evaluate the possible post-fire soil management.

2. Materials and methods

2.1. Materials

Kokam lithium-ion pouch battery Superior Lithium Polymer Battery (SLPB), shown in Fig. 1, with different capacity, 25 and 40 Ah, were used

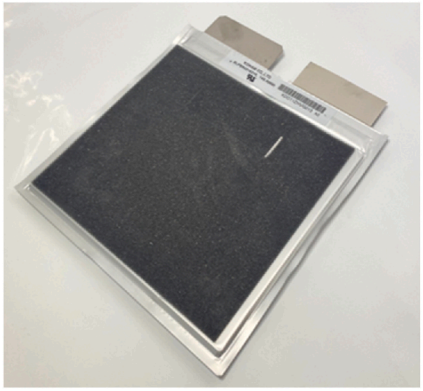

Fig. 1. Kokam SLPM 40 Ah.

for the fire tests. The technical specifications, according to Ref. [25], are reported in Table 1 while the chemical composition of the internal components, expressed in mg of metal per g of the single component, is shown in Table 2.

Before being tested, the cells were loaded using a PS 8000 2U Laboratory Power Supply from Elektro-Automatik. The cells were charged at Constant Current with a maximum voltage limit of 4.2 V, corresponding to the 100 % of SoC.

2.2. Fire tests

The objective of the fire test is to expose a battery to a fire in various ways, such as radiant heat, external fire simulation, or high-temperature hazard [26]. In the present study, the external fire simulation was employed, whereby the cells were directly exposed to the fire generated by a propane burner. The propane bottle had a purity of greater than 95 %, while the ignition source had a power of 7.5 kW. The thermocouples (TCs) selected were the K type, in nickel-chromium-aluminium, which are guaranteed for continuous use in the temperature range between 0 and 1100 °C, with a high temperature tolerance and a high sensitivity.

All the fire tests were carried out according to the following protocol: (i) the cell was placed on a metal grid above the propane burner, (ii) two TCs were fixed to the upper surface of the cell, (iii) the propane flame was lit, (iv) the propane burner was turned off once the cell venting and flame were observed (v) an extinguishing agent was applied for 10 s (i.e., water mist, F-500 and CO_2), after the catastrophic failure of the cell occurred. A metallic tank was positioned below the metal grid to collect the extinguishing agent. Fig. 2 illustrates the test system (a) and the three different extinguishers: water mist (b), F-500 water additive 2 % (v/v) (c) and CO_2 (d). Both the metallic grid and the metallic tank were constructed from inert materials to prevent interference during both the combustion reactions and the sample collection. At the end of each fire test, both surfaces were cleaned to prevent contamination of the sample between the tests.

The test conditions and the relative codes are reported in Table 3. The temperature profile of the cell during the test was obtained by combining the temperature data acquired by the two thermocouples placed on the surface of the cell with the video, recorded by a high-speed camera. The relative times of ignition, venting, fire, catastrophic failure and subsequent extinction were also recorded. At the end of each test, both the solid samples, i.e. the burnt lithium ion cell, and the liquid samples, i.e. the extinguishing agent collected in the tank, were subjected to subsequent analyses in order to determine their chemical composition.

2.3. GC-FID method

The analysis of liquid samples, namely the extinguishing agent collected in the tank after the extinction, was conducted by gas chromatography-flame ionization detection (GC-FID), in accordance with the Environmental Protection Agency (EPA) method 8015D [21], with the objective of identifying and, subsequently, quantifying the BTEX compounds, namely benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene. A PerkinElmer Clarus 500GC with autosampler and coupled with a FID was employed for the analyses. The column utilised was a StabilWax-DA - Restek (30 m length, 0.25 mm i. d., 0.25 μm thickness). For each test 1 mL of liquid sample was aliquoted in 1.5 mL vials, without pre-treatment. A standard solution containing 200 μg/mL of benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene in methanol (BTEX, Restek), was employed as standard to determine the retention time (t_R) of each compound, the calibration line, and the limits of quantification (LOQ) and detection (LOD). The GC-FID analysis method was performed with helium (purity 99.999) as the carrier gas with a flow rate of 1 mL/min. The injector was set at 200 °C and 1.0 μL of sample was injected with a split ratio of 70:1. The analysis involved a programmed temperature profile beginning at 100 °C (2.5 min) and rising to 200 °C (10 min) at a rate of 30 °C/min, for a total run time of about 16 min. The detector was set at a temperature of 270 °C.

Table 1
Kokam SLPB technical specifications [25].

	Kokam 25 Ah	Kokam 40 Ah
Capacity (Ah)	25	40
Voltage (V)	3.7	3.7
Weight (g)	620	935
Width (mm)	215	215
Height (mm)	220	220
Thickness (mm)	6.5	9.0

Table 2
Kokam SLPB chemical composition.

Component	Chemical composition	Metal quantity (mg/g)
Anode active material	Graphite (C)	/
Anode current collector	Cupper (Cu)	32.14 Cu
Cathode active material	$LiMnNiCoO_2$ (NMC)	26.60 Li; 1.30 Mn; 18.28 Ni; 11.32 Co
Cathode current collector	Aluminum (Al)	7.73 Al

2.4. SPME-GC-MS method

The identification and quantification of the volatile organic compounds (VOCs) present in the solid and liquid samples was achieved through the utilisation of gas chromatography-mass spectrometry (GC-MS), in accordance with the Environmental Protection Agency (EPA) 8260D method [22]. The samples were not subjected to any pre-treatment processes and were extracted by solid-phase microextraction (SPME), in accordance with the EPA 5012A method [23].

