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Metal Dusts Explosion Hazards and Protection

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Many industrial processes handle, use, or produce metallic particles small enough to explode in air, thus posing severe explosion hazards. Finishing operations, for example, create very fine particles and have been involved in a growing number of accidents in recent years. New emerging processes, such as 3D printing, are being rapidly developed and directly use micrometric particles to create complete objects by welding layers of material together. Finely divided metals also enter into the composition of plastics, rubber, fibers, paints, coatings, inks, pesticides, detergents, and even drugs; additionally, they are used as catalysts for major industrial chemical reactions, and are even being explored as possible clean alternatives to fossil fuels.

Metal dusts are of special concern due to their peculiar combustion properties, including their higher heat of combustion and pyrophoric nature,. As a result, metal dusts explosions are often much more devastating than explosions involving organic materials. Additionally, due to their high reactivity, many fine and most ultra-fine metal powders can burn in carbon dioxide, water vapor and even nitrogen. Whereas preventive measures may reduce explosion risks efficiently, they rarely are sufficient to eliminate explosions completely, especially when dealing with highly reactive metallic particles. Therefore explosion protection measures usually also need to be considered. The high energetic content of metal dusts poses new challenges to conventional explosion protection systems in terms of robustness and response time. This paper reviews the special hazards of metal dusts and presents the state-of-the-art in terms of explosion protection.

1. Introduction

Metal dusts are a particular class of combustible dusts (Taveau, 2014) as they encompass a large family of energetic materials with diverse explosion sensitivity and severity properties (Table 1). Specifically, metal dusts exhibit higher (adiabatic) flame temperatures ($T_{f,ad}$) than organic dusts, but either lower or higher maximum explosion pressures (P_{max}) and deflagration indexes ($K_{St} = (dP/dt)_{max}V^{1/3}$) depending on the reactivity of the metal involved, the particle size distribution and the presence of an oxide film. In this regard, metal dusts can be classified in first approximation as normally reactive (e.g. iron, steel, zinc), highly reactive (e.g. silicon), or extremely reactive (e.g. aluminium and magnesium), with a corresponding hazard class ranging from St_1 to St_3. In addition to be more reactive, fine metallic particles can be very sensitive to ignition sources (i.e. require very low amount of energy to ignite and start burning). Ultrafine particles (< 1 µm) can even be pyrophoric, i.e. they spontaneously burn when in contact with the air. Fine particles of aluminum, for example, can exhibit high K_{St} (> 300 bar.m/s) and P_{max} (> 10 bar) values corresponding to a St_3 classification, and low minimum ignition energy (MIE < 10 mJ), making difficult the prevention and mitigation of such deflagrations.

The combustion of metal dusts occurs via mechanisms different from those of organic powders. Since most metal powders nearly instantaneously oxidize in contact with air, forming a chemically inert metal oxide layer, both the volatilities of the metal and the relevant metal oxide(s), expressed by their melting and boiling points, these with respect to the flame temperature, need to be considered. Ogle (2017) proposes a combustion classification for metals based on these three specific temperatures: low temperature oxidation where the

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products of combustion diffuse to the surface of the burning droplet, and combustion occurs around the solid surface of the material (iron), surface combustion, and finally vapor phase combustion (aluminium, magnesium).

Table 1: Physical properties of selected metal dusts compared to cornstarch (NFPA 484, 2015; NFPA 652, 2019; Eckhoff, 2003).

Material	$T_{f,ad}$ (°C)	K_{St} (bar.m/s)	P_{max} (bar)	ΔH_C (kJ/mol O_2)	Oxidation products
Aluminum	3790	515	11.2	1100	Al_2O_3
Magnesium	3340	508	17.5	1240	MgO
Silicon	2970	126	10.2	830	SiO_2
Iron	2220	50	5.2	530	Fe_2O_3
Zinc	1800	176	7.3	700	ZnO
Cornstarch	~1500	202	10.3	~400	CO_2, H_2O

Metal dust deflagrations have become increasingly common, and have led to severe accidents in recent years (Taveau et al, 2018). Statistics show that they give rise to a higher death rate due to more severe burns caused by the high temperatures of metal dust flames. Aluminum is the most common metal fuel involved in explosions due to its widespread use in the industry, as well as its extreme ignition sensitivity and reactivity when finely divided.

2. Scaling up the severity of metal dusts deflagrations

The severity of dust explosions is often expressed by the deflagration index K_{St} which is the product of the maximum rate of pressure rise in closed vessels and the cubic root of the vessel volume. This so-called cubic law is widely used to design explosion protection techniques.

