A Review of the Fire and Explosion Hazards of Particulates

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Abstract
Particulate fires and explosions cause substantial loss of life and property. With the goal of understanding, preventing, or at least mitigating particulate fire and explosion hazards, we review basics. We distinguish between ‘hazard’ and ‘risk’ and discuss the fire and explosion hazards of particulates, the many factors determining such hazards, hazard indexes, and ways to reduce fire and explosion hazards. While our primary goal is to improve safety, we briefly discuss how fundamental knowledge can be extracted from weapon technology based on particulate combustion. We review the prevention of and protection against particulate explosions and discuss ongoing and future research.

Keywords: fire, explosion, (nano)particles, hazard indexes, prevention, protection, modeling

1. Introduction; hazard versus risk
Although the basics are well understood, fires and explosions of solid particulates (powders, ‘dusts’) and liquid particulates (‘mists’), especially the former, continue to cause considerable material damage and loss of life. Particle safety therefore remains important. In discussing particulate safety we distinguish between the concepts of ‘hazard’ and ‘risk’.

Hazard is the potential to create an adverse effect. Typical hazards of particulates are fire and explosion. Hazards can be quantified using certain substance properties, often expressed as hazard indexes, which are discussed later. Quantitative values of hazards are always relative, never absolute.

As a technical concept, risk is composed of two quantifiable factors: an adverse effect (e.g. number of deaths) and the probability (0 to 100%) of that adverse effect occurring. If both of these factors are accurately quantified, risk can, at least in principle, have a correct absolute value. In practice, however, calculated risks are often subject to large uncertainties.

Particulate hazards include fire and explosion, which for a given particulate, are determined by its properties, such as its chemical composition, particle size distribution, etc. The risk of a given particulate is, however, not solely determined by its properties, but also by factors external to the particulate itself, such as amounts, conditions (e.g. pressure, temperature), size and strength of containment, (distance to) possible ‘targets’, good management, adherence to legislation, etc. Here we discuss particle hazards and their reduction. The more extensive concept of particle risk falls outside the scope of this review1).

2. Fire and explosion hazards of particulates: the basics
Fire is a (usually relatively continuous) combustion (burning) process consisting of exothermic (= heat-producing) chemical reactions involving a fuel and producing besides combustion products, such as water and carbon dioxide, heat and, via flame, also light. In addition to simply burning, an insidious form of fire called smoldering can occur when large volumes of a combustible powder are stored, typically in a pile for an extended time period. Through oxidation of the surface of the particulates, heat is generated, and if the rate of heat generation exceeds the rate of heat loss (as can occur in a large pile), the temperature within the pile can reach the ignition temperature. The result is a relatively slow burning (slow because oxygen must diffuse into the pile and reaction gases/vapors out). Aside from generating poisonous gases (e.g. carbon monoxide), smoldering can lead to fires and even explosions. We mention smoldering further in Table 2 (under Minimum Ignition Temperature). In the following text, we shall focus on dust explosions.

Given the right conditions, most unoxidized materials can burn. Most substances industrially produced (e.g. plastics, oils) or processed (e.g. wood, petroleum) are unoxidized or not fully oxidized and can therefore burn. One
must be aware that:

ALL POWDERS THAT CAN BURN CAN ALSO EXPLODE

ALL LIQUIDS THAT CAN BURN CAN—AS PARTICULATES (MISTS)—ALSO EXPLODE

No definitive, quantitative definition of the term ‘explosion’ exists. Characteristic of explosions are: ‘much energy’ (Joules, J), “in a short time” ((fraction of) seconds(s); thus high power (J/s)), “in a small volume” (m³, thus high power density (J/s m³)). Further: creation of a ‘blast’ as a pressure wave (Fig. 1, left) or a more destructive shock wave (Fig. 1, right), both of which can wound/kill people, destroy buildings, and create deadly high-velocity fragments. The energy source of explosions can be physical (e.g. lightning) or chemical (e.g. combustion). Here we discuss the explosion hazards of particulates, and therefore we consider only explosions caused by chemical reactions, i.e. combustible substances undergoing combustion in air or oxygen.