The Agilent Technologies 7890B GC System was employed for the analysis, with an EST (Flex) analytical autosampler coupled to an Agilent 5977B GC-MS. The column utilised was a HP-5MS Agilent Technologies Inc. (30 m length, 0.25 mm i. d., 0.25 μm thickness). For each test 10 mL of liquid residue and 5 g of solid residue were aliquoted in separate 20 mL headspace vials. Additionally, an internal standard (ISTD), was added to all samples prior to the analysis. The concentration of the ISTD was 3 μL for the solid samples and 10 μL for the liquid samples of BTEX (Restek). The extraction method was based on solid-phase microextraction (SPME), utilising a 100 μm polydimethylsiloxane (PDMS) fiber (Supelco), which permits the adsorption of non-polar compounds. At the beginning of each analysis session, the PDMS fiber was conditioned for 30 min at 200 °C. Prior to analysis by GC-MS, the sample was heated in an oven maintained at 75 °C for 15 min with stirring. The fiber was then exposed in the headspace of the samples for 15 min at 75 °C. The operating conditions of the gas chromatograph were the transfer line at 250 °C and helium (purity 99.999) as the carrier gas. The analysis is performed at a programmed temperature: from 45 °C (3 min) to 250 °C (10 min) at a heating rate of 1 °C/min, for a total run time of 33 min. The mass spectrometer operates in electronic ionization (EI) mode at 70 eV and the source was maintained at a temperature of 230 °C. Mass spectra were acquired in scan mode, with m/z between 40 and 400. The mass spectra of the samples were compared with those of the NIST mass spectra library.

2.5. ICP-OES method

To identify and quantify the metals in the solid and liquid samples, analyses were carried out by ICP using a pre-treatment procedure consisting of acid digestion with a mixture of nitric and hydrochloric acids according to the EPA 200.8–1 method [24].

Fig. 2. (a) Test system. Extinguishing agents: (b) water mist; (c) F-500; (d) CO_2.

Table 3
Experimental test conditions and relative test code.

Test code	Li-ion cell	SoC (%)	Burner	Extinguishing agent
K25–W	Kokam 25Ah	100	Propane	Water mist
K25–F5	Kokam 25Ah	100	Propane	F-500
K25–CO_2	Kokam 25Ah	100	Propane	CO_2
K40–W	Kokam 40Ah	100	Propane	Water mist
K40–F5	Kokam 40Ah	100	Propane	F-500
K40–CO_2	Kokam 40Ah	100	Propane	CO_2

The samples were previously homogenized using a laboratory porcelain mortar and then approximately 0.150 g was weighed on an analytical balance, transferred to glass flasks and 10 mL of reverse aqua regia was added. Digestion was carried out at room temperature (20 °C) and all samples were shaken on a "Mini Rocker-Shaker mr-1" for 3 h. At the end of digestion, the samples were transferred to a Falcon and diluted with ultrapure water up to a final volume of 50 mL, then filtered. To remove any residual carbon still present in the form of CO_2, all the samples were placed in a sonicator for 15 min and centrifuged at 7000 rpm for 8 min. A 2 mL aliquot of the supernatant from solid samples and a 10 mL aliquot of the supernatant from liquid samples were taken and placed into a 10 mL conical bottom Falcon tube. All samples were finally analysed by Thermo Fisher Scientific iCAP 7200 ICP-OES [27,28]. Standard solutions were prepared by serial dilutions starting from standard solution (Merck KGaA). Thermo Fisher Scientific Qtegra Intelligent Scientific Data Solution (ISDS) software was used to create LabBooks for sample analysis and for data acquisition, processing and reporting.

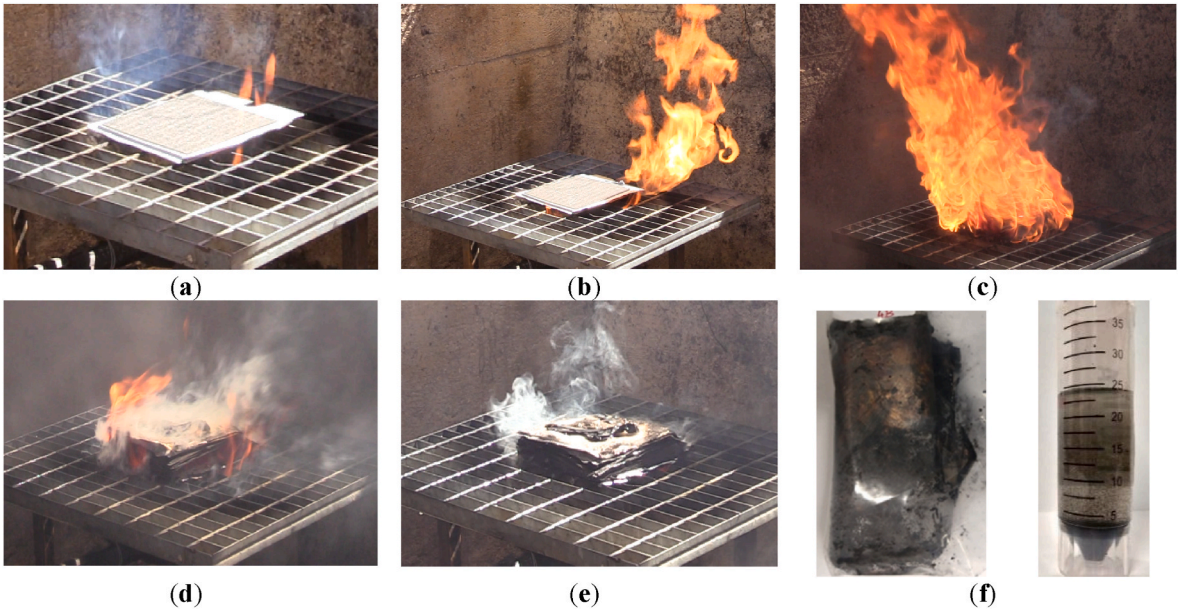

Fig. 3. Key events for K40–W fire test: (**a**) ignition, 0 s; (**b**) venting, 90 s; (**c**) catastrophic rupture, 100 s; (**d**) extinction, 110 s; (**e**) post extinction, 120 s; (**f**) samples collection.