Previous experimental campaigns (Lunn et al., 1988; Bucher et al., 2012; Taveau et al., 2013) reported by Taveau et al. (2019a) have shown the limitations of standardized explosibility parameters (especially the K_{St} factor) to fully describe metal dusts deflagration severity, particularly in the case of aluminum. Recent closed vessel tests carried out by the authors (Taveau et al., 2019a) with four well-characterized metal powders in a 20-l sphere and in a 1-m^3 chamber have confirmed that K_{St} value is not sufficient to describe the volume dependence of metal dusts deflagration severity (Table 2).

Table 2: Explosibility of metal dusts in 20-l sphere and 1-m^3 chamber

Material	20-l sphere		1-m^3 chamber	
	K_{St} (bar.m/s)	P_{max} (bar)	K_{St} (bar.m/s)	P_{max} (bar)
Cornstarch	206	8.4	214	8.9
Iron	50	3.6	64	4.5
Zinc	68	4.7	97	6.0
Silicon	285	8.0	124	9.1
Aluminum	162	8.0	328	10.1

In fact, K_{St} values of iron, zinc and aluminum powders, can be much more severe when measured in the 1-m^3 chamber compared to values found in the more commonly used 20-l sphere. The K_{St} value of aluminum, in particular, can double in the larger vessel. This has been further confirmed by Puttick (2017). This increase in the larger vessel has been attributed to the effect of thermal radiation (Taveau, 2014), which can be an order of magnitude greater for metal dusts compared to common organic dusts (Taveau et al, 2019a). Since most of combustible dusts in the industry are tested in a 20-l sphere due to cost considerations, this phenomenon can lead to an underestimation of explosion risks, and corresponding undersizing of mitigation techniques. As a precaution, it has been proposed to measure the explosion severity of metal dusts taking the possible effects of scale into consideration by using a chamber whose volume is at least 1-m^3 (Taveau, 2015a; 2015b). This recommendation has already been included in the 2018 edition of NFPA 68 for the most reactive metal dusts, and is being considered for a future revision of ASTM E1226.

3. Explosion protection for metal dusts

The higher reactivity of metal dusts brings new challenges to both passive (venting) and active (suppression, isolation) explosion protection systems. NFPA 484 (2015) just started to include warnings and recommendations for the application of protection techniques to metal dusts deflagrations hazards in its Chapter 9 and Annex A based on some early research presented to the Committee (Taveau et al., 2013; Taveau, 2013). As already discussed in section 2, metal dusts comprise a large family of materials, for which it is difficult to propose common explosion protection design rules. Until clear industry guidelines are issued, large-scale testing constitute an essential step to gain understanding of the specific hazards posed by these different metal dusts in order to adapt conventional explosion protection solutions. Considerations by type of explosion protection technique are presented in the following sections.

3.1 Explosion venting

Explosion venting is the simplest and often preferred approach for the protection of an enclosure against a dust deflagration. It enables pressure developed during a deflagration to be safely released into the environment, preventing the process enclosure from being damaged or destroyed. Key features of a suitable explosion vent panel for metal dusts applications include:

- low and reliable static burst pressure, to ensure the vent will open in the early stages of the deflagration,
- fast opening, to quickly discharge the overpressure created by the deflagration,
- strong design, to avoid fragmentation of the panel during the venting process.

These characteristics can only be fully validated by large-scale testing under realistic deflagration conditions.

Previous experimental campaigns (Moore & Cooke, 1988; Lunn et al., 1988; Taveau et al., 2013; Taveau, 2013) showed that vent area can be underpredicted by NFPA 68 for metal dusts. Recent 2-m^3 vented tests (Figure 1) have confirmed that current NFPA 68 venting equation can underpredict the maximum reduced explosion pressure reached during a vented metal dust explosion, especially when explosibility parameters are determined in a 20-l sphere (Taveau et al., 2019b). Vent areas are, for example, well estimated for cornstarch, but largely underpredicted for iron.

Further experiments in 0.5, 2 and 5.6-m^3 chambers have highlighted a scaling issue associated with the venting of aluminum dust deflagrations, which raises doubts concerning the adequate protection of industrial-scale equipment (Figure 2). The lack of agreement between experimental vent area and estimation using the NFPA 68 equation may be related to the inability of the cubic law to capture the volume dependence of metal dusts deflagration severity that has been previously mentioned in section 2.

