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TECHNICAL MEMORANDUM

Project name	**Emission Factors for Select Compounds Formed from Thermal Runaway and Fires from LFP Batteries**
Project no.	**324001292**
Client	**Tanager Power, LLC**
To	**Nadira Basdeo**
From	**Biljana Cosic, Ph.D., and Shirley Lam, Ph.D., P.Eng.**

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1 Introduction

Tanager Power, LLC, in cooperation with Los Esteros Critical Energy Facility, LLC (both subsidiaries of Calpine LLC and collectively hereafter, Calpine) is proposing to develop a 200 MW megawatt (MW) battery energy storage system (BESS) in San Jose, California – Los Esteros Tanager BESS Project (03-AFC-02C). The company intends to conduct an Offsite Consequence Analysis (OCA) to assess the risks associated with potential Lithium-ion batteries (LiB) thermal runaways, fires, and emissions from such events.

The proposed project will utilize Lithium Iron Phosphate (LFP or $LiFePO_4$) battery technology. LFP batteries are recognized for their safety due to their thermal and chemical stability, which results in higher resistance to the possibility of thermal runaway, as characterized by their higher thermal runaway temperatures relative to other types of LiBs.[1,2,3,4]

Ramboll was retained to assist with the evaluation and characterization of emission factors for select species that could be released during such thermal events. In particular, Calpine required emission factor estimates for the following contaminants: hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen cyanide (HCN), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), acrolein (C_3H_4O), formaldehyde (HCHO), phosphoryl fluoride (POF_3), carbonyl fluoride (COF_2), and particulate matter (including ultrafine particulates) for purposes of dispersion modeling of additional toxic air contaminants (TACs), as requested by the CEC in its Project Staff's Data Request Set 3, A64 through A71, regarding Calpine's Petition for Post-Certification Modification to allow construction of Tanager BESS. The emission factors could be used as one of the inputs in the OCA that is being conducted by a third party.

This memorandum documents the technical approach that was used to evaluate and characterize the emission factors estimates and presents the results of the analysis.

[1] PowerTech. Safety of Lithium-Ion batteries. Available at: https://www.powertechsystems.eu/home/tech-corner/safety-of-lithium-ion-batteries/

[2] Rorder P. et al. (2013) Impact of delithiated Li0FePO4 on the decomposition of LiPF6-based electrolyte studied by accelerating rate calorimetry. Journal of Power Sources, 236. Available at: http://dx.doi.org/10.1016/j.jpowsour.2013.02.044

[3] A. Zhukov (2023). Cell-to-pack LFP Lithium Batteries Outperform NMC. Available at: https://www.onecharge.biz/blog/cell-to-pack-lfp-lithium-batteries-outperform-nmc/ accessed on March 14, 2024

[4] NX. Lithium Battery Chemistry: LFP vs NMC explained. Available at: https://nx-tech.com/insight-hub/lfp-vs-nmc-batteries/

2 Technical Approach

To evaluate and characterize the emission factors for this scope Ramboll relied on publicly available data sources that reported emissions of HF, HCl, HCN, NO_2, SO_2, C_3H_4O, HCHO, POF_3, COF_2, and fine particulate matter from LFP battery thermal events. The sources considered included peer reviewed journal articles, technical reports, battery certification tests, and other reputable sources of information. This approach is consistent with the one that Ramboll used to estimate emission factors for the OCA prepared for the Vistra Morro Bay BESS Project in March 2024, hereby known as the "2024 Vistra Report".[5]

For this Calpine study, Ramboll revisited the technical literature considered in the Vistra Report and revised Table 3-2 of the 2024 Vistra Report to only retain emission factors for LFP battery fires for the species of interest. Through this process, some of the references and corresponding emission factors that were not applicable to LFP batteries were removed. Ramboll subsequently conducted a search to identify any recent additional publications that focus on emissions from LFP battery fires only.

3 Results and Discussion

Table 3-1 and **Table 3-2** summarize the studies reviewed. For completeness, all the references from the 2024 Vistra Report (References 1 through 13) are included in the table. Additional descriptions for the prior studies are available in the 2024 Vistra Report. References 14 through 28 in **Table 3-1** and **Table 3-2** summarizes the new and relevant material reviewed. The blue, pink, and green shading in **Table 3-1** were used to distinguish between the studies for which emission factors were not reported because they: (i) did not include sufficient information to calculate the emission factors per mass unit basis (blue); (ii) did not report data on LFP batteries (pink); or (iii) did not include data for the species of interest (green). The remaining emission factors from the original references 1 to 13 were revised to only reflect LFP battery emission factors. Note that the revised and/or retained estimates may still include emission factors that are not representative or specific to LFP batteries. For example, Reference 10 reported average release rates derived from multiple tests involving various type of batteries including LFP, which were used by Ramboll to derive emission factors for HF, HCl, and HCN presented in **Table 3-1**.

Emission factors derived from Reference 11 are also not specific to LFP batteries because the study measured emissions from burning bulk electrolytes. While the derived emission factors were appropriately scaled to the unit mass, the electrolyte volatilization (or loss) rate and associated air emissions measured using burning bulk liquid may not necessarily be representative of the electrolyte loss rate during an actual LFP battery thermal runaway event. In addition, the tests may not have captured the effect from other battery components for the overall partitioning and speciation of electrolytes during battery thermal runaway. The emission factors from such studies were included nevertheless for information because these electrolytes could be used in LFP batteries. In the event that more appropriate emission factor estimates from battery tests are not available, these estimates could be potentially used as the next best surrogates.

[5] Ramboll (2024). OFFSITE CONSEQUENCE ANALYSIS VISTRA MORRO BAY BATTERY ENERGY STORAGE SYSTEM (BESS) PROJECT. Available at: https://www.morrobayca.gov/DocumentCenter/View/19401/Ramboll-Report_BESS-Offsite-Consequence-Analysis-OCA_March-2024

Table 3-1: Summary of Emission Factors Reported or Derived from Different Studies (mg/kg basis)