3. Results

3.1. Fire tests

All the tests reported in Table 3 were carried out using the procedure described in section 2.2. As an example, Fig. 3 shows the main events occurring during the test carried out on the K40 cell extinguished with the water mist (W) agent: (a) ignition of the propane flame, (b) venting of the gases/vapours, (c) catastrophic failure of the cell and appearance of the flame, (d) application of the extinguishing agent, (e) cooling of the system, (f) collection of solid and liquid samples.

After lighting the propane burner and subjected the cell to continuous heating, the internal pressure of the LIB increased due to the vaporization and decomposition of the electrolyte, which led to the opening of the area with a lower resistance seal, and the venting of the gas/vapor (Fig. 3b). The venting phase was characterized by the swelling of the cell, followed by a hissing explosion and the spraying of a large quantity of white aerosol consisting mainly of the electrolyte solution, which ignited immediately. Due to the exothermic reaction, the temperature rise became more violent and involved the whole system, causing the catastrophic failure of the cell (Fig. 3c).

Fig. 4 shows the temperature profiles of the tests carried out on (a) K25 and (b) K40 cells with the three selected extinguishing agents, water mist (W), F-500 (F5) and CO_2.

A similar behaviour between the extinguishing agents used is clearly evident, regardless of the capacity of the cell. It is important to note that the fire tests with CO_2 as extinguishing agent required three applications of the extinguishing agent: two with CO_2 and one with water mist for final cooling of the system. From these graphs in Fig. 4, the temperature values of each event are evaluated as shown in Table 4.

From the data, it is possible to calculate the rate of temperature increase leading to venting (v_V) by equation (1), and the rate of cooling (v_C) by equation (2), during the application of the extinguishing agent. The values, expressed in °C/s, are given in Table 5.

$$v_v = \left(T_{venting} - T_{initial}\right) / \left(t_{venting} - t_{initial}\right) \quad (1)$$

$$v_c = \left|\left(T_{end\ extinction} - T_{start\ extinction}\right) / \left(t_{end\ extinction} - t_{start\ extinction}\right)\right| \quad (2)$$

The average of the v_V values for the K25 and K40 are 1.6 ± 1.1 °C/s and 1.2 ± 0.7 °C/s respectively, which allowed to exclude a significant difference in the response due to the cell capacity parameter. On the contrary, significant differences were observed in the cooling rate when the agents were varied: the rate varied from 30.5 ± 4.9 °C/s for water mist, 36.5 ± 6.4 °C/s for F-500 to a lower value of 20.0 ± 1.4 °C/s for CO_2, in reference to the first extinction. These values highlighted the greater cooling ability and inhibition capacity of the water-based agents compared to the gaseous ones.

Once the system had reached a safe temperature, solid and liquid samples were taken. Table 6 shows the weight of the solid samples (g), the percentage of mass loss (%), the humidity of the solid samples (%) and the volume of the liquid samples (mL).

It was observed that the weight loss increases as the capacity of the cells increases, in fact for the K25 there is an average loss of 88.78 ± 20.93 g while for the K40 the loss is of 150.11 ± 40.13 g. The amount of liquid residue collected from the containment tank at the end of the tests varies considerably. This variability may be due to partial evaporation of the extinguisher in the case of the water mist and F-500 tests, whereas in the case of the CO_2 test, the final water was applied in abundance to extinguish the fire definitively. Regardless of the amount of extinguishing agent used, the moisture content of the solid sample did not differ significantly, with an average value of 25.3 ± 5.6 %.

3.2. BTEX analysis by GC-FID of liquid samples

The liquid samples were analysed by GC-FID and the quantification of benzene, toluene, ethylbenzene, p-xylene, m-xylene and o-xylene (BTEX) was obtained by interpolation of the areas with the calibration lines of the standards. In all samples the analyte concentrations are

