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Explosion Parameters of Aluminium Dust in Different Volumes: the Limits of the Cube Law

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Since the development of laboratory apparatus for determining safety parameters in the form of the explosion pressure P_{ex} and the maximum rate of pressure rise $(dp_{ex}/dt)_{max}$ a large number of dusts have been studied experimentally and the values obtained published in databases (GESTIS-DUST-Ex, 2018). It is assumed for the purpose of these studies that the parameters of a dust determined under ideal laboratory conditions are more critical – and therefore constitute a safer basis for the planning of safety measures – than the values actually arising in an explosion in an industrial installation. This generally holds true for the explosion pressure, which is attributable essentially to the basic thermodynamic variables of the heat of reaction, the specific heat capacity and the concentration. It is not the case however for the kinetic variable of the maximum rate of pressure rise, which is dependent upon the volume, as well as the turbulence and dust distribution. To facilitate comparison of the dp/dt values obtained with the use of different laboratory apparatus, the maximum rates of pressure rise are adjusted for the standard volume of 1 m^3 by means of the cube law. The $dp_{ex}/dt*V^{1/3}$ value calculated in this way also enables the dp/dt values to be applied to very large volumes. It must be noted here that application of the cube law to the laboratory test apparatus is subject to very strict conditions. Important criteria include the ignition geometry, sphere geometry, ignition delay time, etc. Even when these boundary conditions are observed, non-organic dusts frequently exhibit substantial deviations from the cube law. Systematic experimental studies of aluminium dust in a range of test volumes demonstrate that the cube law cannot be used without qualification. The reasons for this difference in reactive behaviour are discussed, and the limitations of the cube law thereby also revealed.

1. Introduction

Aluminium is used for a wide range of purposes owing to its low density and the swiftness with which it forms a barrier layer of Al_2O_3. Aluminium and its alloys are used wherever low weight is required for reduction of fuel consumption in combination with high stability. The aluminium dusts occurring in industrial production frequently exhibit a high reactive behaviour, which has led to numerous accidents (CSB, 2004) in collection and filtration installations (Li et al., 2016). For this reason, the safety parameters for explosion protection are of great importance for the planning and execution of safe installations. The measured maximum rates of pressure rise (Equations 1 and 2) are used for specification of the pressure relief areas or the response times of the suppression systems (DIN EN 14491, 2012). Studies of aluminium dusts in a range of test volumes (Taveau, et al., 2018) have revealed that the cube law cannot be used without qualification to adjust the dp/dt values to a standard volume of 1 m^3; greater volumes have been shown to lead to higher dp/dt values, an observation that violates the cube law and can give rise to considerable safety problems.

2. Experiment

The maximum explosion pressure P_{ex}, and the rate of pressure rise dp_{ex}/dt and standardized maximum rate of pressure rise, i.e. the K_{st} value (Equations 1 and 2 respectively), were determined in closed 20 l and 1 m^3 vessels in accordance with EN 14034 Part 1 (EN 14034-1, 2011) and Part 2 (EN 14034-2, 2011). The oxygen

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concentration in the residual gas was determined (Servomex 570A oxygen analyser) immediately following the explosion reaction in the 1 m^3 vessel. In order to determine the influence of dispersion upon the dp/dt value, tests were performed in both vessels with an rebound nozzle and a half-ring nozzle. In the 20 l sphere, a dispersion cup was used in addition that enables the dust within the reaction vessel to be raised pneumatically.

In order to determine the aluminium turnover, the reaction vessel was flushed with argon immediately following the explosion reaction. Following a cooling-down phase of 2 to 3 hours, the sample material remaining following completion of reaction was removed completely from the vessel, and a representative sample obtained by grinding (Fritsch Pulverisette 14) and sieving (710 µm, Retsch AS 200). The sample prepared in this way (300 mg) was dissolved in 4% sodium hydroxide solution with the formation of hydrogen (NaOH/H_2 method). The quantity of hydrogen released is proportional to the fraction of non-reacted, metallic aluminium. 300 mg aluminium foil was used as standard for pure aluminium. In the test, this produced 403 ml hydrogen, corresponding to the stoichiometric calculation.