Study	Cell Type	Mass of Tested Cell/Battery, Module, Rack, or Container	Emission Factor [mg/kg of battery]											Additional Information
			Hydrogen Flouride	Hydrogen Chloride	Hydrogen Cyanide	Sulfur Dioxide	Nitrogen Dioxide	Nitric Oxide	Particulate Matter with Diameter ≤ 2.5 µm	Acrolein	Formaldehyde	Phosphoryl fluoride	Carbonyl fluoride	
		[kg]	HF	HCl	HCN	SO_2	NO_2	NO	$PM_{2.5}$	C_4H_4O	CH_2O	POF_3	COF_2	
1	Unspecified LMO pouch type	0.095	Emission factors were calculated for other types of batteries.											Species tested or observed in the study include HF, HCl, SO_2, CO, NO, SO_2, CO_2, THC.
2	LFP, unspecified laptop battery	0.64-1.23	2,973 - 11,320											The study reported emission factors in mg/Wh. Sufficient information was provided to convert the values to mg/kg battery. The study included pouch and cylindrical LFP cells with the maximum emission factors measured for pouch cells (3990.6 mg/kg - 11,320 mg/kg) and the minimum for cylindrical cells (2,994 mg/kg).
3	LFP, LCO, NCA-LATP, 18650	unknown	Not enough data to determine mg/kg EF									ND	Not enough data to determine mg/kg EF	HF and POF_3 emission factors reported in mg/Wh. Reported emission factors for HF from LFP batteries are in the range of approximately 21 – 203 mg/Wh with the lowest values measured for prismatic LFP cells (21-40 mg/Wh) and the maximum values for pouch LFP cells (56-203 mg/Wh). Information on the battery models and/or mass tested not provided to derive with confidence emission factors per battery mass basis. POF_3 was below detection limit in all LFP battery tests. It was only detected for one LCO battery test at SOC 0%.
4	NMC	0.87	Emission factors were calculated for other types of batteries.											Species tested include CO, CO_2, HCl, H_2; F quantified in solids only; Additional organic gases quantified (in addition to those reported in this table), HCl, and a number of elements within the PM sample (C, Ni, Cu, Al, V, Cr, etc.)
5	NMC	28.75	Emission factors were calculated for other types of batteries.											Species quantified include HF, CO, Benzene, Toluene, Xylene, Styrene, metal compounds including Mn, Li and Co. Additional species reported but without sufficient information to derive emission factors include NO, PH_3, H_3PO_4, F aerosol, NO_2, CO_2, TVOC, aromatics.
6	LFP	0.075	>253											Additional species tested include CO, PF_3, DMC, CO_2, EMC, H_2, C_2H_4, C_2H_5F, CH_3OCH_3, CH_3OCHO, CH_4, CH_3F, C_2H_5OH, C_2H_6, C_3H_6, etc.
7	LFP, NMC, LMO	0.236 cell 1.18 (5-cell stack)	1,525 - 3,559											The study tested automotive grade pouch LFP cells, a stack of 5 cells. Other species quantified include CO_2 and VOCs. Additional species identified include CO, DEC, DMC, EMC.
8	NMC, LMO	70 est.	Emission factors were calculated for other types of batteries and without sufficient information to determine emission factors in mg/kg EF											Gas compounds quantified: HF, HCl, HBr, CO, CO_2, SO_2, NO, THC, PAHs, PM and elements within the PM (Ni, Li, Co). For an estimated battery pack mass of 70 kg, derived emission factors for HF, HCl and CO would be within the range of those reported in this table.
9	LFP, NMC	2.026 - 2.097	ND	2,575										Additional species tested include CO, CH_4, C_2H_4, C_3H_6, CO_2, H_2, NH_3.
10	LFP, NCM, BM-LMP	Approx. 0.5-6.5	Insufficient information to discern data specific to LFP batteries.											Species tested HF, HCl, HCN and CO. Emission rate in g/s per 30-minute burn event reported as an average or representative value derived from multiple tests and cells of different types and sizes. Information on the battery mass in individual tests not provided. Emission factors estimated from the reported emission rates and cell mass range considered in the study (approximately 0.5 kg/cell to 6.5 kg/cell). Emission factors in mg/kg battery derived conservatively assuming the reported emission rate in g/s per 30 min was released from the smallest cell (0.5 kg).
11	No battery testing. Burning of LiPF6 or LiFSI-based electrolytes in bulk	Not applicable	2,816 - 9,520		64	11,312		480	128 - 2,112		64 - 144	496		Not actual battery tests. Evaluation of emissions from burning various $LiPF_6$ and LiFSI-based electrolytes which are used in LFP batteries. Both type of electrolytes are used in LFP batteries. Additional species quantified include CO, CO_2, POF_3, NO, SO_2, C_2H_4, CH_4, C_2H_2, HCOH, THC, SiF_4, soot. Emission factors derived assuming 16% mass share of electrolyte in battery.
12	LFP, LCO and NMC	0.039-0.044	Emission factors for species of interest not available.											Species tested include CO, CO_2, H_2, CH_4, C_2H_4, and C_2H_6.
13	LFP, NMC	Not reported	Not enough data to determine emission factors in mg/kg EF or mg/W											Information on the battery mass tested not provided to derive with confidence emission factors per battery mass or energy capacity basis. Species tested include HF, HCl, HCN, CO_2, NO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, CH_3OH, C_2H_5OH, benzene, and toluene.
14	LFP	5.6 cell 680 mod 6,500 rack	Emission factors for species of interest not available.											BESS Rack Test. Species tested include CH_4, C_2H_4, CO, CO_2, H_2, $C_5H_{10}O_3$, $C_4H_8O_3$, $C_3H_6O_3$.
15	LFP	20.4 cell 1,170 mod 9,360 rack 37,440 container	319	992	67									BESS Container Test. The burn test involved the entire content of a fully equipped BESS container. HF, HCl and HCN concentrations reported in ppm. Total volume of generated gases not measured. The maximum exhaust gas flow rate estimated using fume hood ventilation data.
16	LFP	5.4 cell 70 mod 2870 rack	161.4	344.2	840.7									BESS Rack Test. Test did not specify if more than one module was burned in the experiment. However, the photos indicate that at minimum one entire module and cells were damaged by fire. To estimate emission factors it was conservatively assumed that one module was burned. This assumption produces the highest estimates.
17	LFP, LCO	0.042	3,069 - 7,294	34 - 138					4,849 - 13,552					The study investigated the size distribution and composition of $PM_{2.5}$ that was released from thermal runaway. The PM fractions measured included organic matter, elemental carbon, fluorides (F-), phosphates (PO_4^{3-}), elemental phosphorus (P), and selected metals. Gaseous species measured included acidic gases and their corresponding anions including HF/F^-, HCl/Cl^-, HNO_3/NO_3^-, H_2SO_4/SO_4^{2-}. The supplementary Table S3 provided EFs in mg/Wh which were converted to mass-based emission factors using battery energy capacity of 3.63 Wh. Emission ranges were provided based on the minimum (i.e., average – standard deviation) and maximum (i.e., average + standard deviation) values.
18	LFP, LTO, NMC	0.076	162 - 300		9 - 39					92 - 748	46 - 416			The emission factors were calculated based on the maximum triplicate experimental value for each experiment. Species tested included HF, HCN, CO, CH_4, CO_2, NH_3, C_2H_4, C_3H_6, CH_2O, C_3H_4O
19	LFP, NMC, LCO, NCA, LMO-NMC, and others	Not reported	Not enough data to determine mg/kg EF											Emission factors for HF, HCl, and CO was reported in mg/Wh. Some reported emission factors were estimated based on authors' assumptions on the batteries tested in other studies. Reported emission factors for HF from LFP batteries for the 5 studies not included elsewhere in Table 3-1 range between 4.12 – 107.14 mg/Wh with the lowest value measured for prismatic LFP cell (4.12 mg/Wh) and the maximum value for pouch LFP cells (107.14 mg/Wh). Other species tested or observed include NO_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, and others.