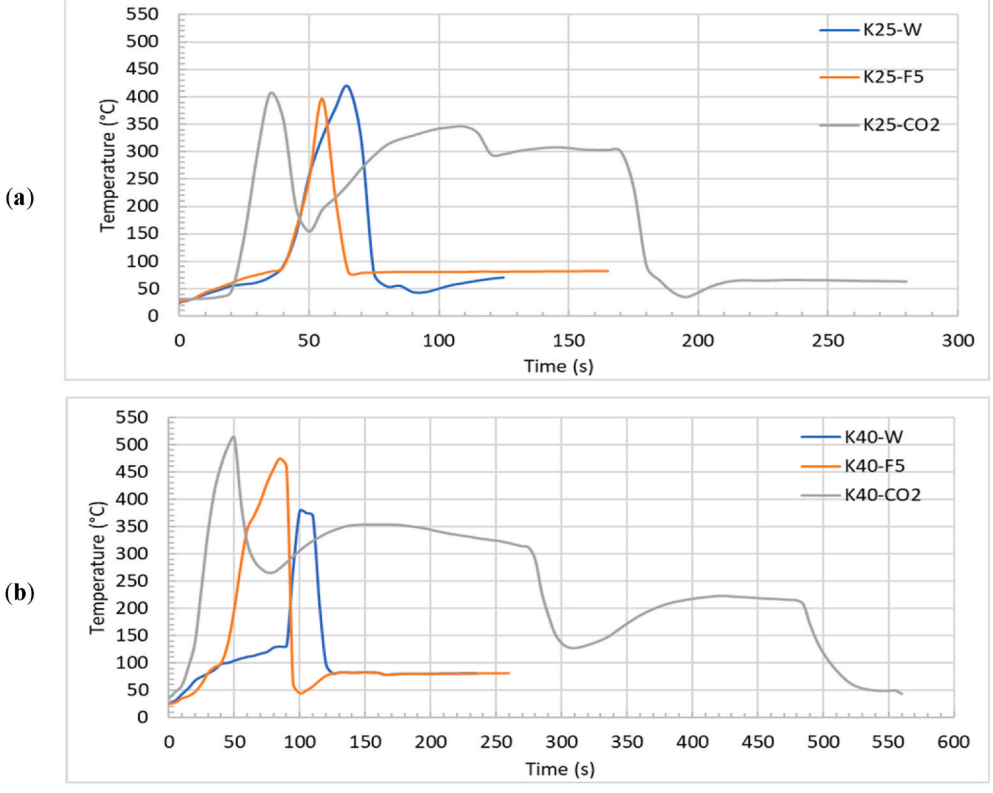

Fig. 4. Temperature profile for fire tests on cells: (**a**) K25; (**b**) K40.

Table 4
Temperature (°C) of key events for each fire test.

Temperature of key event	K25–W	K25–F5	K25–CO_2	K40–W	K40–F5	K40–CO_2
$T_{initial}$ (°C)	25	26	29	25	26	26
$T_{venting}$ (°C)	150	89	35	132	100	31
$T_{catastrophic\ rupture}$ (°C)	419	396	406	379	475	406
$T_{start\ extinction}$ (°C)	419	396	406	370	459	512
$T_{end\ extinction}$ (°C)	78	80	195	98	45	319
$T_{start\ extinction'}$ (°C)	–	–	345	–	–	289
$T_{end\ extinction'}$ (°C)	–	–	295	–	–	187
$T_{start\ extinction''}$ (°C)	–	–	300	–	–	207
$T_{end\ extinction''}$ (°C)	–	–	91	–	–	101

Table 5
Values of cooling rate v_c (°C/s) for the different agents.

Test code	v_v	v_c	$v_{c'}$	$v_{c''}$
K25–W	2.8	34	–	–
K25–F5	1.6	32	–	–
K25–CO_2	0.6	21	5	21
K40–W	1.2	27	–	–
K40–F5	1.9	41	–	–
K40–CO_2	0.5	19	10	10

Table 6
Solid and liquid samples after each fire test.

Test id	Weight of solid samples (g)	% weight loss (%)	Humidity (%)	Volume of liquid samples (mL)
K25–W	446.90	19.5	24	185
K25–F5	488.46	12.0	20	298
K25–CO_2	463.30	16.5	31	1092
K40–W	755.66	9.5	28	482
K40–F5	639.50	23.4	18	158
K40–CO_2	681.50	18.4	31	not collected

below the LOD, 200 ppb for benzene and 1 ppm for the other compounds, except for sample K40–F5 which has a benzene concentration of 500 ppb.

3.3. Volatile organic compounds analysis by SPME-GC-MS

The solid and liquid samples were analysed by SPME-GC-MS, and Table 7 and Table 8 show the identified compounds with the corresponding retention time, t_R expressed in min, and the concentration, expressed in ppm for the solid and in ppb for the liquid.

In both solid and liquid samples, the compounds identified are similar, in terms of classes, but the order of magnitude of the concentration is different: in solids they are in the order of ppm, while in liquids they are in the order of ppb. For samples with the same extinguishing agent applied, the compounds identified are similar for cells with different capacities, as are the concentration levels. There is a difference between solid and liquid samples due to the ability of the VOCs to remain in the samples. In the case of liquids, the lower concentration (ppb) observed compared to solids may be due to the lack of affinity between the matrix and the compounds. For solids, higher concentrations of VOCs were observed after application of F-500 than for other agents, and this may be due to the property of the agent to encapsulate a specific class of compounds, such as hydrocarbons. In fact, especially for the K25–F5 test, the concentrations of hydrocarbons are one order of magnitude higher than the concentrations of the other compounds: 42030 ppm for biphenyl, 1127 ppm for octadecane, 1962 ppm for hexadecane and 1027 ppm for heptadecane.

3.4. Metals analysis by ICP-OES

The solid and liquid samples were analysed by ICP-OES and the metal concentrations, expressed in ppm, are given in Tables 9 and 10.

It can be observed that the contribution of each metal in the different solid samples is similar in terms of total amount. These trends between the metals can be traced back to the percentages of metals present in the cell, as indicated in the MSDS. In fact, the anodic material, including the copper metal collector, is approximately 15–35 wt%, the cathodic material is approximately 20–50 wt%, and the electrolyte solution is 10–20

Table 7
Compounds identified in solid samples with their respective t_R (min) and concentration (ppm).

