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Dust Explosion Risks in Battery Recycling

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Executive Summary

Combustible dust hazards remain a persistent threat across various industries, as dust is an inevitable byproduct of many processes. Managing combustible dust hazards at the battery recycling plants is one of the key factors to minimize the incidents and down time and, therefore, to improve the work environment, and to increase the profitability of the business. The present work aims at exploring the dust explosion risks of black mass in battery recycling. Four black mass samples are investigated. Microscope images, particle size distribution, water content and organic carbonates are analyzed. Dust explosion experiments are performed in a 20-L vessel. Results show that a 10 kJ ignition energy cannot generate high explosion overpressure, whereas an ignition energy of 20 kJ yields an explosion overpressure above 6 bar. The experimental results are compared with published data on various explosion-related characteristics of other dusts in battery recycling, in particular, aluminum and graphite dusts.

Keywords: dust explosion, lithium-ion battery, recycling, black mass, process safety.

1 Introduction

Combustible dust hazards remain a persistent threat across various industries, as dust is an inevitable byproduct of many processes. While a fire needs fuel, oxygen, and an ignition source, a dust explosion requires two additional elements: particle dispersion and confinement. A dust explosion occurs when fine combustible particles, mixed with the air reaching an optimal concentration in an enclosed equipment, are ignited, resulting in a violent and explosive combustion. Incidents statistics collected by Yuan et al. [1] reveal a strong link between dust explosion occurrences and industrial activities. As the battery recycling capacity is expected to grow exponentially in the coming years, managing combustible dust hazards at the battery recycling plants will be one of the key factors to minimize the incidents and down time and, therefore, to improve the work environment and to increase the profitability of the business.

This paper (i) provides a concise overview of the lithium-ion battery (LIB) recycling process, (ii) evaluates the risks of dust explosions associated with recycling operations, (iii) reviews documented dust explosion incidents in the battery industry, (iv) specifies personal protective equipment required for conducting related experiments, (v) characterizes the material properties of battery recycling materials, focusing on four types of black mass derived from Nickel-Cobalt-Manganese (NCM) battery chemistry, (vi) presents findings from dust explosion experiments conducted with the black mass, and (vii)

compares the dust explosion parameters of the black mass from this study with those of graphite and aluminum dusts reported in the literature. This work builds upon a completed project report (in Swedish) [2] and a journal article [3].

2 Lithium-ion battery recycling

The growing number of LIBs in various applications presents a serious waste-management challenge at the battery end-of-life (EoL). Furthermore, the pressing need for battery recycling has become increasingly evident due to the significant social, economic, and environmental issues associated with the mining of critical raw materials for batteries, including lithium, cobalt, nickel, and graphite [4]. For instance, lithium mines in South Africa consume the limited water resources, which pose a negative impact on the local farmers. The production of a ton of lithium requires 1 900 tons of water [4]. Furthermore, chemicals used for processing lithium contaminate the water, soil, and air [5]. When compared to lithium, cobalt is considered to be more dangerous for creating bottleneck for electrification. Huge quantities of cobalt are found in geopolitical unstable regions like Democratic Republic of Congo. Cobalt can harm the eyes, skin, heart, and lungs and can cause cancer. Unsafe work conditions and employment of child labors by small-scale mines raise serious ethical concerns of cobalt mining.

To build a sustainable and globally competitive battery value chain, the European Commission proposed a new battery regulation aiming at making batteries long-lasting, safe and sustainable [6]. In particular, the EU is promoting battery recycling through the newly approved Regulation 2023/1542, which replaces the current Battery Directive (2006/66/EC) governing batteries in the EU [7]. With the help of this new legislation, future batteries should have less of an impact on the environment, include fewer hazardous compounds, use fewer raw materials from non-EU nations, and be collected, reused, and recycled mostly within Europe. For instance, starting in 2027, industrial batteries, electric-vehicle and automotive batteries will be required to declare the content of recycled cobalt, lead, lithium and nickel. By 2030, these batteries will have a compulsory minimum recycled content of metal, i.e., 12 % cobalt, 85 % lead, 4 % lithium and 4 % nickel.