Study	Cell Type	Mass of Tested Cell/Battery, Module, Rack, or Container	Emission Factor [mg/kg of battery]											Additional Information
			Hydrogen Flouride	Hydrogen Chloride	Hydrogen Cyanide	Sulfur Dioxide	Nitrogen Dioxide	Nitric Oxide	Particulate Matter with Diameter ≤ 2.5 µm	Acrolein	Formaldehyde	Phosphoryl fluoride	Carbonyl fluoride	
		[kg]	HF	HCl	HCN	SO_2	NO_2	NO	$PM_{2.5}$	C_4H_4O	CH_2O	POF_3	COF_2	
20	LFP	1.25	Not enough data to determine mg/kg EF											Concentrations profiles for HF, HCl, SO_2, NO_2 and NO are available for SOC 0%, 50%, 75%, and 100% but there is insufficient information to derive emission factors. Comparison of NO_2 and NO concentration profiles indicate that total generation rate (integrated mass) of NO_2 is smaller than the generation rate of NO (at 42% to 80% of NO mass for different SOCs). Given the limited availability of NO_2 emission factors for LFP batteries, the NO emission factors could be potentially considered reasonable and conservative surrogates.
21	LFP	5.27 est.	304 - 1,537	129 - 150		332 - 820		65 - 495						Study reported on the mass of generated gases such as HF, HCl, SO_2, NO, NH_3 and others. Information on the specific battery model tested was not provided. Specifications on the battery nominal capacity and dimensions were used to identify the battery type and mass which was used to estimate SO_2 emission factor. Emission factors for NO estimated for reference where equivalent emission factor for NO_2 would be 99-759 mg/kg, assuming 100% NO to NO_2 conversion.
22	LFP and sodium-ion battery	2.83				653.5								The study reported relative composition (fractions) of the gases produced including H_2, EMC, CO, CO_2, SO_2, C_3H_8 and other VOCs. Emission factors for some of these species were also reported in L/Wh. The emission factor and battery mass provided were used to estimate emission factor for SO_2.
23	LFP	1.98 est.				594.4								The mass of generated gases including SO_2, CO, CO_2 and H_2 was estimated from the information provided. Information on the specific battery model tested was not provided. Specifications on the battery nominal capacity and dimensions were used to identify the battery type and mass which was used to estimate the SO_2 emission factor.
24	LFP	0.038	263 - 11,500			3,105 - 5,263								The study evaluated impact of $LiPF_6$- and LiFSI-based electrolytes on the mass of produced gases such as HF, CO and SO_2. The data were used to estimate emission factors for HF from $LiPF_6$- and LiFSI-based cells and SO_2 from LiFSI cells.
25	LFP, LCO	0.042	Not enough data to determine mg/kg EF											The study focused on chemical characteristics and composition of fine particulate matter.
26	LFP, NMC	6.72							ND - 57,454					Authors reported emissions of $PM_{2.5}$, black carbon and particle numbers in g/hr which they interchangeably refer to as "emissions" and "emission rates". The reported value can be potentially interpreted as total emissions released during an experiment or a short-term release rate during the period of active release. At present $PM_{2.5}$ emission factors were conservatively derived assuming the reported values in g/hr represent total emissions released during the event. Assuming that the reported in g/hr values represent short-term release rates, the derived emission factors would be lower (ND - 21,960 mg/kg). The study also monitored CO_2, CO, CH_2O, NO, NO_2, HCl, HF, HCN, CH_4, and C_3H_8 using FTIR without sufficient information needed to derive emission factors for these species.
27	LFP, NMC	1.129							8.9 - 2,285					Authors reported measured emissions of $PM_{2.5}$, black carbon and particle numbers in g/hr which are interchangeably refer to in the paper as "emissions" (prevalent terminology) and "emission rates". The distinction has direct implication on the interpretation of the values and derivation of emission factors. Considering other information presented in the paper which indicates that duration of measured releases were considerably shorter than an hour, the emission factors were conservatively estimated by assuming that reported $PM_{2.5}$ emissions (in g/hr) represent total emissions (mass) released during the entire event.
28	LFP, LCO and NMC	0.040	142 - 198	1,208 - 2,415						ND - 12	ND - 166		19 - 40	The study evaluated volumes of gaseous species including HF HCl, CO, COF_2, CH_2O, C_4H_4O, and electrolytes which were reported as theoretical contaminated volumes per PAC-1. This information was used to reconstruct the actual volumes and mass of relevant species which were then used to derive emission factors. Reconstruction of actual volumes requires the use of PAC-1 values which were not provided by the authors.

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Notes:

Rack and container mass represent the total mass of all modules in a rack/container tested.

ND indicates that concentration was below detection limit or non-detect.

Table 3-2: A summary of the methods and conditions used in the experimental studies in quantifying emissions from battery fires