A key difference between fire and explosion is that in fire, the fuel (e.g. burning candle) and the oxidizer (air) are clearly separated. Oxygen molecules, necessary to maintain the occurrence of combustion, reach the flame largely by diffusion. By contrast, explosions are characterized by a pre-mixing of fuel and oxidizer. Examples of increasing intimacy of pre-mixing are: a cloud of combustible dust or mist (combustible particles suspended in air); an explosive gaseous mixture (e.g. methane molecules and oxygen molecules in air); a solid high explosive, such as TNT (atoms of fuel (carbon and hydrogen) adjacent to atoms of oxidizer (oxygen) in the same molecule). It is this pre-mixing of fuel and oxidizer, and its degree of ‘intimacy’ (most ‘intimate’ at the atomic level, as in an explosive such as TNT), that form the basic reason why explosions occur (much) more rapidly than fires do, thereby resulting in a (much) higher (volumetric) rate of energy release, i.e. power (W or W/m³).

Explosions of powders, commonly called dust explosions and/or explosions of liquid particulates, called mist explosions; are almost always a type of explosion called deflagration. The propagation mechanism of deflagration is heat conduction: heat is transferred from the hot reaction zone (the flame) to the much cooler unreacted material ahead of the flame, thus preheating it until it reaches its ignition temperature, at which it ignites and burns (combusts).

Behind the flame, expanding hot, oxidized gaseous products and (possibly) unburned material are present. Characteristic of deflagrations is that the flame speed, \( S_f \), is always subsonic (i.e. flame propagates at less than the speed of sound, which in air at ambient conditions is ca. 330–340 m/s). At non-turbulent conditions, deflagrative flame speeds in air at ambient conditions typically range between a few m/s and about 10 m/s.

In a closed vessel filled with a flammable mixture undergoing deflagration and ignited in the center, the flame expands spherically from the vessel’s center until it reaches the vessel’s wall. During this process, the pressure in the vessel continuously rises. Both the pressure and the rate of pressure rise reach a maximum when the flame reaches the vessel’s wall. Characteristic of deflagrations in a closed vessel are therefore a maximum explosion pressure, \( P_{\text{max}} \), and a finite maximum rate of pressure increase, \( \frac{dP}{dt}_{\text{max}} \). (In practice, pressure is often expressed as bara (= bar absolute, 1 bara (= atmospheric pressure) being \( 10^5 \) Pa) and rate of pressure rise expressed in bar/s.) Maximum pressure, \( P_{\text{max}} \), and maximum rate of pressure increase, \( \frac{dP}{dt}_{\text{max}} \), are found at optimal particulate concentration.

While deflagrating flames propagate less rapidly than the speed of sound, the pressure waves produced by the expanding flame propagates ahead of the flame at sonic velocity; i.e. 330–340 m/s. Therefore in deflagrations, the flame (subsonic velocity) and pressure waves (sonic velocity) are separated from one another, pressure waves preceding the flame.

Only at conditions rarely existing in industrial applications can particulates explode via a mechanism other than deflagration: the detonation. A detonation is a chemically reactive shock wave. A shock wave (Fig. 1, at right) is a special case of a pressure wave. Like pressure waves, shock waves have a maximum pressure, \( P_{\text{max}} \), but differ from pressure waves by having an almost infinite rate of pressure rise, \( \frac{dP}{dt} \). Additionally, the flame speed of a detonation is supersonic, i.e. faster than the speed of sound. Also in contrast to deflagrations, in which the deflagrative flame and pressure waves are separate from one another and propagate at different speeds, both the detonation flame and the shock wave propagate at the same (supersonic) speed, with the combustion occurring within the shock wave, ignited by the high temperature resulting from the sudden compression. In general, per unit mass of material exploding (e.g. per kg), detonations are much more devastating than deflagrations because detonation pressures are much higher (ca. 2 to 16 times greater) than maximum deflagration pressures and rates of pressure rise near infinite. Detonations are also much more difficult to protect against than deflagrations, since detonations propagate supersonically.

For deflagrations occurring in a closed volume at an initial pressure not far from atmospheric (i.e. ca. 0.1 to 10
The ideal gas law expresses the maximum explosion pressure simply and usually sufficiently accurately (< 10% error):

\[ P_{\text{explosion}} \approx \left( \frac{n_{\text{explosion}}}{n_{\text{initial}}} \right) \cdot \left( \frac{T_{\text{explosion}}}{T_{\text{initial}}} \right) \cdot P_{\text{initial}} \quad (1) \]

where:
- \( P_{\text{explosion}} \) = final pressure (bara) of the explosion for given conditions of mixture composition, etc.
- \( n_{\text{explosion}}/n_{\text{initial}} \) = ratio of number of gaseous moles produced by the explosion relative to the initial number, including, in both cases, the inert gas molecules;
- \( T_{\text{explosion}}/T_{\text{initial}} \) = ratio of absolute explosion temperature (K) relative to initial temperature (K).
- \( P_{\text{initial}} \) = initial pressure (bara).