Further analytical methods were applied in the form of electron microscopy imaging, photometric methods for determining the particle-size distribution (Retsch Camsizer XT) and methods for determining the minimum ignition energy and minimum ignition temperature (DIN EN ISO/IEC 80079-20-2, 2016).

2.1 Sample material

The aluminium dust sample used was produced by the spray method in an inert gas (median: 26 µm, Figure 1b). The NaOH/H_2 analysis produced 395 ml H_2, i.e. an aluminium content of 98%. At a median of 26 µm, this equates to an oxide layer of approximately 10-15 nm, which is in the region of the native formation of the alumina barrier layer in air. In order to increase the depth of the oxide layer, sample material was tempered for 48 hours at 200 °C under atmospheric conditions for the purposes of a test.

At the same time, a second aluminium material sample sourced from a blasting plant (blasting material, aluminium wire shot, Figure 1a was tested in the 20 l vessel. This aluminium sample has silicon and magnesium fractions of up to 1%. The process lends the particles a different surface structure.

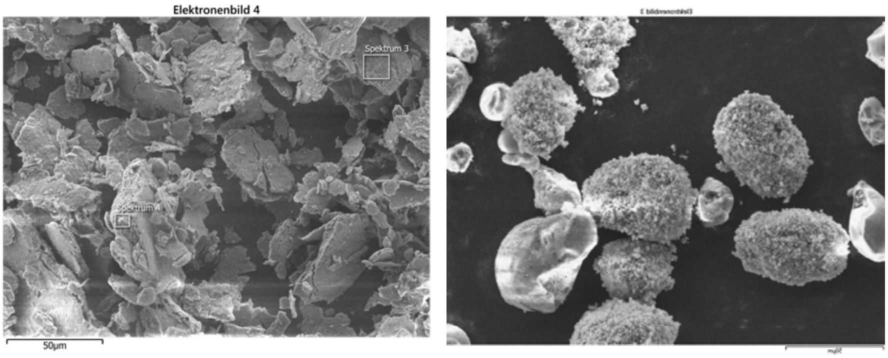

Figure 1a, left: SEM-EDX image, aluminium alloy/blasting dust, Figure 1b, right: Aluminium dust produced by the thermal spraying process

3. Experimental results: explosion pressure and rate of pressure rise of aluminium in the 1 m^3 vessel and 20 l sphere

Figures 2a and 2b plot the characteristics of the explosion pressure P_{ex} and the rate of pressure rise $dp_{ex}/dt^{*}V^{1/3}$ against the concentration, for both reaction vessels. The dp_{ex}/dt values from the 20 l sphere were adjusted to the standard volume of 1 m^3 by means of the cube law, Equation (1).

$$\frac{dp_{ex}(V)}{dt} \cdot V^{1/3} = \frac{dp_{ex}(1m^3)}{dt} \tag{1}$$

$$\left(\frac{dp_{ex}(1m^3)}{dt}\right)_{max} = K_{st} \tag{2}$$

The rebound nozzle was used in the 20 l sphere for dispersion, the half-ring nozzle in the 1 m^3 vessel. The dp_{ex}/dt values differ by a factor of 3, and do not obey the cube law. The transfer of K_{st} values (Equation 2) for aluminium dust determined in smaller reaction vessels is therefore subject to limitations. This is relevant to safety technology and the calculation of pressure relief areas. The cube law was derived from the physical description of spherical gas explosions. It can be applied to dust explosions when a number of boundary conditions are met. These include homogeneous dust distribution, a spherical vessel, ignition in the centre, atmospheric conditions, and constant flame propagation speed in a radial direction. The literature also assumes that differences in surface area/volume (A/V) ratio can be disregarded for spherical test apparatus of 16 l or more (Bartknecht, 1993).

A further difference, which can be seen in Figure 2b, is that the $dp_{ex}/dt*V^{1/3}$ values in the 20 l sphere do not reach a maximum. Each increase in concentration leads to a small increase in the $dp_{ex}/dt*V^{1/3}$ values. This means that each increase in concentration has increased the fraction of reactive particles, without the total increase in material in the reaction chamber having an extinguishing effect (Cashdollar, et al., 2007).