Study	Cell Type	Type of Abuse	SOC [%]	Duration of Emissions	Ignition	Atmosphere	Notes
1	Unspecified LCO pouch type	Thermal (Fire)	0-100	~1-10 min	Yes	Ambient	Cell level tests.
2	LFP, unspecified cobalt-based chemistry laptop battery pack (pouch, cylindrical and unspecified)	Thermal (Fire)	0-100	~15-30 min	Yes	Ambient	Tests conducted on multiple cells in close proximity or mechanically fastened together; laptop battery packs including multiple cells, electrical connectors, electronic circuits and plastic housing.
3	LCO, LFP, NCA-LATP, 18650	Thermal (Fire)	0-100	~30 min	Yes	Ambient	Tests conducted on multiple cells not electrically connected to each other and a laptop battery pack including the plastic box, electronics and cables.
4	NMC	Thermal (External heating)	100	>14 min	No	Inert (N_2)	Cell level tests.
5	NMC	Physical (Mechanical: piercing; blunt force; high velocity projectile); & Thermal (Fire)	100	16-26 min	Yes	Ambient	Module (8 cells) level tests with the total mass of approximately 29 kg. Experiment carried out in large tunnel, with sampling point far from fire. Potential deposition/drop-out.
6	LFP	Electrical (Overcharge – charge cell beyond its limit)	135	6.25 hr	Unknown	Ambient	Cell level tests. Emissions of certain compounds (e.g., HF) were still present at end of test.
7	LFP, NMC/LMO (Pouch cells Automotive grade)	Thermal (Heating)	100	~45 min (LFP), ~4.5 min (NMC/LMO)	No	Inert (N_2)	Tests conducted on multiple cells clamped together (5-cell stack).
8	NMC/LMO	Thermal (Fire)	~80	5-30 min	Yes	Ambient	Battery pack, module and cell level tests. Information on the battery mass tested not provided to derive with confidence emission factors per battery mass basis. The study also quantified emissions from battery car fire tests which included contribution from other car components. Emission factors from these tests were not considered and quantified for the purpose of this assessment.
9	LFP, NMC (LFP prismatic)	Thermal (External heating)	100	30-60 min	Yes	Ambient	Module level tests (4 cells) with no electrical connection between cells.
10	NCM/LFP/ BM-LMP	Thermal (Heating) Electrical (Overcharge)	25-100	~13-83 min; Average ~42 min	Some cells self-ignited	Ambient	Cell level tests. Module level tests also conducted, but emissions not quantified.
11	No battery testing. Tests involved burning of LiPF6 or LiFSI-based carbonate electrolytes	Thermal (Heat flux using infrared heaters)	N.A.	Up to ~15 min	Yes	Ambient	Fire behavior of LiPF6 and LiFSI-based electrolytes was studied.
12	LCO/NMC, NMC, LFP	Thermal (External heating)	Battery at Cutoff Voltage	Test duration up to ~2 hours; Gas venting events a fraction of the time	No	Inert (Ar)	Cell level tests.

Study	Cell Type	Type of Abuse	SOC [%]	Duration of Emissions	Ignition	Atmosphere	Notes
13	NMC, LFP	Thermal (External heating), Electrical (Overcharge), External short circuit	50-100, Overcharge, and External Short Circuit	~20-35 min	Yes	Ambient	Cell level tests.
14	LFP	Thermal (External heating)	100	~120 min	No	Ambient	BESS Rack Test.
15	LFP	Thermal (External heating and pulse igniter)	100	~5 hours	Yes	Ambient	BESS container Test
16	LFP	Thermal (External heating)	100%	~3 hours	Yes	Ambient	BESS Rack Test.
17	LFP, LCO	Thermal (External heating)	0, 30, 50, 75, 100	~30 min	Yes	Ambient	Cell level tests.
18	LFP, LTO, NMC	Electrical (Increase of heat form DC Voltage regulator)	10, 25, 50, 75, 100	~20 to >90 min	Yes	Ambient	Cell level tests.
19	LFP, NMC, LCO, NCA, LMO-NMC and others	Varied	0 – 100	Varied	Varied	Ambient and Inert	Cell, battery pack and module level tests.
20	LFP	Thermal (External heating)	0, 50, 75, 100	~30 min	Yes	Ambient	Cell level tests.
21	LFP Prismatic	Thermal (External heating)	0, 50, 100	~30 min	Yes	Ambient	Cell level tests.
22	LFP and sodium-ion battery	Thermal (External heating)	100%	~30 min	No	Ambient	Cell level tests.
23	LFP	Thermal (External heating)	50, 75, 100	~60 min	Yes	Ambient	Cell level tests.
24	LFP	Thermal (Combustion calorimeter)	0, 50, 100	~10 min	Yes	Ambient	Fire behavior of LiPF6 and LiFSI-based electrolytes was studied.
25	LFP and LCO	Thermal (External heating)	0, 30, 60, 80, 100	~10 min	Yes	Ambient	Cell level tests.
26	LFP and NMC (LFP Cylindrical)	Nail penetration and overcharge	100	~4 to ~23 min	Unknown	Ambient	Module level tests.
27	LFP and NMC (LFP Prismatic)	Thermal (External heating)	10, 30, 50, 100	Not specified; inferred from other information to be significantly less than 1 hour	Unknown	Ambient	Cell level tests.
28	LCO, NMC, and LFP	Penetration and pyrolysis	0 to 100	Unknown	Unknown	Ambient and Inert	Cell level tests.

Note that airborne emissions from battery fires are driven by many variables beyond battery chemistry, cell design, state of charge (SOC), or energy density. External factors such as the type of abuse that was used to induce thermal runaway, the scale and design of experiment, type and arrangement of containment, availability of excess air, and others would also play a role.[6] The combination of these internal and external factors govern the battery fire dynamics, which includes the prevalence of different gasification regimes (combustion vs. pyrolytic) and subsequently chemical speciation and partitioning of material between phases (e.g. gases, liquids and solids). Ideally, emission factors should be based on representative source-specific data and obtained using reliable and widely accepted test procedures. Emission factors are considered more robust and reliable if they are based on many observations that would capture the variability of emissions under different process conditions and over time.[7]

So far Ramboll has not identified any reference in the public domain that reports emissions or emission factors from LFP (or any other type of LiBs) that were derived from the observations of actual (accidental) BESS fires. As shown in **Table 3-2**, most of the studies with quantifiable emission data are experimental investigations of battery thermal runaways in controlled environments. The majority of studies involved bench-scale experiments on individual battery cells or loose modules. Only a limited number of references (16) identified by Ramboll included UL9540A battery tests from accredited testing laboratories. The standardized test is specifically designed to evaluate thermal runaway and fire propagation in battery energy storage systems (BESS). It involves testing of battery cells and modules mounted on racks in the setting representative of BESS project installations. Of the 16 UL9540A tests identified only three (Reference 14, 15, and 16) involved testing of LFP battery racks that are representative of a BESS installation.

Two of the UL9540A test reports (Reference 14 and 15 in **Table 3-1**) were provided by Calpine's proposed vendor (Xiamen Hithium Energy Storage Technology Co. Ltd.) and one test report (Reference 16 in **Table 3-1**) was found from the UL database.[8] The UL9540A test associated with Reference 14 did not quantify the species of interest. Reference 15 represents a UL9540A test on a similar but somewhat larger battery cell model with the same LFP chemistry, manufactured by the same vendor, and using a similar BESS container design. The test involved a targeted burn of an entire container-based BESS unit fully equipped with battery racks and other auxiliary equipment. This test, hereby referred to as the "Large Scale Fire Test Report", is, to Ramboll's knowledge, the most representative test for a BESS fire. The species of interest measured during the test included HF, HCl, and HCN.