The presence of roughly 80% inerts (nitrogen + argon) in air causes the factor \( n_{\text{explosion}}/n_{\text{initial}} \) to be approximately unity. Therefore Equation 1 simplifies to:

\[ P_{\text{explosion}} \approx \left( \frac{T_{\text{explosion}}}{T_{\text{initial}}} \right) \cdot P_{\text{initial}} \quad (2) \]

Under optimal conditions \( P_{\text{explosion}} \) becomes the maximum possible explosion pressure \( P_{\text{max}} \). Equation 2 predicts that the maximum possible explosion pressure of a deflagration within a closed vessel is reached when the maximum possible temperature is obtained. For gases, this occurs to a (near) stoichiometric mixture composition. For particulates, it is in a fuel-rich area. The maximum combustion temperature is the adiabatic flame temperature, ‘adiabatic’ referring to ideal conditions in which no heat loss occurs. The adiabatic flame temperature is a chemical thermodynamic property; i.e., it is determined solely by the chemical properties of the substances involved (e.g., its heats of combustion), mixture composition (e.g., oxygen concentration), and initial temperature and pressure of the system.

Generally the faster the explosion process, the less time to lose heat, and the closer adiabatic conditions are attained, manifesting itself as a closer approach to the theoretical maximum adiabatic explosion temperature and thus greater rate of temperature rise, \( dT/dt \), and pressure rise, \( dP/dt \). Maximum adiabatic flame temperatures for common organic powders (i.e., plastics, coal) and/or droplets of combustible liquids exploding in air (e.g., oils) typically range between 1,500 and 3,000 K. Eq. 2, based simply on the perfect gas law, predicts that maximum explosion pressures for particulate explosions (deflagrations) of most particulates occurring in air in closed vessels initially at atmospheric pressure (1 bara) and ambient temperature (\( T = \text{ca. 300 K} \)) should typically be in the range of ca. 5 to 10 bara (= 4 and 9 baro (baro = bar overpressure)); in practice this is indeed the case³.

Two parameters essential for assessing particulate explosion severity (Table 1) are maximum explosion pressure, \( P_{\text{max}} \), and maximum rate of pressure rise, \( (dP/dt)_{\text{max}} \), the latter usually volume-normalized and called the \( K_{\text{St}} \) factor (or simply \( K \) factor; see Table 1). As Eq. 2 shows, the maximum possible explosion pressure of deflagrations is largely determined by the adiabatic flame temperature.

The (volume-normalized) rate of pressure rise is largely determined by the speed of the flame, \( S_f \). For a deflagration occurring in closed spherical equipment and ignited at its center, the time duration of the explosion, \( \Delta t \), is, by approximation, simply the radius of the sphere, \( R_{\text{sphere}} \), divided by the flame speed, \( S_f \). Therefore the faster the flame, the quicker the explosion occurs, and thus the faster the pressure rise. Indeed, the following approximations can be easily derived⁴,⁵,⁶:

\[ dP/dt = \Delta P/\Delta t = (P_{\text{max}} - P_{\text{initial}})/(R_{\text{sphere}}S_f) \quad (3) \]

\[ K_{\text{St}} = (dP/dt)_{\text{max}} \cdot T^{1/3} \propto P_{\text{initial}} \cdot S_f \quad (4) \]
in which \( P_{\text{max}} \) and \( P_{\text{initial}} \) are, resp., the maximum explosion pressure and the initial pressure, \( R_{\text{sphere}} \) the radius of the sphere in which the explosion occurs, and \( S_{f} \) the averaged flame speed; the symbol \( \mu \) means ‘proportional to’. More exact models are available, see e.g. Dahoe et al.6)

In the absence of turbulence, the flame speed, \( S_{f} \), being the propagation velocity of the flame front, is the vector result of the laminar burning velocity, \( S_{l} \), and the expansion of the hot gas. In a closed vessel, the latter is large at first, when pressure is still near the initial value, and zero at the end when maximum pressure is reached. In a tube open at one end and closed at the other, and ignited at the open end, as the flame propagates into the tube, the hot reaction gases flow out of the tube and thus in a direction opposite (i.e. countercurrently) to that of the flame. In this special case, and assuming laminar conditions: \( S_{f} = S_{l} \).