Compound	t_R (min)	K25–W	K25–F5	K25–CO_2	K40–W	K40–F5	K40–CO_2
1-butanol	2.24	–	–	1581	–	–	–
2,4-dimethyl-1-heptene	4.91	–	–	5439	–	–	–
1,3-propanediamine	7.14	99	–	–	89	–	–
undecane, 2,2-dimethyl	7.16	–	–	434	–	–	–
1-hexanol, 2-ethyl	7.63	–	725	–	–	147	–
tetradecane	9.55	–	494	–	–	413	–
decane, 3-bromo	9.57	–	–	–	176	–	110
tridecane	10.55	–	743	–	–	415	–
biphenyl	11.40	–	42030	–	–	–	–
octadecane	11.45	–	1127	–	–	222	–
undecane, 4,7-dimethyl	11.47	–	–	–	–	–	389
biphenyl-ether	11.59	47	–	–	93	–	–
5-octadecene	13.06	–	926	–	–	–	–
1,4-butanediol	13.10	56	–	–	–	–	–
hexane, 3,3-dimethyl	13.12	–	–	–	–	–	346
hexadecane	13.13	–	1962	–	–	177	–
undecane, 5,7-dimethyl	13.17	–	–	–	250	–	–
heptadecane	13.83	–	1027	–	–	–	–
isophthalic acid	14.93	1401	–	–	2434	3789	–
terephthalic acid	16.58	–	–	1397	2264	–	1949

-: compounds not detected; the compounds belonging to the hydrocarbon class are underlined.

Table 8
Compounds identified in liquid samples with their respective t_R (min) and concentration (ppb).

Compound	t_R (min)	K25–W	K25–F5	K25–CO_2	K40–W	K40–F5
octanal	7.32	0.2	–	–	–	–
1-hexanol, 2-ethyl	7.64	1.0	–	1.1	2.1	–
1-octanol	8.14	1.4	nq	–	0.6	73
nonanal	8.55	0.4	–	1.2	0.2	–
hexanoic acid, 2-ethyl	8.62	0.2	–	–	0.5	–
decanal	9.64	0.5	–	–	1.0	–
1-decanol	10.28	6.8	444	4.0	4.4	1387
undecanal	10.63	0.1	–	–	0.2	–
biphenyl	11.38	7.5	14	74	0.6	173
tetradecane	11.46	0.5	–	–	0.2	nq
biphenyl-ether	11.59	0.6	–	–	0.2	–
acenaphthylene	12.07	0.4	–	–	–	–
1-heptadecene	12.24	–	6.6	–	–	–
hexadecane	13.13	–	–	–	0.2	–
3-heptadecene	13.83	–	7.2	–	–	–
phenanthrene	14.71	1.2	–	0.8	–	–
1-octadecanol	14.56	–	5.7	–	–	–
hexadecanal	14.75	–	9.6	–	–	14

-: compounds not detected; nq: concentration under the limit of quantification (LOQ); the compounds belonging to the hydrocarbon class are underlined.

Table 9
Metals concentrations (ppm) in solid samples.

Test code	Co (ppm)	Cu (ppm)	Li (ppm)	Mn (ppm)	Ni (ppm)
K25–W	1052 ± 380	1886 ± 131	7669 ± 500	826 ± 48	2936 ± 173
K25–F5	1671 ± 515	3364 ± 232	9274 ± 587	1107 ± 174	3018 ± 546
K25–CO_2	1356 ± 723	3491 ± 239	6305 ± 386	1030 ± 163	3434 ± 205
K40–W	1085 ± 196	7521 ± 522	4898 ± 315	909 ± 57	2480 ± 234
K40–F5	1554 ± 130	8788 ± 614	5607 ± 332	860 ± 76	2983 ± 665
K40–CO_2	1216 ± 502	7091 ± 495	7282 ± 466	902 ± 63	4330 ± 146

Table 10
Metals concentrations (ppm) in liquid samples.

Test code	Co (ppm)	Cu (ppm)	Li (ppm)	Mn (ppm)	Ni (ppm)
K25–W	66 ± 6	48 ± 5	73 ± 7	111 ± 12	62 ± 6
K25–F5	106 ± 11	30 ± 3	142 ± 14	59 ± 6	96 ± 9
K25–CO_2	85 ± 9	20 ± 2	58 ± 6	49 ± 5	127 ± 11
K40–W	108 ± 11	89 ± 10	116 ± 12	122 ± 12	88 ± 8
K40–F5	80 ± 8	66 ± 6	68 ± 7	35 ± 4	31 ± 3

wt%. Lithium is the most concentrated metal due to its presence in the cathode material and in the electrolyte solution as salt ($LiPF_6$).

Although at concentrations two orders of magnitude lower than in the solids, traces of the same metals were also found in the post-extinguishing liquid samples, as shown in Table 10. This means that the extinguishing agent not only extinguished the fire, but also carried metal particles with it, thus modifying the initial composition of the agent itself and also altering its environmental impact.

4. Discussion

From the results of the various fire tests, it is clear that the use of different extinguishing agents (i.e., water mist, F-500 and CO_2) leads to significant differences both in terms of the cooling rate, according to data shown in Tables 5, and in the chemical composition of the solid and liquid samples taken, according to the data shown in Tables 7–10

The first consideration can be made on the temperature profile of the fire tests recorded by the thermocouples in the upper surface of the cell. The descriptions of the main events, in terms of temperature, are given in Table 4. Table 4 allows the similarities and differences to be highlighted according to the parameters involved. The main similarity between the temperature trends, which is independent of both the capacity of the batteries and extinguishing agents, is the initial heating and the rate of ignition of the cell. However, the maximum temperature reached differs, being very close between the three tests in the case of the K25, with an average of 407 ± 12 °C, whereas in the case of the K40 there is a greater discrepancy in the values, with an average of 447 ± 72 °C. The capacity of the cell therefore influences the maximum temperatures that can be reached during a fire. The main difference, however, lies in the extinguishing phase, where completely different trends are observed depending on the class of extinguishing agent used, i.e. water-based or gaseous.