Of the 14 UL9540A battery tests that Ramboll identified in public domain, nine (9) were for LFP batteries. The majority of the tests quantified releases of species such as carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), and organic combustion by-products and did not sample the species of interest. Of the 9 LFP test reports, only one (Reference 16) included enough information to derive emission factors for HF, HCl, and HCN. A brief description of the UL9540A tests (Reference 15 and 16)

[6] Wang et al. (2019) Thermal runaway and fire behaviors of large-scale lithium-ion batteries with different heating methods. Journal of Hazardous Materials, 379, 120730. https://doi.org/10.1016/j.jhazmat.2019.06.007; Zhang et al. (2019) Quantitative identification of emissions from abused prismatic Ni-rich lithium-ion batteries. eTransportation, 2, 100031. https://doi.org/10.1016/j.etran.2019.100031; Ribière et al. (2012) Investigation on the fire-induced hazards of Li-ion battery cells by fire calorimetry, Energy Environ. Sci. 5, 5271–5280. https://doi.org/10.1039/C1EE02218K; Swiss Federal Laboratory for Materials Science and Technology. (2020) Elektromobilität und Tunnelsicherheit – Gefährdungen durch Elektrofahrzeugbrände. https://plus.empa.ch/images/2020-08-17_Brandversuch-Elektroauto/AGT_2018_006_EMob_RiskMin_Unterird_Infrastr_Schlussbericht_V1.0.pdf

[7] US EPA. AP-42: Compilation of Air Emissions Factors from Stationary Sources (AP-42). Introduction. Available at: https://www.epa.gov/system/files/documents/2024-01/introduction_2024.pdf

[8] UL Solutions. UL9540 Database. http://www.ul.com/ul9540a-database

and the underlying data that were used to derive emission factors for the three species of interest is provided below.

3.1 Large Scale Fire Test Report (Reference 15)

The UL9540A test is unique since it is the only large-scale BESS fire test reviewed by Ramboll which was designed to purposefully burn an entire, fully equipped BESS container to evaluate whether thermal runaway would propagate to other adjacent and nearby containers. In contrast, the majority of UL9540A tests reviewed by Ramboll are designed to evaluate thermal runaway propagation or containment on a smaller scale, such as between adjacent cells or adjacent and nearby modules. The BESS unit (container) used in the large-scale fire test consisted of 4 racks (8 modules per rack with each module weighing 1,170 kg each, and with 52 cells per module) with a total of 1,664 cells (with each cell weighing 20.4 kg each) amounting to 37,440 kg of battery material burnt per container. The test was conducted on an outdoor partially enclosed platform which included the initiating BESS container (enclosure A), and three additional partially equipped (target) BESS containers (B, C and D) as shown in the images below. In this case, the thermal runaway did not propagate to the adjacent or nearby containers.

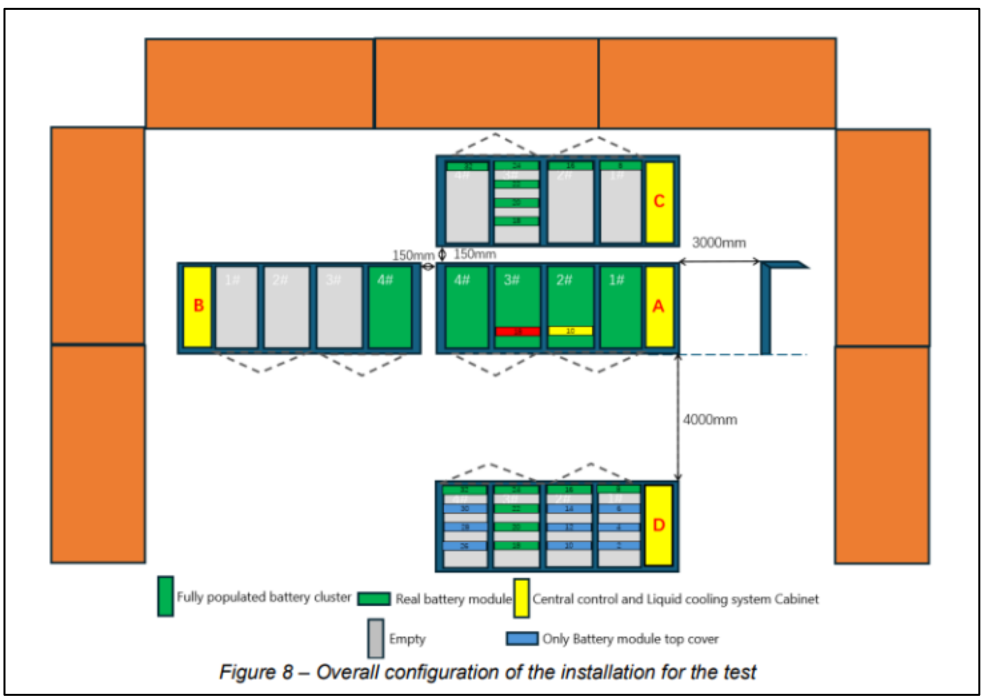

Figure 3-1: Excerpt from the Large-Scale Fire Test[9]

[9] 4792101499-6.25MWh battery energy storage system-LSFT Report-Final.pdf, page 16