Like the adiabatic flame temperature, the laminar burning velocity is determined only by substance properties, mixture composition, and initial temperature and pressure conditions. Typical laminar burning velocities for gases/vapors in air at stoichiometric concentrations are roughly 0.4 m/s or less; for most powders they are less, typically roughly 0.25 m/s. However, unlike the maximum explosion pressure which follows directly from chemical thermodynamics, the laminar burning velocity is also strongly influenced by chemical kinetics (e.g. reaction mechanism). Chemical kinetics is usually much more complex than chemical thermodynamics, which is a reason why laminar burning velocities usually cannot be calculated from theory. As we discuss later, while laminar burning velocities are typically in the 1 m/s range, through turbulence flame speeds can accelerate enormously (to more than 600 m/s) causing pressure increases of several bars. Explosion behavior is determined by a complicated interplay between chemical thermodynamics, chemical kinetics, and turbulence-generated physical transfer phenomena.

Surprisingly small overpressures can cause considerable damage. An overpressure of 0.1 baro typically shatters glass windows and lethal effects start also at this pressure; 1.0 baro damages typical industrial equipment used for handling powders such as silos, and totally destroys normal buildings (houses, office blocks), causing their collapse and killing those inside. Normal structures react to even small overpressures because pressure is force/area, e.g. overpressures of 0.1 and 1 baro correspond to forces of, respectively, 1 ton/m² and 10 tons/m². Typical vertical surfaces of buildings (e.g. windows, walls) cannot withstand such huge lateral forces and are thus highly vulnerable7).

In dust or mist explosions, typically deflagrations, occurring in closed systems such as silos, it is the maximum pressure, \( P_{\text{max}} \), that largely determines the explosion’s destructiveness. For explosions occurring in open systems, however, such as in the open air, the situation is different. In this case it is the combination of maximum pressure, \( P_{\text{max}} \), the duration of the explosion (shown as \( \Delta t \) in Fig. 1), and even the form of the pressure wave (e.g. its \( dP/dt \)) that determine explosion destructiveness. The combination of explosion overpressure and explosion duration, i.e. the integral of the overpressure over time, is called the explosion impulse, \( I_{\text{explosion}} \):

\[
\text{Explosion impulse} = I_{\text{explosion}} = \int P \, dt
\]

In practice, the explosion impulse can often be approximated sufficiently accurately by assuming a right triangle for the pressure or shock wave (i.e. right-hand side of Fig. 1), so that

\[
\text{Explosion impulse} = I_{\text{explosion}} = \int P \, dt \approx \frac{1}{2} P_{\text{max}} \cdot \Delta t
\]

Once certain thresholds of over-pressure and impulse are reached to be able to create damage, explosion destructiveness generally increases as explosion impulse increases, i.e. increasing \( P_{\text{max}} \) and/or increasing explosion duration, \( \Delta t \).

We again distinguish between an explosion occurring in a closed system or in an open system and deflagrations versus detonations. As discussed above, in a closed system (e.g. reactor or silo), an explosion—deflagration and detonation—manifests itself as a sudden pressure rise leading to a maximum pressure. In a completely open system, for example an explosion occurring in the open air, a typical deflagration generally results in a large (hot) gas volume increase, but only in a very small pressure increase (i.e. \( \Delta P << 0.1 \text{ baro} \))8). This fact follows from the ideal gas law, as applied to an open system (i.e. constant pressure system, as in the atmosphere):

\[
V_{\text{explosion}} = (T_{\text{explosion}}/T_{\text{initial}}) \cdot V_{\text{initial}}
\]

By approximation, the adiabatic flame temperature and thus the explosion temperature of a given substance remains roughly the same independent of whether the system is at a constant volume (i.e. closed system) or at constant pressure (i.e. open system); i.e. the factor \((T_{\text{explosion}}/T_{\text{initial}})\) remains approximately constant. Therefore Eq. 7 shows that in an open system, the ratio of the volume of the explosion products \((V_{\text{explosion}})\) to the initial unexploded volume \((V_{\text{initial}})\) will be approximately the same as the pressure ratio obtained in a closed system, namely 5–10. It is also because deflagrations occur relatively slowly (typical flame speeds being only about 10 m/s) that deflagrations occurring in completely open areas do not usually produce large overpressures, but they can when occurring in congested areas.

However, detonations occurring in open air behave quite differently. Detonation pressures of particulate clouds are typically around 20 times the initial pressure in both open
and closed spaces. Also, because of aerodynamic phenomena caused by supersonic flow, pressures resulting from reflections of detonative shock waves can be much higher—ca. 40 to even 160 times the initial pressure. Because of these huge initial detonation pressures and even higher reflected pressures, detonation is much more destructive than deflagration, especially in the open air.