Water-based extinguishing agents, i.e., water mist and F-500, have a rapid and sustained cooling effect, unlike CO_2, which has a lower cooling effect, causing the temperature to rise again. In fact, in the case of water mist and F-500, one application was sufficient to cool the device to below 100 °C, whereas in the case of CO_2, even after the second application, temperatures of 300 °C and 150 °C were recorded for the K25 and K40 cells, respectively. Numerically, this behaviour can be expressed by the cooling rate (v_c), expressed in °C/s, and calculated by equation (2). From the individual results shown in Tables 5 it is possible to obtain an average value for each extinguishing agent. The higher average value of v_c is obtained with F-500, 36.5 ± 6.4 °C/s, followed by water mist, 30.5 ± 4.9 °C/s, and finally by CO_2, 20.0 ± 1.4 °C/s. Cell capacity has no significant affect on this parameter. The difference in effect can be explained both by the physical properties of the agents and by the cooling mechanism. In fact, the water mist and the F-500, being liquid, sprayed in the form of micro-drops, can penetrate inside the cell, allowing internal cooling. The greater cooling effect of the F-500 over water mist is due to the ability of F-500 to encapsulate the burning fuel elements in the micelles, inhibiting combustion and consequently heat release. Although CO_2 could suppress the LIB fire by smothering it, it is not able to reduce the internal temperature of the LIBs to stop the internal exothermic reactions. This is the reason why the heat capacity of carbon dioxide is so low that it cannot cool the battery down for a long time.

Differences between the extinguishing agents are also observed in the compounds identified in both solid and liquid samples by GC-FID and ICP-OES. Analyses on solid and liquid samples were carried out to identify and quantify VOCs and metals and to classify the waste, both solid and liquid, according to the European Regulation N. 2008/98/CE [18], and, after modification, the EU Regulation N. 1375/2014 [19], to which the Italian Legislative Decree n.152 [20] refers. The concentrations of BTEX, obtained by GC-FID analysis on the liquid samples, are

similar among the liquid samples: toluene, ethylbenzene and xylene isomers are below the LOD, equal to 1 ppm in all liquids, while benzene is below the LOD of 200 ppb in all the samples except for the sample of the K40–F5 test, which contains 500 ppb of benzene. The limit values for these substances in waste, according to the EU Regulation N. 2008/98/CE, are: 100 ppm for benzene, 30000 ppm for toluene, $2.25*10^5$ ppm for ethylbenzene and $2.00*10^5$ ppm as the sum of the xylenes. All the values obtained are well below the legal limits and therefore the solid and liquid residues cannot be classified as hazardous waste with regard to VOCs.

With regard to the identification and quantification of the compounds present in the solid and liquid samples, reported in Tables 7 and 8 respectively, it should be noted that the values in Table 7 are expressed in ppm, while those in Table 8 are expressed in ppb, so that the concentration of VOCs was more than three orders of magnitude higher in the solid samples than in the liquid ones. In general, the low concentration and number of VOCs, regardless of the extinguishing agent, may be due to the maximum temperatures reached by the cell, above the surface temperature of 427 ± 46 °C. In particular, the solid samples obtained from the F-500 tests, for both cell capacities (K25–F5 and K40–F5), contained petroleum distillate compounds, such as tetradecane, tridecane, octadecane and hexadecane. On the other hand, water mist samples contain acids and eters, such as isophthalic acid and diphenyl ether, respectively. In the case of liquid samples, however, most of VOCs were identified in the water mist samples, albeit at very low concentrations. The liquid samples from the CO_2 tests also refer to the water mist used after two extinction steps with gas: it was observed that these first two steps resulted in a high loss of VOCs.

The differences observed in the number of compounds and the relative concentrations are related to the type of extinguishing agent used. In fact, due to the encapsulant capacity of F-500, this agent shows a higher concentration of VOCs, especially for the hydrocarbon class. This class of compounds is regulated by the EU Regulation N. 1375/2014 [19], where the limit and threshold concentration values for the hazard classification and the relative codes depend on the sample matrix. For solid samples, hydrocarbons are divided into two classes based on the number of carbon atoms (C5–C8 and C11–C39), for liquid samples C5–C39 hydrocarbons are considered altogether. The compounds belonging to the hydrocarbon class have been reported as underlined text in Tables 7 and 8: it can be noted that in the case of the solid samples no light hydrocarbons were identified, but only heavy hydrocarbons. In Table 11, the sums of the concentrations of C11–C39 hydrocarbons for the solid samples and the sum of C5–C39 hydrocarbons for the liquid samples are reported with the concentration limits according to the EU Regulation N. 1375/2014 [19].

The concentration values of the solid samples are all below the threshold values of the HP14 code (ecotoxic), except for the sample of the test K25–F5 that is above the threshold values of the HP14 code but significantly below the limit value. In the liquid samples, the concentrations are significantly lower than the limit of the HP5 code (harmful). Therefore, for the class of hydrocarbons, there is no correlated hazard for either solid or liquid samples.

Similarly, in the case of the quantification of metals by ICP analysis both for solid (Table 9) and liquid (Table 10) samples from the different fire tests, the range of concentrations of metals in the solid samples is significantly higher (one order of magnitude) than those in the liquid ones. The highest concentrations in the solids are found for Cu, which constitutes the anode collector, and Li, while lower concentrations are observed for the other metals of the cathode, which is made up of lithium-nickel-manganese-cobalt oxides. The higher concentration of lithium is due to the presence of the metal both in the active cathode material, in the form of an oxide, and in the electrolyte solution, in the form of a dissolved salt ($LiFeP_6$). These concentrations have been compared with the limit values for metals in waste set out in EU Regulation N°2008/98/EC. They refer only to Cu and Ni with different limit concentrations, which lead to a different code and therefore a different specific hazard. Table 12 shows the concentration values of Cu, expressed as $CuSO_4$, measured in the solid and liquid samples and the reference limit concentration and the threshold concentration for the purpose of hazrad according to EU Regulation N. 1375/2014 [19]. The same results are reported in Table 13 for Ni, expressed as $NiSO_4$.