Historically, the primary goal of LIB recycling has been to recover cobalt due to its high value [8]. Yet, interest in recovering additional materials has increased as cobalt content in batteries decreases and obligatory recycling regulations requiring recovery of materials to a higher degree come into effect in the EU [7].

The battery recycling technology has been continuously evolving depending on the materials sought for recovery. Currently, the EoL LIBs are recycled through three main process types including (i) pyrometallurgy via smelting, (ii) hydrometallurgy through leaching and (iii) direct recycling using physical processes [8-10]. Pyrometallurgy uses high temperature to convert metal oxides into metals or mixed metal alloy [8]. This process is characterized by high energy consumption and low material yield. Other materials like aluminum, graphite, and organic solvents are generally not recovered [8]. Hydrometallurgy uses acids to extract metal ions out of the cathode materials, and then extracted using organic solvents [8,9]. Direct recycling separates different components of the active material powder from shredded cells by physical process with minimal treatment and avoiding chemical alterations [8]. The dominant recycling technique in Sweden consists of preprocessing or pretreatment of LIBs; see Fig. 1. A final product, black mass, which contains relatively high concentrations of precious metals and graphite, and a granular material made up of the shredded cathodes and anodes of the batteries, is obtained for further hydro- or pyrometallurgical extractions.

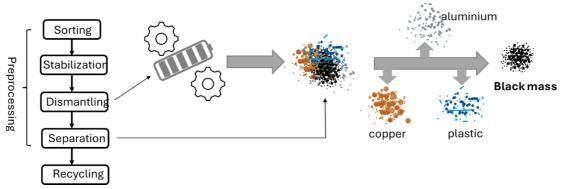


Figure 1: Overview of the LIB recycling process, adapted from Ref. [10].

3 Dust explosions

A dust explosion occurs when fine combustible particles, thoroughly mixed with the air in an enclosed equipment, are ignited, resulting in a violent and explosive combustion (see Fig. 2) [11]. To start a fire, it requires a fuel (dust), oxygen, and an ignition source. However, a dust explosion requires two more elements to occur, i.e., dispersion and an enclosure; see Fig. 3. In a preprocessing or mechanical recycling process, there are many steps that involve handling of combustible dust (see [10] and Fig. 1). For instance, the dismantling process involves mechanically dismantling the battery packs by ripping, shredding, crushing, and milling into a black material of varying sizes and shapes. Further on, materials such as plastic, steel, aluminum, and copper, are separated from the black material by various techniques such as sieving, magnetic, electrostatic, eddy current and gravity density separations [10]. The final product black mass is obtained for further extractions. The composition of black mass varies widely due to differences in feed material and shredding processes, with no standardized composition.



Figure 2: A vented dust explosion in an industrial-scale vessel, used under Creative Commons CC-BY license [11].

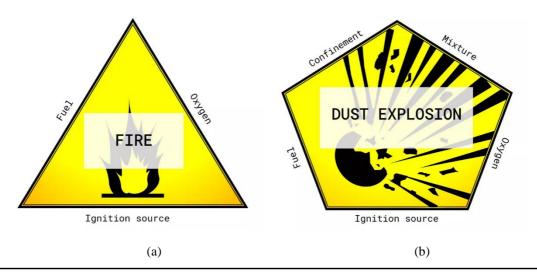


Figure 3: Illustrations of (a) a fire triangle and (b) a dust explosion pentagon, adapted from Ref. [15].