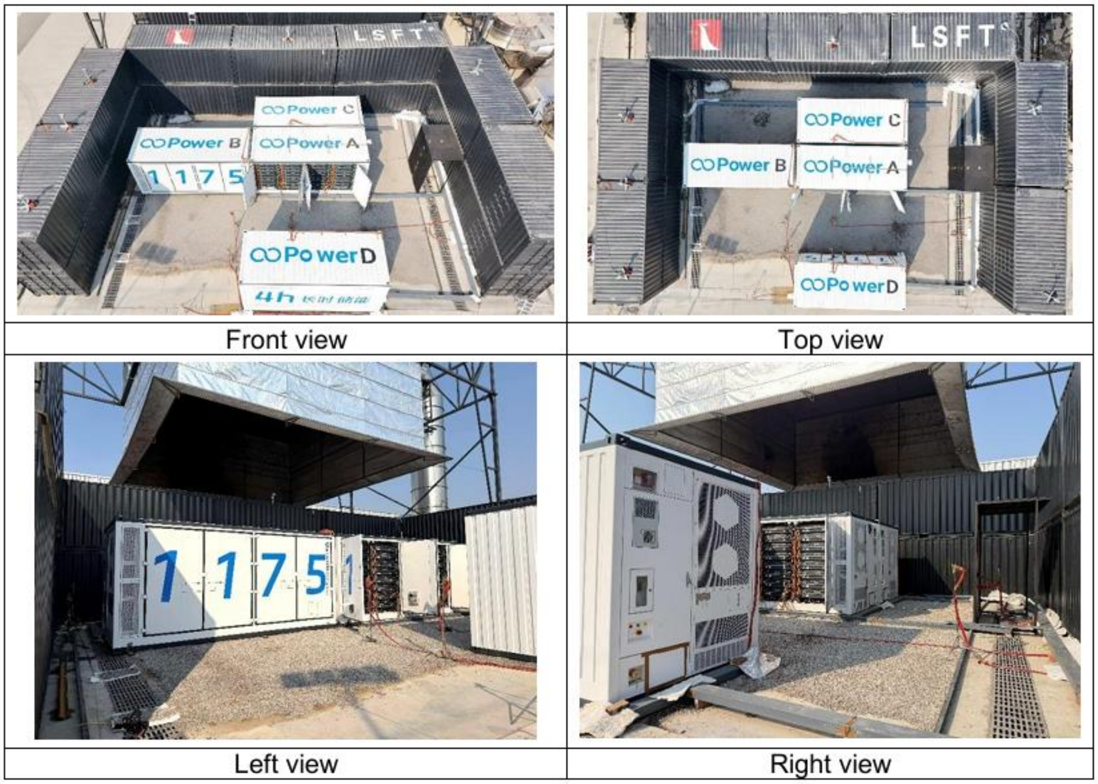

Figure 9 – pictures of the overall configuration

Figure 3-2: Pictures of the overall configuration of the Large-Scale Fire Test[10]

The test was designed to fully ignite and burn the entire container and its contents. To accomplish this, three cells in the initiating BESS unit (one in the initiating module and two cells in the back up initiating module) were driven into thermal runaway which was propagated to other cells. To facilitate thermal runaway propagation, a pulse ignition arc and a heating wire was used to ignite combustible gases during the venting of the initiated cells. The liquid-cooling system in the initiating container was also turned off during the test (the coolant was present but not circulating). During the test the four doors of the battery cabinet and the ventilation vent windows were open and the fan was off.

While the entire test ran for about 16 hours, the majority of visible burning took place for approximately 5 to 6-hour period from when the initiating cell was deliberately pushed into thermal runaway to the time when there was no visible fire or burning on the initiating container. During the test, the combustion gases were captured by a hood powered by a fan with the maximum capacity of 156 m^3/s. The images below show: (top) an early stage of the BESS flame propagation (approximately 2 hours and 45 minutes after thermal runaway was initiated) and (bottom) the period associated with peak thermal activity (approximately 4 hours after the initiation).

[10] *Id.*

(l) Flame Propagation
[02:47:05]

(aa) Flame Propagation Peak
[04:03:20]

Figure 3-3: Images of flame propagation and visible emissions in different stages of BESS fire

As noted, all cells and the entire contents of the initiating container (A) burned down during the test. Thermal runaway did not propagate to the cells in the adjacent and nearby containers.

Figure 54 – Top view of post test

Enclosure A

Front view

Figure 3-4: Images of the initiating unit after the test

Composition of the exhaust gases was tested by collecting six 1-L bag samples at discrete periods at 15:30, 17:00, 17:30, 18:00, 18:30, and 19:00 local time which appear to correspond to approximately 1 hour, 2.5 hours, 3 hours, 3.5 hours, 4 hours, and 4.5 hours after the start of the experiment. Sampling was done from the gas port on the top of container as illustrated in the figure below. Each 1-L bag sample was collected over a period of 30 to 60 seconds. Concentrations of the gases tested, including HF, HCl and HCN, were reported as relative volumetric (molar) fractions (e.g. ppm and vol.%).

Figure 3-5: Location of sampling port

The flow rates or total volume measurements of the gases released during the large-scale fire test are not available. Ramboll used information on the ventilation system and plume images from the testing report to make a conservative estimate of the maximum flow rate of vented and combustion gases that were released during the BESS fire test. The photographs indicate that through most of the test period, the exhaust gas flow rates were well within the hood capacity (e.g. see top image on **Figure 3-3**). The exception is the period corresponding to and close to the peak flame propagation. During which the fume hood did not appear to effectively handle the total exhaust gases as evidenced by the apparent spill over and accumulation of the visible plume in the test area, accumulation at the test site, and spill over (e.g. see bottom image on **Figure 3-3**). For that period, Ramboll estimated very conservatively, a total exhaust flow rate 3 times the hood exhaust fan capacity (i.e. 468 m^3/s under standard conditions). The total volume of exhaust gases generated during the active test period was estimated by assuming that the maximum flow rate persisted over the entire 6 hours despite the images of the visible plume indicating that the rates were likely substantially below the maximum hood capacity of 156 m^3/s.

The maximum estimated gas generation rate is consistent with an estimate developed using another independent approach. Based on Ramboll’s experience, the total air entrained by uncontrolled fires could be as high as 10, 20 or more times the stoichiometric air. Considering all flammable battery components in the container, Ramboll estimated the theoretical air for the entire event of approximately 155,000 m^3. To account for other uncertainties, including the presence of additional flammable materials in the BESS unit, Ramboll conservatively estimated the total entrained air as being 100 times that of theoretical air (or 15,500,000 m^3 over 6 hours). By assuming a similar volume of gas in the exhaust stream, the average flow rate was calculated as 714 m^3/s over the 6-hour period. This back of the envelope approach yields an estimate which is consistent (the same order of magnitude) as the estimate obtained using ventilation data.

As a final common-sense check, the two estimates were used to calculate the corresponding hood's face velocity (speed at which air is drawn into the hood). Properly designed hoods should operate in the neighborhood of 100 fpm (feet per minute) and up to approximately 350 fpm (for hot sources).[11] For the given hood area (12 m x 12 m) and estimated exhaust flow rates of 468 m^3/s and 714 m^3/s, the calculated velocities are 2,730 fpm and 4,170 fpm, respectively. These values are substantially higher than typical or recommended velocities, suggesting that both flow rate estimates are conservative, even during the peak period when the hood capacity may have been exceeded.