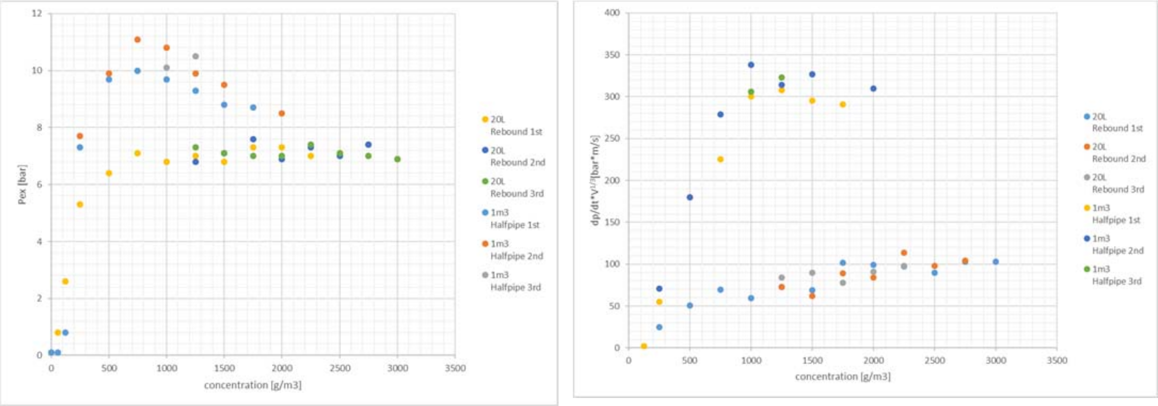

Figure 2a (left): P_{ex} of aluminium dust in the 20 l sphere and the 1 m^3 vessel, Figure 2b (right): dp_{ex}/dt values for aluminium dust in the 1 m^3 vessel and 20 l sphere (converted by means of the cube law)

4. Searches: GESTIS dust explosion database

Aluminium dust rarely occurs in pure form in the dust exhaust installations and machining centres of industrial plants. The experimental observations described above prompt the question of how the industrial aluminium dusts are distributed between the different dust explosion classes. The GESTIS dust explosion database of the German Social Accident Insurance (GESTIS-DUST-Ex, 2018) contains data records on a total of 510 studied aluminium dust samples, of which 235 samples were used for the evaluation.

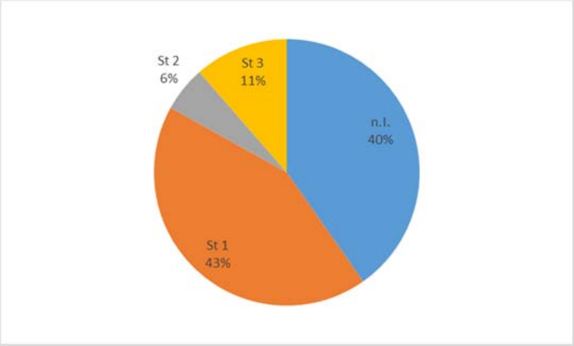

Figure 3: Distribution of the aluminium dusts between the dust explosion classes (N=235, (GESTIS-DUST-Ex, 2018))

Figure 3 shows the distribution of the dusts in percent between the dust explosion classes. Aluminium dusts that are not explosive (n.I. = no ignition) are generally very rich in oxides (such as in welding or electroplating processes), or their particle size is very coarse, with median values greater than 300 µm (such as aluminium grit). Aluminium dusts in the range of dust explosion class St 3 are very fine, with median values below 30 µm, such as aluminium powder or fine abraded material from aluminium grit or similar. These dusts frequently tend to smoulder (burning class BC=4). Dust explosion class St 1 is relevant to the problem of the non-cubic behaviour of aluminium dusts. Very few data were obtained by means of the 1 m^3 vessel; consequently, for St 1 aluminium dusts for which the drop in reactivity cannot be explained by the admixtures (e.g. aluminium (80-88%)/tin (9-11%)/corundum (<2%), grinding), studies in a 1 m^3 vessel may potentially yield higher K_{st} values. This is the case for approximately 20% of the St 1 dusts studied.