Safe operation at a battery recycling plant is crucial for the battery business to comply with the latest EU regulations. From the public perspective, dust is seldom considered to be a cause of explosion when compared to solid explosives, e.g., Trinitrotoluene (TNT), flammable gases or pressurized vessels. However, according to the Swedish Work Environment Agency's statistics, 237 incidents related to combustible dust were reported during 2012 – 2017 [12]. Nessvi and Persson [13] estimated that the frequency of dust explosion incidents in Sweden was once per week, a significant increase compared to the previously reported frequency of once per month, as indicated by the Swedish Work Environment Agency's statistics. Therefore, it is crucial to identify the dust explosion risks for the battery recycling plants, such as in the conveyer belt, mill, drying equipment, dust collector, etc. Also needed are mitigation strategies such as placement of detectors for spark, ATEX (European Directives for controlling explosive atmospheres) approved equipment, and cleaning routine. Furthermore, to properly design explosion protection equipment, it is necessary to know the dust explosion characteristics. Last, other factors are as equally important as technical solutions, such as (i) ensuring lessons learned through educations, (ii) willingness of understanding root causes of incidents instead of blaming human errors, (iii) correct common cultural errors such as suppressing bad news, lowering incident severity categorization, and so on [14].

4 Incidents related to combustible dust at battery recycling plants

The LIB recycling industry is a new and quickly expanding business in Sweden as well as in Europe. Incidents statistics collected by Yuan et al. [1] show that dust explosion incidents are in close relationship with industrial activities. As the Swedish battery recycling capacity is expected to grow exponentially in the coming years, managing combustible dust hazards at the LIB recycling plants will be one of the key factors to minimize the incidents and down time and, therefore, to improve the work environment, and to increase the profitability of the business. For instance, an explosion occurred at an old battery recycling plant of Contemporary Amperex Technology Corporation (CATL) with a capacity of 15 000 ton/year for battery ternary precursors on January 7th, 2021. It was unclear if the explosion was directly related to combustible dust. However, according to the recycling firm, the explosion was caused by waste aluminum foil caught fire in a garbage dump. The blast generated a mushroom cloud in the sky that could be seen from several kilometers away. The incident led to one fatality and 20 injuries [16, 17]. Another incident involved a 25-year-old man who sustained serious injuries during an explosion at a battery factory in northern Sweden on November 4th, 2023. The explosion took place during maintenance work on a cleaning equipment. The injured individual passed away more than one month later in the hospital. Investigations revealed that the explosion was linked to aluminum dust [18].

There are many challenges in obtaining relevant dust explosion incidents data. Andrew Hopkins, emeritus professor at the Australian National University, has long experience in industrial safety and accident analysis. In an interview with Trish Kerin, director of IChemE Safety Centre, Andrew listed two most disheartening behaviors in dealing with chemical incidents [14]. First, some companies invested significant effort in justifying why an incident should be categorized as lower severity, rather than focusing on resolving the issue promptly. The second behavior is suppression of bad news. Accidents with less damage tend to be neglected and therefore are not reported to the related agencies [1]. Moreover, the fire brigade tends to classify the reported incidents as a fire instead of an explosion [12]. Nevertheless, there are some sources where we can learn incidents data. For instance, the U.S. Chemical Safety Hazard and Investigation Board (CSB) incidents database contains valuable incident investigation reports regarding combustible dust hazards [19]. Furthermore, an online database contains recent dust explosion incidents [20]. Currently, there is a very limited amount of reported and identified incidents directly linked to combustible dust in the context of LIB recycling. The reasons may stem from the fact that this is a new business, and underreporting challenges mentioned earlier.

5 Personal Protecting Equipment (PPE) for handling black mass

Risks associated with handling of black mass for performing chemical analysis and dust explosion experiments are multiple. The primary risk is the inhalation of carcinogenic black mass dust particles. In general, the black mass contains 20 - 50 % cathode active powder, 25 - 50 % anode active powder, and

a limited amount of other materials including copper, aluminum, organic solvents, lithium hexafluorophosphate (LiPF₆), polyvinylidene fluoride (PVDF), etc.; see a sample of black mass in Fig. 4. For instance, batteries with Nickel-Manganese-Cobalt (NMC) chemistry are generally noted as NMCabc, e.g., NMC111 or NMC811, representing Li(Ni_xMn_yCo_z)O₂, where x + y + z = 1 and x = a/(a + b + c), y = b/(a + b + c), z = c/(a + b + c), respectively [7]. Accordingly, the cathode active powder for NMC chemistry is lithium-nickel- manganese-cobalt-oxide, which is a carcinogenic substance.