In estimating total emissions from the large-scale BESS fire test, Ramboll applied additional safety factors to account for potential uncertainties associated with the quantification of gaseous species in the exhaust stream. The test report indicates that the reported HF, HCl and HCN concentrations (in ppm) were quantified using the HJ 84-2016 method, which uses ion-based chromatography to measure inorganic ions in water solution.[12] According to Hithium, the recovery rate was close to 100%, therefore, no additional safety factors were included for the mass transfer from gas to liquid. The test report provided only the average concentrations from all 6 samples. Without information on the individual samples, it is not possible to assess the variability in concentrations and emissions on a shorter time scale that is relevant in an OCA. As a result, Ramboll applied an additional safety factor of 6 to the reported average concentrations to estimate the potential maximum concentrations in any of the 6 individual samples. In summary, total emissions and emission factors associated with the burn of the entire BESS container were estimated using the reported average concentrations adjusted up by a factor of 6 and the conservative flow rate estimate of 468 m^3/s assuming they persisted for the entire 6-hour period considered.

3.2 Wood County BESS Project Report (Reference 16)

The second UL 9540A test that included sampling of the same three species HF, HCl and HCN is a test for the battery model considered for the proposed Wood County battery energy storage system in Wisconsin. The report is hereby referred to as the "Wood County BESS Report". The test included two racks (units), an initiating and an adjacent target rack. Each rack was equipped with 41 modules (70 kg per module) with each module containing up to 10 cells (5.4 kg/cell). The test was performed indoors with two racks staged "back to back". A heater was used to force two cells in the initiating module into thermal runaway. While all cells in the initiating module were destroyed due to thermal runaway, there was no propagation to the adjacent or nearby modules. The entire test lasted for approximately 2 hours and 40 minutes. In this test, the composition, velocity, and temperature of the vent gases were measured within the calorimeter's exhaust duct. Gas composition was monitored using a Fourier-

[11] "ACGIH, Industrial Ventilation: A Manual of Recommended Practice for Design, 31st Edition.

[12] China Standard Store. HJ 84-2016 English Version. Available at: https://www.chinastandard.net/i/HJ84-2016.html

Transform Infrared Spectrometer. The reported total cumulative volumes of the gases generated during the test were calculated by integrating the respective flow rates.

As seen from the description, the scale of the test and the induced thermal runaway is limited to a single (70 kg) battery module. Most of the UL 9540A tests reviewed by Ramboll are of a similar general design and have similar outcomes where the test is limited only to the total destruction of a single module. Although these tests are not entirely representative of large-scale BESS fires, they are relevant because the tested batteries are representative of those used in BESS installations. Furthermore, the capture, characterization, and quantification of the generated gases and emissions from indoor controlled standardized tests conducted at a smaller scale tend to be more reliable than in large-scale open-fire tests.

3.3 Other Studies

In addition to the UL9540A test reports, Ramboll also identified and reviewed approximately 90 new research papers and technical documents which refer to LiB batteries and emissions from battery fires that were not included in the review presented in 2024 Vistra Report. A large portion of these documents were found to discuss emissions from LFP battery fires in general terms without providing any original data from battery testing. Of the 90 documents, approximately 30 were identified to include some original testing data that could be potentially used to derive emission estimates. From those 30 papers, only 12 contained information for LFP batteries. And further of the 12 LFP subset, only 9 documents (References 17,18, 21-24, 26-28 in **Table 3-1** and **Table 3-2**) had sufficient information to derive emission factor estimates for LFP batteries and focused on the compounds of interest. The remaining references (approximately 20 research papers) either did not contain original data or did not include sufficient information to calculate emission factors for the species of interest.

As noted above, many of the newly reviewed studies including References 17, 18, 24, and 28 involved bench-scale experiments. The studies evaluated at least one of the target contaminants, but the individual cells and/or type and size of cells may not necessarily be representative of a utility-scale BESS application. In this case for example, the tests included individual cells with LFP chemistry, such as pouch or cylindrical batteries (such as those used in a remote controller) with weights in a range between 38 g and 76 g per battery. The scale and size, and nature of these tests are obviously not representative of BESS installations or resulting fires. The type, size, and design of such batteries and in particular the different surface-to-volume ratio of small batteries, can have material impact on the thermal runaway dynamics, speciation, and relative contribution of releases associated with battery components vs. battery casing. Despite the obvious differences between these batteries and those used in BESS installations, the emission factors from these studies were reported with an intent to be used when more representative estimates are not available.

As noted earlier, the emission factors derived from the tests that involved burning bulk electrolytes may not be representative of those associated with actual battery thermal runaway (see Reference 11 and Reference 24). The results from these studies are included for informational purposes because the electrolytes tested ($LiPF_6$ and LiFSI) are used in LFP batteries. These estimates could potentially be used in situations where more representative battery tests are not available.

The primary goal of this review was to identify and present the new and original work for the emissions from LiBs with a focus on LFP chemistry. Reference 19, a review paper by Rappsilber et al., is an exception, as it was briefly addressed in the 2024 Vistra Report. Having been published and identified by Ramboll only shortly before the 2024 Vistra Report was released, a fuller consideration was warranted. Rappsilber et al., produced a meta-study that included a comprehensive review of the published literature and data on gaseous emissions from various types of LiB fires. It provides a summary of LiB tests from 76 research papers from the 2000 to 2021 period studying potential emissions from battery thermal runaway events. Based on Ramboll's review of the supplementary material provided with the paper, 21 of the studies included some testing of LFP batteries, 9 of which included quantifiable emission factors for the species of interest. Note that some of the emission factors reported in the review paper were derived by the authors using available information from the referenced studies. Four of these studies have been already identified in **Table 3-1** and **Table 3-2** as References 3, 7, 9, and 13.[13] The remaining 5 studies reported emission factors for HF only.[14] These studies did not include sufficient information to derive emission factors on mass basis. For information, the range of emission factors from these 5 studies (in mg/Wh) were included in **Table 3-1** under Reference 19 (column Additional Information). Note that for this type of application, i.e., estimating emissions from large-scale BESS fires and/or worst-case release scenarios, Ramboll considers mass-based emission factors more appropriate than those based on the battery energy capacity.