Concerning explosion behavior in general, Abbasi et al., 2009\(^9\) and Mannan, 2012\(^10\) provide detailed description of types and characteristics of explosions, including deflagrations and detonations.

### 3. Fire and explosion hazard indexes

The more energy released during combustion and the faster this occurs, the greater the destructiveness—the severity—of the resulting fire/explosion. The less energy needed to initiate combustion, the greater the sensitivity to ignition (to fire and/or explosion), and thus the greater the probability of a fire/explosion occurring. Fire and explosion hazards of particulates (and also of gases and vapors) are therefore expressed in terms of severity indexes and sensitivity indexes, which Tables 1 and 2 list, along with meaning and significance.

Assessment of the fire and explosion hazards of particulates requires knowing the values of the indexes listed in Tables 1 and 2\(^11\). We stress that with the possible exception of \(P_{\text{max}}\) and \(S_{\text{f}}\), which in principle are invariant, values for most explosion indexes either cannot or not yet reliably be predicted theoretically. It is essential to be aware that the index values are influenced by testing procedures and equipment (which have been standardized; e.g. for temperature, pressure, turbulence, etc.). Note further that values found in the literature are often not directly applicable to one’s own case, as these index values are affected by ambient changes (e.g. temperature, pressure, turbulence)\(^12\). Additionally, indexes of a given type of particulate (e.g. grain dust) may vary greatly, depending on which type of grain (species and sub-species), average particle size and particle size distribution, and even weather conditions (temperature, humidity) under which the powder has been stored, and for how long (this related to possible adsorption/absorption of moisture from air and its effect on particle size). The literature gives a detailed discussion of test methods and their evaluation\(^13\).

While test methods are standardized, research leads to new insights and improved testing improvements. Gao et al., 2013, describe examples of how sensitive explosion behavior is to variations in testing procedures\(^14\). This is also true for an essential explosion severity index, the \(K_{\text{St}}\) value, once thought to be invariant. Proust et al. show that the assumption that it is independent of the two standard types of testing equipment is not generally true\(^15\).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Hazard severity indexes of particulates dispersed in air (or other oxidative gases)</th>
</tr>
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<tbody>
<tr>
<td><strong>Severity index</strong></td>
<td><strong>Meaning/significance/dimensions of severity index</strong></td>
</tr>
<tr>
<td>Tendency towards detonation</td>
<td>Per kg of material, detonation is the most destructive explosion type. Generally, the tendency towards detonation increases with increasing mixture reactivity and decreasing particle size.</td>
</tr>
<tr>
<td>Maximum explosion pressure, (P_{\text{max}})*</td>
<td>For deflagrations the maximum explosion pressure is largely determined by the maximum explosion temperature (Eq. 2); (bara (absolute pressure) or baro (overpressure)). Explosion hazard increases with greater maximum explosion pressure.</td>
</tr>
<tr>
<td>Maximum rate of pressure rise, ((dP/dt)_{\text{max}})*</td>
<td>Maximum rate of pressure rise, with initial conditions of 1 bara and room temperature; usually expressed as bar/s. Usually cannot be calculated and must therefore be measured. Explosion hazard increases with greater maximum rate of pressure rise.</td>
</tr>
<tr>
<td>Maximum volume-normalized rate of pressure rise, called (K_{\text{St}}) factor (or simply (K) factor), where: (K_{\text{St}} = (dP/dt)<em>{\text{max}}^{1/3} \times (dP/dt)</em>{\text{max}}) (relationship often called ‘cubic law’)</td>
<td>Maximum rate of pressure rise (bar/s), normalized to a sphere of 1 m(^3) volume, with initial conditions of 1 bara and room temperature. (This equation is called the ‘cubic law’.) Since it depends on ((dP/dt)<em>{\text{max}}), the (K</em>{\text{St}}) factor must be measured; usually expressed as bar m(^{-1}) s(^{-1}). Explosion hazard increases with increasing value of (K_{\text{St}}) factor. Both the maximum rate of pressure rise and the volume-normalized rate of pressure rise are largely determined by the flame speed, (S_f), see Eqs. 3 and 4.</td>
</tr>
<tr>
<td>Flame speed: Laminar burning velocity, (S_{\text{L}}), m/s; (turbulent) flame speed, (S_{\text{T}}), m/s</td>
<td>Speed of flame relative to stationary observer, (S_f). Laminar burning velocity, (S_{\text{L}}), is the speed of flame relative to the unburnt gas at completely laminar (i.e. non-turbulent) conditions and stoichiometric concentration; at constant pressure this is only possible if the expanding hot combustion gases flow away backwards countercurrently to the moving flame front. (S_{\text{T}}) is typically in the range of ca. 0.2–0.4 m/s. Through turbulence, the flame speed ((S_f)) can accelerate from a few m/s to near sonic velocities, and even to supersonic during a deflagration-detonation transition: DDT</td>
</tr>
</tbody>
</table>