Another risk is the production of hydrogen fluoride (HF) when black mass is heated. HF is an extremely toxic and corrosive gas and liquid. It is a weak acid. In the gaseous form, it is a colorless with a strong irritating odor. It can react with moisture and fat of the skin, penetrate the tissue, react with calcium, and result in severe burns. When in contact with eyes, it can cause blindness. Occupational Safety and Health Administration (OSHA) limit of HF is 3 ppm averaged over an 8-hour work shift.



Figure 4: A sample of black mass.

There is a small amount of LiPF₆ in black mass, i.e. less than 5 % by weight according to the black mass safety datasheet from the supplier. LiPF₆ is thermally stable up to 107 °C [21]. In the presence of water, the decomposition onset temperature is lower, around 87 °C. The HF generation reactions are [21, 22]:

$LiPF_6 \rightarrow LiF + PF_5$	(1)
$PF_5 + H_2O \rightarrow POF_3 + 2HF$	(2)
$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF$	(3)
$POF_3 + H_2O \rightarrow POF_2(OH) + HF$	(4)

Since this was the first time the authors handled black mass, a comprehensive PPE and safety procedure was adopted at the first time of the dust explosion experiments. The PPE includes (i) disposable overall, (ii) battery powered air purifying respirators with helmet with filters, (iii) disposable nitrile gloves, (iv) portable gas detector for HF, and (v) calcium gluconate gel in case of skin exposure; see Figs 5 and 6. Furthermore, the first experiments were performed after normal working hours to minimize the risk of exposure of hazardous particles and gases to unprotected workers.

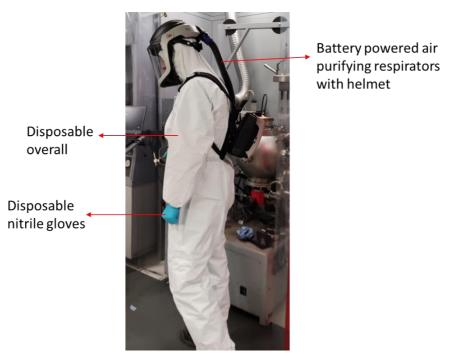


Figure 5: A technician wears PPE during experiments.



Figure 6: A portable gas detector for HF in (a), and calcium gluconate gel in case of skin exposure for HF in (b).

Table 1 shows the large and small respiratory protection equipment used in the experiments. The larger respiratory protection equipment is the same one as the technician wore on his body in Fig. 5. Note that the discussion of detailed categories of respiratory protection equipment is beyond the scope of this work, and only a general description of filter types is listed in Table 1.

Table 1: Two types of respiratory protection equipment used during the experiments.



^{*}A: color code Brown, against certain organic gases and vapors with a boiling point higher than 65 °C.

Hg: color code red, against metallic mercury.

P: color code White, particle filters.

The first experiments were performed outside the normal work hours, after 16 o'clock. Gas detector for HF did not alarm for any dangerous levels. Therefore, in subsequent experiments, normal working clothes were used without disposable overall. A smaller mask (see Table 1) was used in combination with the larger one to allow for easy movement during the work. The experiments were performed during normal working hours, but the lab area was isolated to avoid unprotected workers coming close.

6 Black mass samples

Four types of black mass material were provided by two battery recycling firms. These samples were obtained in mechanical processes using batteries associated with NCM chemistry. In the following, the samples are named A, B, C, and D. The first three samples were provided by one battery recycling factory and sample D was given by another battery recycling facility. Before explosion tests, certain material properties were measured.