As summarized in **Table 3-1**, the current review has shown that there is still a very limited number of studies, in particular those representative of BESS battery systems and associated fires, that reported emissions for the contaminants of interest. After removing data for other LiB types, Ramboll has so far identified 18 studies with sufficient information to derive emission factors on a mass basis for some or all of the species of interest. Within this limited set of studies, there is still a considerable range and variance in the estimated emission factors from LFP battery fires due to a battery state of charge, cell geometry, type of abuse, atmospheric conditions, and other factors. For example, References 2 and 3 show that LFP pouch cells result in higher HF emissions relative to LFP cylindrical (References 6, 17, and 18) and prismatic cells (Reference 16). Specifically, the maximum emission factor for HF reported in Reference 24 for a pouch cell (38 g/cell) was 11,500 mg/kg, which represents the overall maximum emission factor for HF reported in all references reviewed. Reference 2 also produced a similar emission factor for HF for a pouch cell (1,227.6 g/cell) of 11,320 mg/kg. For comparison, the emission factor for HF for a cylindrical cell (734.8 g/cell) reported in Reference 2 was 2,994 mg/kg. Similar observations were reported in Reference 3, which tested emissions of HF for pouch and prismatic LFP cells. While Reference 3 did not include sufficient information to derive emission factors on a mass basis, the reported emission factors in mg/Wh indicate that HF levels measured for LFP pouch cells were systematically higher than those for prismatic cells. Specifically, the reported HF emission factor ranged from 56 mg/Wh - 203 mg/Wh for pouch cells and 21 mg/Wh - 40 mg/Wh for prismatic. Note that most

[13] Emission factors for References 7 and 9 are already presented in **Table 3-1** per unit mass basis (mg/kg battery). Note that Ramboll included References 3 and 13 in the original literature review (2024) because they contained some relevant information on thermal runaways and associated emissions although the emission factors from the two studies were not reported due to lack of sufficient information to convert the measured data to emission factors in mg/kg (Reference 3) or in mg/kg or mg/Wh (Reference 13). In spite of that Rappsilber et. al. reported emission factors for HF, HCl and HCN from Reference 13 in mg/Wh. Our review of the supplementary material indicates that the authors likely made some assumptions on the battery types and energy capacities (which were not provided in the original report) to make these estimates. For this reason Ramboll does not consider the emission factor estimates reported by Rappsilber for Reference 13 reliable.

[14] While some of these studies were known to Ramboll at the time of the original review in 2024 they were not included in **Table 3-1** and **Table 3-2** for varied reasons including that they could not be converted to mg/kg basis and/or the magnitude of the emission factors was relatively low in comparison to the factor already that point.

of the more recent BESS projects, including the one now proposed by Calpine, utilize the prismatic LFP cell type.[15]

References 21 to 23, 26 and 27 also involved bench-scale experiments, but the size and capacity of batteries tested may be closer to the batteries employed in a utility-scale BESS. However, even within this subset, some of the battery types evaluated are not necessarily representative of those used in BESS applications, such as automotive and/or cylindrical battery types that were evaluated in References 26 and 27.

Considering the species of interest and their representation in the literature review, Ramboll was able to identify and derive emission factors on a per mass basis for all species with exception of NO_2. While a number of studies monitored NO_2 concentrations (e.g. References 13, 19, 20 and 26) none of them included sufficient information to derive emission factors. However, two of those studies that reported data on NO (Reference 11 and Reference 21) could be potentially used as a point of reference and/or surrogate for emission factors for NO_2 considering that NO generation rates on volumetric basis (in BESS and more broadly in other fires) are typically higher than that of NO_2 (as also evidenced by the NO and NO_2 concentrations reported in Reference 20).

Carbonyl fluoride is another species with limited data with a single emission factor estimate available (Reference 28). Phosphoryl fluoride and acrolein have two emission factor estimates each.[16] All other remaining species of interest have three or more emission estimates.

3.4 Emission Factor Selection

In general, the emissions used in an OCA should be representative of the reasonable worst-case release scenarios in the event of a maximum credible fire event. There are several factors to consider when selecting appropriate emission factors, such as data representativeness, reliability, and conservatism. One of the main challenges associated in selecting emission factors in this instance is that the published data, as shown in **Table 3-1**, represent a very diverse data set with estimates for some contaminants varying many orders of magnitude. The level of variability in reported emission factors is not surprising considering the large number of variables that could potentially influence emissions associated with battery thermal runaway.

Ramboll proposes a tiered approach to select an emission factor for each compound. The first step involves screening of the emission factor database (**Table 3-1**) for the estimates associated with the battery categories representative of BESS applications, such as LFP prismatic cells with individual cell mass 1 kg or higher. From the given data set, the maximum emission factor should be selected due to its size and uncertainties surrounding the available data. If the literature values are not available for the representative BESS battery type, the emission factor will be based on the maximum reported value from all available studies. Using this general approach, Ramboll produced a list of the recommended emission factors for use in an OCA presented in **Table 3-3**.

[15] TUV, 2023. Test report number: CN244DBX 001. Client reference number: 2347845. Client: Xiamen Hithium Energy Storage Technology Co., Ltd.

[16] NO, PM_{10} and TSP fractions are also among the contaminants with two emission factor estimates each. Ramboll understands that they are not of interest at this time but were included to the current review for information and context.

Table 3-3: Recommended emission factors for an OCA of BESS fires

Species	Emission Factor [mg/kg of battery]	Basis
HF	1,537	Maximum of the studies involving representative LFP cell size and geometry (prismatic) (Reference #9, #15 and #16 and #21)
HCl	2,575	Maximum of the studies involving representative LFP cell size and geometry (prismatic) (Reference #9, #15 and #16 and #21)
HCN	840	Maximum of the studies involving representative LFP cell size and geometry (prismatic) (Reference #9, #15 and #16 and #21).
SO_2	820	Maximum of all battery studies reviewed (Reference #21).
NO_2	2,400	Due to the limited data on NO_2 emissions one may consider using the maximum estimate for NO from Reference #21 (495 mg/kg) which is equivalent to NO_2 emission factor of 759 mg/kg, and applying a safety factor of 3 (e.g. 3x800 mg/kg).
$PM_{2.5}$	2,285	The only value reported for the representative batter cell size and geometry (prismatic) (Reference #27).
C_4H_4O	748	Maximum of the two available studies (Reference #18 and #28).
CH_2O	416	Maximum of the two available studies (Reference #18 and #28).
POF_3	496	Maximum of two studies (Reference #11). Note that the study quantified emissions from burning electrolyte. The other study (Reference #3) that evaluated unspecified LFP battery size reported concentrations below detection limit.
COF_2	40	The only value reported for any batter type (Reference #28).

4 Closing Remarks

Ramboll conducted a comprehensive review of the data available in the public domain to evaluate and characterize emission factors for the various compounds of interest potentially associated with an LFP battery thermal runaway. The current review identified limited new information pertaining specifically to the emissions from utility-scale BESS fires. Ramboll proposed a tiered approach to select the most conservative and representative emission factor for each compound. In some instances, when no representative data for a BESS application was available, the estimates were based on the maximum reported value from all LFP battery studies. The maximum emission factor estimates for LFP BESS fires are presented for consideration in the worst-case scenario for offsite consequence analysis.