5. Influence of the measuring apparatus upon the dp_{ex}/dt value

The safety parameters dp_{ex}/dt is dependent upon the test apparatus used, such as its volume, vessel geometry, ignition delay time and dispersion method. The aluminium test dust was dispersed in the 20 l vessel by means of three different methods. In addition to the rebound nozzle and the half-ring nozzle, a dispersion cup was used in which the sample dust was placed in the reaction vessel and raised pneumatically. Following adjustment to the standard (Equation 1), the $dp_{ex}/dt*V^{1/3}$ values measured are in the range from 60 to 110 bar m/s (Figure 4). None of these methods attains the $dp_{ex}/dt*V^{1/3}$ values obtained with the 1 m^3 vessel. The different dispersion methods necessitate adjustment of the ignition delay time t_v. In the 20 l vessel, longer delay times with lower turbulence lead to a further reduction in the dp_{ex}/dt values. A shortening of t_v and thus an increase in the level of turbulence would be desirable; in the experiment however, this led to pressure coupling with the sample container and therefore a pressure drop in the reaction chamber.

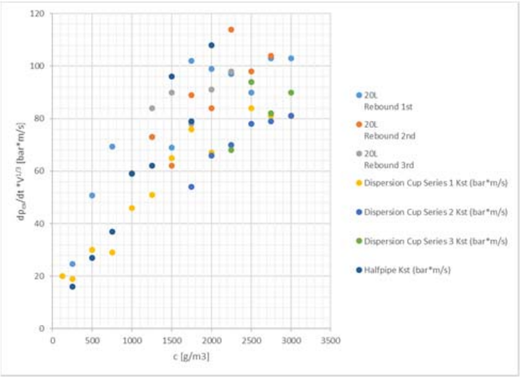

Figure 4: Aluminium $dp_{ex}/dt*V^{1/3}$ values in the 20 l sphere for different dispersion methods

In the 1 m^3 vessel, the rebound nozzle was used as well as the half-ring nozzle. The rebound nozzle led to a reduced K_{st} of 200 bar m/s. Reducing the ignition delay time t_v by 50-100 ms had no influence upon this result. It was also demonstrated that in both volumes, a reduction in the ignition energy from 10 kJ to 2 kJ did not lead to any significant change in the P_{ex} and dp_{ex}/dt values with a measurement uncertainty of (± 20%) (TÜV Süd Schweiz AG, 2016).

5.1 Change in dust characteristics caused by the test apparatus and storage

The manufacturing process lends the aluminium test dust a specified particle size distribution with a defined oxide layer. Storage in air at 200 C for 48 hours does not result in a change to the oxide layer, as was demonstrated by means of the NaOH/H_2 method. Dispersion by means of the half-ring nozzle in the 1 m^3 vessel also causes no change in the particle size of the aluminium test dust. In order to rule out the oxide layer being damaged by the injection process and the dust thereby acquiring a higher reactivity, a sample was preconditioned with the half-ring nozzle without ignition and subsequently tested with the rebound nozzle. Within the experimental uncertainty, no difference was detected between this and the tests performed without preconditioning.

5.2 Reactive conversion

At a concentration of 1,000 g/m^3 in the 1 m^3 vessel with the half-ring nozzle, the NaOH/H_2 analysis revealed a conversion of 772 g aluminium and thus a conversion rate of approximately 80%. The oxygen concentration in the residual gas was 1.4% by volume. The stoichiometric aluminium concentration for the formation of alumina (Al_2O_3) under atmospheric conditions (20.8% O_2 by volume) at 100% oxygen conversion is 309 g. Correction with the residual oxygen content yields 286 g aluminium; the remainder of the total conversion determined under low-oxygen conditions leads to the formation of aluminium nitride (AlN). Comparison with a sample that was not cooled down in argon, but obtained following pressure equalization a few minutes after the reaction, yields a similar conversion rate within the measurement uncertainty ($NaOH/H_2$ analysis ± 10%). This shows that with complete dispersion, conversion is complete once the maximum explosion pressure has been reached. For the reaction in the 20 l vessel, a concentration of 1,250 g/m^3 yields a conversion of 508 g aluminium and thus a conversion rate of 42%. The lower conversion rate explains the reduction of 2 bar in the maximum explosion pressure, since the formation of AlN is lower. The limiting oxygen concentration for aluminium under nitrogen atmosphere is 5% (molar content in the gas). The formation of AlN is therefore possible only by oxidation as a pre-reaction.