Black mass was investigated using a stereo microscope from Olympus SZX 16. The obtained microscope images show that samples from one recycling plant contain large pieces of particles, probably copper and aluminum foil; see Fig. 7.

B: color code Grey, against certain inorganic gases and vapors (excluding CO).

E: color code Yellow, against sulfur dioxide and other acidic gases and vapors like HF.

K: color code Green, against ammonia and organic ammonia derivatives.

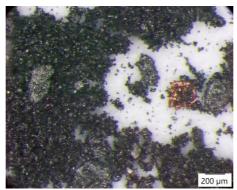


Figure 7: Microscope images of one black mass sample.

Particle size distributions were measured using traditional sieving method with sieve mesh sizes of 20, 32, 63, 75, 125, 180, 250, 350, 500 μ m. Here, D_{10} , D_{50} , and D_{90} represent the particle diameters associated with 10%, 50%, and 90%, respectively, of the total particle mass, e.g., the mass of particles smaller than D_{10} is equal to 10% of the total mass. Moreover, the following parameter

$$\sigma_d = \frac{D_{90} - D_{10}}{D_{50}} \tag{5}$$

represents the span of a particle size distribution.

The water content (weight) in the samples were determined using a Karl-Fischer Titration method. The organic solvents may also exist in black mass as impurities and may influence the dust explosion characteristics. The black mass underwent extraction using dichloromethane (DCM) and was subsequently subjected to Gas Chromatograph Mass Spectrometer (GCMS) analysis. The characteristics including particle size, water content and organic carbonate content of the samples were reported in Tabel 2.

Table 2: Characteristics of particle size distributions, water contents and ethylene carbonate contents.

Parameters	Sample A	Sample B	Sample C	Sample D
D ₁₀ [μm]	12.76	3.55	12.62	11.90
D_{50} [μm]	32.00	20.18	37.16	23.40
D ₉₀ [μm]	140.40	97.67	163.66	45.11
σ_d [-]	3.99	4.66	4.06	1.42
Water content [weight %]	0.70%	0.36%	0.19%	0.36%
Ethylene carbonate [weight %]	2.99 %	0.014 %	_	3.00 %

7 Dust explosion experimental setups

The dust explosion experiments were conducted in a 20 L vessel, as sketched in Fig. 8. First, a vacuum pressure of -0.6 bar gauge was created by evacuating air from the spherical vessel. Second, the dust sample was loaded into a pressurized container at 20 bar gauge. Third, the dust was injected into the spherical chamber via a fast-actuating valve and a rebound V-shape nozzle. After the dust injection, a relatively homogenous dust-air cloud was formed and the pressure within the vessel stabilized at approximately 1 atm. Fourth, pyrotechnical igniters were employed to ignite the dust cloud after a variable ignition delay time, i.e., time interval between the dust injection and ignition. Fifth, the pressure curve P(t) was recorded using dynamic pressure sensors. Finally, the rate of pressure rise was calculated by differentiating P(t).

8 Results and discussions

Different parameters including material, dust concentration, ignition energy, and ignition delay, were varied to study black mass dust explosion. Totally, around 70 experiments were performed in the 20-L vessel. Only a summary of results is presented here, and the readers can refer to Refs. [2, 3] for more detailed results.

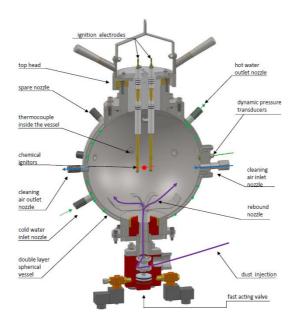


Figure 8: 20-litre spherical vessel.

Black circles in Fig. 9 (a) show that black mass dust explosion experiments with the 10 kJ ignitor have yielded an overpressure around 1 bar for all studied samples, thus, indicating weak explosion process. On the contrary, the 20 kJ ignitor is able to initiate sufficiently intense combustion of black mass, which yields a relatively high explosion overpressure; see red squares in Fig. 9 (a), with dependence of the maximum explosion overpressure on dust concentration being typically of a parabolic shape. However, a further increase in the ignition energy weakly affects P_{max} for sample C, cf. red squares and blue diamonds. Dependence of the deflagration index, $K_{St} = (dP/dt)_{\text{max}}V^{1/3}$, on dust concentration also has a parabolic shape when using the 20 kJ ignitor; see Fig. 9 (b).