Figure 1: Photographs of 2-m3 vented tests with cornstarch, iron and aluminium dusts (Taveau et al, 2019b)

Figure 2: Photographs of a 5.6-m^3 vented test with aluminum powder and obtained vent area ratios (vent area installed for the experiments $A_{v,e}$ divide by the vent area as calculated using NFPA 68 equation $A_{v,c}$) as a function of the test chamber volume for the same aluminum sample (Taveau et al, 2019b)

3.2 Explosion suppression

Explosion suppression is the process of controlling deflagrations, mainly by absorbing the energy produced by the combustion reaction. An explosion suppression system typically consists of a pressure sensor, a control panel, and a high rate discharge (HRD) suppressor. After detection of the pressure waves emitted by the deflagration, suppressant discharge is initiated to extinguish the fireball by reducing the temperature of the combustible dust. Suppression has generally been considered very difficult for metal dusts. Indeed, materials such as aluminum or magnesium exhibit higher rates of pressure rise (i.e. a faster pressure generation and less time available for the suppression system), and also higher flame temperatures (i.e. more suppressant is needed to absorb the heat generated by the combustion reaction).

Few examples of attempts to suppress metal dust deflagrations exist in literature. Bartknecht (1989) reported on the suppression of aluminum dust in a 1-m^3 vessel using Sodium Bicarbonate. At a low aluminum concentration, suppression was effective. However, at concentrations of and above 500 g/m^3, suppression was not successful. Moore & Cooke (1988) investigated metal dust suppression in more details using aluminum flake (K_{St} = 321 bar.m/s, P_{max} = 10.7 bar, dust concentration of 500 g/m^3) in a 6.2-m^3 vessel with a detector activation pressure of 0.05 bar. Various suppressant agents were screened: china clay, copper dust, talc, silicon oil, metal halide, mono ammonium phosphate (MAP), sodium bicarbonate (SBC) and calcium carbonate. Only the last two materials showed some potential, but the final total suppressed pressure (TSP) was still too high (3 bar). Injecting 12.9 kg/m^3 of SBC reduced the TSP to 1.8 bar.

Table 3 summarizes more recent suppression tests carried out with organic dusts (coal, wheatstarch, cornstarch) and metal dusts (silicon, aluminum) in a 1-m^3 chamber. Low TSP were easily achieved for organic dusts and silicon. Aluminum dust deflagrations, on the other hand, were more difficult to mitigate: while TSP was only 0.26 bar for cornstarch (K_{St} = 220 bar.m/s), it resulted in 2.05 bar for aluminum (K_{St} = 300 bar.m/s) with twice the amount of suppressant. A suppressant concentration of 9.1 kg/m^3 was required to reduce TSP_d below 1 bar. Additional tests were performed by a third-party laboratory (FSA) in Germany to study the scalability of suppression in a larger 4.4-m^3 vessel (Figure 3). This experimental campaign provided evidence of the feasibility of aluminium deflagrations suppression, but also stressed limitations in terms of dust concentration and maximum K_{St} (Taveau et al. 2015). A low activation pressure, in combination with an increased concentration of suppressant agent has proven to successfully quench the fireball at its incipient stage and result in much reduced TSP.

Table 3: 1-m^3 chamber suppression tests (Taveau et al., 2013; Taveau et al., 2015).

Material	K_{St} (bar.m/s)	Suppressant concentration (kg/m^3)	TSP (bar)
Coal	100	2.3	0.19
Wheatstarch	150	2.3	0.22
Cornstarch	220	2.3	0.26
Silicon	120	2.3	0.33
Aluminum	300	4.5	2.05

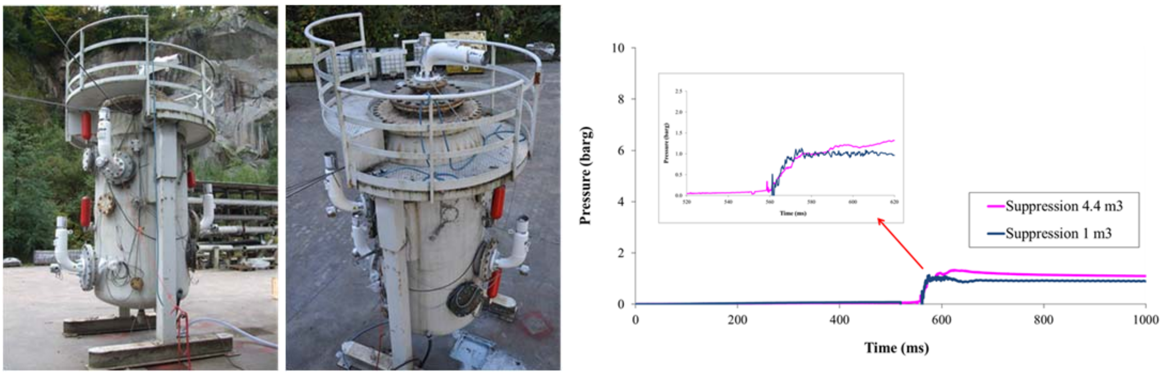

Figure 3: 4.4 m3 vessel (FSA) used for the suppression tests and comparison of the explosion pressure curves from 1-m3 and 4.4-m3 suppression tests with 500 g/m3 of aluminum dust (Taveau et al., 2015)

3.3 Explosion isolation

The use of pipes to connect vessels and convey particulate materials is a common practice in the process industry. Isolation techniques are used to prevent pressure and/or flame travelling from its point of ignition to other parts of the process. This is particularly difficult to achieve when flame speeds and explosion pressures are high as it is the case for metal dusts.