6. Comparative analyses with an aluminium alloy

Searches in the GESTIS dust explosion database identified an aluminium dust (alloy blasting dust) that exhibits high K_{st} values (> 300 bar m s^{-1}) in the 20 l sphere. The safety parameters of the two dusts are compared in Table 1.

Table 1: Comparison of the aluminium sample studied with an aluminium alloy blasting dust exhibiting high K_{st} values in the 20 l sphere

Parameters	*Aluminium dust sample*	*Aluminium alloy blasting dust (sample for comparison from the GESTIS dust explosion database)*
P_{ex}	*10.4 [bar] (1 m^3)*	*9.9 [bar] (20 l)*
K_{st}	*316 [bar m/s] (1 m^3)*	*510 [bar m/s] (20 l)*
LEL	*60 [g/m_3] (1 m^3)*	*30 [g/m^3] (20 l)*
Aluminium content ($NaOH/H_2$ method)	*98%*	*76%*
Manufacturer's information	*100%*	*AlSi1MgMn (surface material)*
Minimum ignition temperature	*660 °C (GG oven)*	*560 °C (GG oven)*
Minimum ignition energy	*30-100 mJ*	*10-30 mJ*
Burning class	*BC 1*	*BC 4*
Median	*26 µm*	*29 µm*
Volumetric fraction < 10 µm	*2%*	*13%*
Fusion temperature	*660 [°C]*	*585-650 [°C]*

The data in Table 1 indicate that the essential differentiators are the burning class, the minimum ignition temperature and the fraction of very fine dust particles with a particle size of < 10 µm. The last of these has a decisive influence upon the reactive surface area (Castellano, et al., 2014). The different morphological structures are also visible under the scanning electron microscope (Figures 1a and 1b). The aluminium sample for comparison is filter dust from a blasting process involving aluminium wire shot; this explains the elevated fine particle fraction with its larger reactive surface area.

7. Conclusions

The experiments performed enable various influences of the test method to be ruled out as the cause of the dependency of the $dp_{ex}/dt*V^{1/3}$ value upon the volume for aluminium dust. These influences include a change in the particle size distribution due to dispersion, damage to the oxide layer, oxidative ageing and differences in ignition energy. The comparison with the aluminium alloy shows that the parameters of the fine fraction, fusion temperature, and the associated minimum ignition temperature describe the difference in the reactive behaviour. The model of a solid ceramic shell of Al_2O_3 with melting aluminium core (Dufaud, et al., 2010) as a pilot stage for the reaction explains the difference in the alloy's reactive behaviour (Bernard, et al., 2017) since the chemical properties of the alloy and the pretreatment result in the ceramic layer being less pronounced. The surface area/volume ratio of the apparatus, and therefore the different radius of the test vessel affects strongly the turbulence of the dispersed particles, which explains the differences for the $dp_{ex}/dt*V^{1/3}$ values. Siwek and Bartknecht determined the reaction volume above which conversion of dp_{ex}/dt values to the 1 m^3 standard volume is possible with the cube law to be 16 l (Siwek, 1989). The two-stage reaction of aluminium dust, first to Al_2O_3 and at a defined high temperature to AlN are sensitive to turbulence and heat sink surfaces (A/V ratio), resulting in the maximum $dp_{ex}/dt*V^{1/3}$ values not being reached in smaller vessels, i.e. under less favourable conditions for spatial dispersion. The NaOH/H_2 conversion analyses, the residual oxygen content and the reaction enthalpies for Al_2O_3 and AlN (CRC Press LLC, 2000) enable a total released thermal energy of 12.7 MJ/kg calculated for a concentration of 1,000 g/m^3 in the 1 m^3 vessel. This corresponds to 3.0 kg of TNT. Under purely adiabatic conditions, i.e. where energy is absorbed only by products and by educts (gases and solids) after reaction. This high energy would lead to explosion pressures of approximately 12 bar with an adiabatic temperature increase of approximately $\Delta T=5{,}000$ K in the residual gas phase. The calculation based on the half concentration approach for products and educts including melting and partly vaporization and reduction of O_2 and N_2 in the gaseous phase.

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