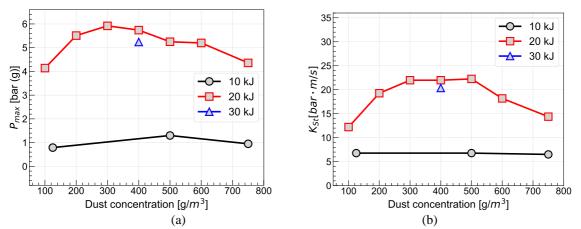


Figure 9: Maximum explosion overpressure (a) and deflagration index (b) versus concentration of black mass sample C at different ignition energies.

9 Comparison with other dusts

Comparison among black mass, graphite, and aluminum dust explosion parameters is shown in Fig. 10. Note that P_{max} and K_{St} are average values of 35 graphite dust samples and 107 aluminium dust samples. For black mass dusts, a relatively low ignition energy, i.e., 10 kJ, generates mild explosions, which means low values of P_{max} and K_{St} ; see dark blue circles in Fig. 10. However, a relatively high ignition energy, i.e., 20 kJ, generates high explosion overpressures, around 6 bar for black mass sample C; see Fig. 10 (a). Aluminum dust is the most hazardous dust among the three, with an average P_{max} being 9. 8 bar and an average K_{St} being 263 bar·m·s⁻¹. Note the logarithmic scale of the ordinate axis in Fig. 10 (b).

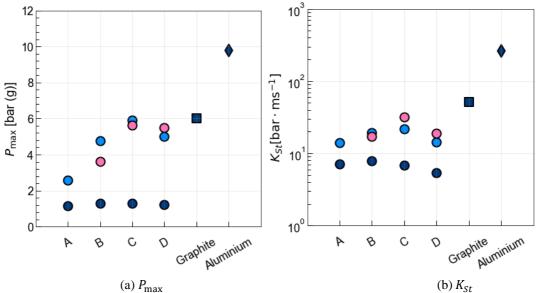


Figure 10: Comparison of dust explosion characteristics P_{max} and K_{St} among four types of black mass, A, B, C, D, graphite [23-26], and aluminum [15, 23, 24, 27].

10 Conclusions

Four black mass samples from different battery recycling plants were analysed to obtain dust sample microscope images, particle size distributions, water contents and organic solvent contents. Subsequently, dust explosion experiments were performed in a 20-L vessel by varying the dust concentration, ignition energy, ignition timing, and dust injection pressure. Results show that an ignition energy of 10 kJ is not sufficient to generate a high explosion overpressure, whereas an ignition energy of 20 kJ can yield an explosion overpressure above 6 bar for black mass sample C at a concentration of 300 g/m³. So high ignition energy could be released during hot works like welding, fire, gas explosion due to smoldering or battery failure. Comparison of dust explosion characteristics measured for black mass samples in this study with the counterpart characteristics for graphite and aluminum dusts, taken from the literature was carried out. The aluminum dust generates the highest explosion overpressure and deflagration index among these dusts, indicating the highest risks in the battery recycling plants.

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Presenter Biography



With a solid background and extensive experience in simulations using numerical tools, particularly Computational Fluid Dynamics (CFD), encompassing areas such as chemical kinetics, combustion, multi-phase flow, turbulence, and more. Proficient in both commercial and open-source CFD codes, as well as commercial multi-physics codes and open-source data analysis tools like Python. Holds a PhD in thermal and fluid dynamics awarded in 2014 from Chalmers University of Technology. Possesses a keen interest in combustible dust safety and occupational safety. Considerable experience in battery fire and thermal propagation simulations.