Little has been reported on the propagation or isolation of metal dust deflagrations. Bartknecht (1989) tested an aluminum dust (K_{St} = 625 bar.m/s) at a concentration of 500 g/m^3 in a 400-mm diameter, 30-m long pipe closed at one end. After only 20 m of propagation, the flame speed was already greater than 1,500 m/s and the pressure exceeded 25 bar. Chemical isolation performed well in this pipe using detection at 1 m and an extinguishing barrier at 10 m. Flame did not pass the barrier and pressure was reduced to 3 bar. The suppressant conditions were not specified; however, it appears that 12 kg of MAP were injected. Adding a 2.4-m^3 initiating vessel caused flame jet ignition and a more severe deflagration, with the velocity and pressure exceeding 3,000 m/s and 36 bar respectively at 30 m. Attempts to use mechanical isolation at 10 m or greater led to massive deformation of the gate. The installation of vents, with an area of 4.5 times the cross section of the pipeline, was effective at reducing the pressure at the mechanical valve.

Further tests conducted by Fike Corporation (Going & Snoeys, 2002; Taveau et al., 2013) at DMT GmbH testing site using an aluminium dust with K_{St} > 300 bar.m/s in a 5-m^3 initiating vessel and 400-mm pipe interconnected system indicated that the initial deflagration transitioned into a detonation within the pipe, with pressures up to 30 bar and flame speeds over 450 m/s. The fast acting mechanical isolation valve did stop the explosion flame from propagating down the pipe, however flames escaped through pipe gaskets and valve parts as a result of the excessive heat and pressure. A combined system was developed by adding 2 chemical isolation containers at 4 m from the vessel, each containing 8.2 kg of SBC. This chemical barrier suppressed enough of the flame front so that the pressure at the isolation valves was decreased to an acceptable level, 15 bar, thereby allowing the isolation valve to completely block the flame without being damaged or leaking. More recent tests have been performed using an updated version of the mechanical isolation valve with an even more reactive aluminum dust (K_{St} = 680 bar.m/s, P_{max} = 11.6 bar) in a 1-m^3 contained vessel connected to the 150-mm diameter pipe. The valve was able to stop the explosion both for ignition near pipe and ignition at vessel center, without chemical isolation. Pressure spikes up to 40 bar were measured just in front of the closed valve, but did not damage it. The use of the same valve has also been validated in a 5-m^3 vented vessel connected to a 400-mm pipe representing a typical real-scale explosion scenario in a dust collector (Figure 4).

Figure 4: Mechanical explosion isolation of an aluminium dust (KSt = 450 bar m/s) deflagration initiated in a 5-m3 vented vessel (Taveau, 2017)

4. Conclusions

Our review presents the latest findings related to the evaluation of metal dusts deflagration hazards and the corresponding challenges for explosion protection systems:

- the severity of metal dusts deflagrations does not scale well when using the K_{St} concept and cubic law. The K_{St} value of aluminum, in particular, can double in the 1-m^3 chamber compared to the 20-l sphere. This increase in the larger vessel has been attributed to the effect of thermal radiation which can be an order of magnitude greater for metal dusts compared to common organic dusts. This situation is concerning since it can lead to the undersizing of explosion protection systems. As a precaution, NFPA 68 now recommends to measure the explosion severity of the most reactive metal dusts in a 1-m^3 chamber,
- metal dusts pose unique challenges to explosion protection systems due to their higher reactivity. Current limitations specific to each explosion protection technique (venting, suppression, isolation) have been presented and discussed. A scaling issue related to the venting of aluminum dust deflagrations has been

identified, which raises doubts concerning the adequate protection of industrial-scale equipment and therefore should be addressed by future explosion protection standards,
- explosion protection systems intended to be used against metal dusts deflagrations need to be tested against the specific materials being handled in the industrial process subject to dust deflagration hazards. The use of equipment compliant with relevant explosion protection standards, tested, validated under real deflagration conditions, and certified by a third party is necessary to guarantee proper operation during an accidental deflagration.

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