The Cu concentrations in the solid samples from the K25 fire tests were below the threshold value for codes HP4 (irritant) and HP6 (toxic), but above the threshold for code HP14 (ecotoxic), without exceeding the limit values. On the contrary, the Cu concentrations of the solid samples from the K40 fire tests exceeded the threshold values of all codes, HP4 (irritant), HP6 (toxic) and HP14 (ecotoxic), without exceeding the hazard limits. The difference between the two cell capacities is due to the higher amount of metals in the K40 than in the K25. On the contrary,

Table 12
Cu, as $CuSO_4$, concentration in solid and liquid samples compared to the limit of the EU Regulation N. 1375/2014 [19], expressed in ppm.

Sample matrix	Test code	Cu, as $CuSO_4$ (ppm)	Concentration limit (ppm) for the purpose of danger according to the EU Regulation N. 1375/2014 [19]
Solid samples	K25–W	4392	250000 (HP6) threshold **10000**
	K25–F5	7833	200000 (HP4) threshold **10000**
	K25–CO_2	8129	250000 (HP14) threshold 1000
	K40–W	**17513**	
	K40–F5	**20463**	
	K40–CO_2	**16511**	
Liquid samples	K25–W	112	
	K25–F5	70	
	K25–CO_2	47	
	K40–W	207	
	K40–F5	154	

Table 11
Hydrocarbons concentration in solid and liquid samples compared to the limit of the EU Regulation N. 1375/2014 [19], expressed in ppm.

Sample matrix	Test code	C11–C39 Hydrocarbons concentration (ppm)	Concentration limit (ppm) for the purpose of danger according to the EU Regulation N. 1375/2014 [19]
Solid samples	K25–W	0	250000 (HP14) threshold **10000**
	K25–F5	**48309**	
	K25–CO_2	5873	
	K40–W	250	
	K40–F5	1227	
	K40–CO_2	735	
Sample matrix	Test code	C5–C39 Hydrocarbons concentration (ppm)	Concentration limit (ppm) for the purpose of danger according to the EU Regulation N. 1375/2014 [25]
Liquid samples	K25–W	0.017	100000 (HP5)
	K25–F5	0.049	
	K25–CO_2	0.149	
	K40–W	0.002	
	K40–F5	0.346	

Table 13
Ni, as $NiSO_4$, concentration in solid and liquid samples compared to the compared to the limit of the EU Regulation N. 1375/2014 [19], expressed in ppm.

Sample matrix	Test code	Ni, as $NiSO_4$ (ppm)	Concentration limit (ppm) for the purpose of danger according to the EU Regulation N. 1375/2014 [19]
Solid samples	K25–W	*7741*	1000 (HP7)
	K25–F5	*7957*	**10000** (HP11)
	K25–CO_2	*9054*	*3000* (HP10)
	K40–W	*6539*	**10000** (HP5)
	K40–F5	*7865*	250000 (HP6) threshold **10000**
	K40–CO_2	**11416**	200000 (HP4) threshold 1000
Liquid samples	K25–W	163	100000 (HP13)
	K25–F5	253	250000 (HP14) threshold 1000
	K25–CO_2	335	
	K40–W	232	
	K40–F5	82	

Table 14
PNEC values for freshwater, marine water, STP relative to Co, Cu, Li, and Mn.

Metal	Test code	Concentration (ppm)	PNEC
Co	K25–W	***66*** ± ***6***	**1.06 ppb** (freshwater)
	K25–F5	***106*** ± ***11***	*2*.36 ppb (marine water)
	K25–CO_2	***85*** ± ***9***	0.37 ppm (STP) [29]
	K40–W	***108*** ± ***11***	
	K40–F5	***80*** ± ***8***	
Cu	K25–W	***48*** ± ***5***	**6.3 ppb** (freshwater)
	K25–F5	***30*** ± ***3***	*5*.2 ppb (marine water)
	K25–CO_2	***20*** ± ***2***	230 ppb (STP) [30]
	K40–W	***89*** ± ***10***	
	K40–F5	***66*** ± ***6***	
Li	K25–W	***73*** ± ***7***	**1.65 ppm** (freshwater)
	K25–F5	***142*** ± ***14***	*0*.165 ppm (marine water)
	K25–CO_2	***58*** ± ***6***	22.94 ppm (STP) [31]
	K40–W	***116*** ± ***12***	
	K40–F5	***68*** ± ***7***	
Mn	K25–W	***111*** ± ***12***	**0.34 ppm** (freshwater)
	K25–F5	***59*** ± ***6***	*0*.003 ppm (marine water)
	K25–CO_2	***49*** ± ***5***	100 ppm (STP) [32]
	K40–W	***122*** ± ***12***	
	K40–F5	***35*** ± ***4***	

the Cu concentrations in the liquid samples are all well below the limit values and therefore the liquid samples cannot be classified as hazardous waste according to the EU Waste Regulation.

The Ni concentrations in the solid samples, as shown in Table 13, were all found to be above the threshold of codes HP4 (irritant) and HP14 (ecotoxic) without exceeding the limit values, but above the concentration limits of codes HP7 (carcinogenic) and HP10 (toxic for reproduction). In addition, the Ni concentrations in the solid sample obtained from the K40–CO_2 fire test are above the threshold of code HP6 (toxic) and above the concentration limit of codes HP5 (harmful) and HP11 (mutagenic). Thus, all the solid samples must be classified as carcinogenic (HP7) and toxic for reproduction (HP10), and in addition the solid sample from the K40–CO_2 test may cause specific target organ toxicity (STOT) or aspiration toxicity (HP5) and mutagenicity (HP11). As observed for Cu, the Ni concentration in the liquid samples is also well below all threshold limits. Therefore, the liquid samples can not be classified as hazardous waste according to the EU waste Regulation.

Combining the results obtained, it is possible to make an initial assessment of the environmental impact of the extinguishing agents used on LIB fires. In fact, both the water mist and the F-500 are classified, due to their composition, as not harmful to the environment, non-toxic and completely biodegradable, while CO_2 has the advantage of leaving any residue being applied in the gas phase. However, the results obtained show that both the solid and the liquid samples can no longer be included in this classification due to the accumulation of VOCs and metals well above the legal limits.

Another important aspect to be assessed in a real case is the percolation of liquid from the battery on the ground to the internal soil. In fact, in a real case, the liquid extinguishing agent is not properly collected in a tank during the extinguishing operation, but it is released into the environment and, in particular, into the soil. This can cause it to seep through the soil and reach aquifers and/or flow into a watercourse close to the site. Both scenarios lead to water pollution with consequent risks to aquatic organisms. The concentrations of metals that can cause pollution and the relative risk to aquatic organisms differ both between metals and between freshwater, marine water and sewage treatment plants (STPs). For the different metals, the hazard values for aquatic organisms are expressed as a Predicted No-Effect Concentration (PNEC) and can be obtained from the relevant ECHA dossiers. This is the concentration of a chemical below which no adverse effects are measured in an ecosystem. PNEC values are available for the following metals: Co, Cu, Li and Mn, while for Ni there is currently no information available on the risk to aquatic organisms.

Table 14 shows the concentrations of metals (Co, Cu, Li and Mn) quantified in the liquid samples with the PNEC values for the freshwater, marine water and sewage treatment plant.

The PNEC values were compared with the concentration of the metals quantified in the liquid samples of each fire test in order to identify the potential hazard to aquatic organisms. The comparison showed that all liquids remaining at the site after the extinguishing phase have concentrations higher than the PNEC for both the waters and the organisms considered, with the exception of Mn in the samples K25–F5, K25–CO_2 and K40–F5. These results highlight the importance of timely reclamation of the area at risk of extinction in order to avoid the release of liquids into the environment that are dangerous for aquatic organisms.

5. Conclusions

The increased use of LIBs presents new challenges in terms of safety and fire management. One relevant issue is certainly the evaluation of extinguishing agents in order to identify the most suitable and efficient one in terms of cooling and inhibition effects. But it is also important to determine the possible harmful effects on human health and the environment of the solid and liquid wastes generated by their use. Therefore, fire tests were carried out on commercial NMC pouch cells to determine the efficiency of the extinguishing agents and the chemical composition of the liquid and solid samples.

By the monitoring of the temperatures in the different fire tests, it was found that the cell capacities, 25 and 40 Ah, did not significantly affect the temperatures of venting and catastrophic rupture of the cell, but only the maximum temperature reached on the cell surface during the fire. In terms of extinguishing agents, the water-based (i.e., water mist and F-500) showed a greater efficiency than the gaseous one (i.e., CO_2). Water-based agents have a faster and more effective cooling effect due to their ability to penetrate into the cell, allowing temperatures below 100 °C to be achieved after the first application. The higher cooling rate of F-500 is due to its ability to encapsulate the fuel compounds. Therefore, from a cooling efficiency point of view, water-based agents can be considered as the better solution.

The analyses for the identification and quantification of VOCs and metals in the solid and liquid samples collected after the tests demonstrated the hazard of the wastes remaining after a LIB fire. In particular, in the solid samples from the tests with F-500 application, due to the higher ability of micelles to encapsulate hydrocarbon compounds, the concentration of hydrocarbons (C11–C39) was found to be higher than the threshold value, but did not exceed the concentration limit value established by EU Regulation n. 1375/2014 for the classification of a hazardous waste as ecotoxic (HP14). Differences in metal concentrations were found between liquid and solid samples. While the metals

concentrations in the solids reach values in the order of thousands of ppm, traces of metals were identified and quantified in the residual liquid after extinction. Based on these values, all solid samples can be classified as carcinogenic (HP7) and toxic for reproduction (HP10) according to the hazardous waste classification. The liquid samples showed concentrations above the PNEC value for freshwater, marine water, and STP organisms. Thus, from the point of view of the human health and environmental impact, the analysis of the solid and liquid samples after the fire showed criticalities, especially due to the high metal contents. These species, together with the VOCs, modify the initial composition of both the fuel and the extinguishing agents and therefore require a new cataloguing for subsequent disposal.

Therefore, in the event of a fire involving LIBs, a number of measures must be taken to ensure the safety of the site, the environment and people. Firstly, it is necessary to use the extinguishing agent with the highest possible extinguishing capacity in order to cool the system quickly and effectively and to avoid the risk of re-ignition. Secondly, once the fire has been extinguished, the solid residues must be properly collected and taken to the appropriate disposal centres, while the liquid samples must also be collected, where possible, also by suction from the ground to avoid contamination of watercourses, otherwise soil remediation procedures should be applied.

CRediT authorship contribution statement

S. Ubaldi: Writing – original draft, Investigation, Data curation. **C. Di Bari:** Writing – review & editing, Conceptualization. **M. Quinterno:** Investigation, Formal analysis, Data curation. **A. De Rosa:** Supervision, Investigation. **M. Mazzaro:** Supervision, Resources. **G. Ferrigno:** Methodology, Data curation. **D. Secci:** Writing – review & editing, Supervision, Methodology. **P. Russo:** Writing – review & editing, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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