\*Note that in non-optimal composition and hence not maximum output, these quantities are indicated as \(P_{\text{ex}}\) and \((dP/dt)_{\text{ex}}\).
We concentrate here on discussing how particulate properties determine particulate hazards. Reducing hazards requires an understanding of the basics and actively applying this understanding to designing, manufacturing and handling particulates and the design and handling of relevant equipment.

### 4. Chemical and physical factors determining particulate hazards

#### 4.1 Chemical factors

Particulates composed of unoxidized or not fully oxidized
Substances are usually combustible; if combustible they can also explode. Here we divide combustible particulates into three categories: 1. Unstable reactive substances; 2. Stable reactive substances; 3. Stable flammable substances.

Unstable reactive substances are substances whose decomposition is exothermic. By themselves (e.g. no air present), unstable substance therefore tend to spontaneously decompose, and since decomposition is exothermic, heat is generated. When stored with insufficient cooling, unstable substances thus tend to heat up, causing a temperature increase. Since increased temperature generally exponentially increases the chemical reaction rate (of further decomposition, which is exothermic), a vicious cycle may result leading to increasingly fast temperature increase, increasingly fast decomposition reaction, etc., a ‘run-away’, ultimately causing explosion.

Examples of unstable reactive liquid substances produced in large quantities are ethylene oxide, propylene oxide, and organic peroxides; in much smaller quantities, concentrated hydrogen peroxide and nitroglycerine. Examples of solid unstable substances produced in large quantities are ammonium nitrate, TNT, and other high explosives. Most large-volume unstable powders are, however, not commonly used in industry.

Stable reactive substances are stable in that by themselves, they do not decompose or their decomposition is endothermic (i.e., requires heat). They are reactive because they can spontaneously burn or explode—but only when in contact with air or water. Pyrophoric substances form a category of stable reactive substances; these spontaneously burn or explode when exposed to air. Examples are finely divided unoxidized metals, such as iron and aluminum, which spontaneously ignite when exposed to air. Water-reactive substances which spontaneously react violently (burn, explode) in contact with water, form another category of stable reactive substances. Examples are the elements sodium, potassium, rubidium, and cesium and compounds such as aluminum bromide and calcium carbide.

The third category of substances, stable substances, consists of substances that by themselves do not spontaneously decompose and, in contact with air or water, do not spontaneously burn or explode. Stable materials that are non-oxidized (e.g., polyethylene powder, gasoline), or incompletely oxidized (e.g., alcohols, grain dust) are flammable, but will only burn/explode when pre-mixed with air, and additionally are also subjected to an ignition source (e.g., flame, spark) of sufficient energy (i.e., greater than the particulate’s MIE and/or MIT). It is such substances—non-oxidized or only partially oxidized substances, and thus combustible—that by far cause the greatest number of fires and explosions.

In general, explosion sensitivity and in particular explosion severity tend to increase as certain chemical thermodynamic properties, such as heat of combustion, increase (expressed in terms of mass (e.g., kJ/kg) or, even more importantly, in terms of volume (kJ/m³)). Higher heats of combustion usually result in higher adiabatic flame temperatures and thus (Equation 2) higher maximum explosion pressures. Since chemical reaction rates tend to increase exponentially with increasing temperature, substances with high adiabatic flame temperatures also tend to have higher laminar burning velocities and flame speeds, and thus higher rates of pressure increase, \( (dP/dt)_{max} \). Finely divided reactive metals such as aluminum and magnesium have particularly high heats of combustion, thus high adiabatic flame temperatures (up to nearly 3600 K), and thus high maximum explosion pressures (typically around 12 bara) and high \( K_f \) values (well above 300 bar m/s).

### 4.2 Physical Factors

#### 4.2.1 Similarities of Gas/Vapor and Particulate Explosions

Explosions of particulates (i.e., dust explosions, mist explosions) resemble gas and vapor explosions in that they also occur via chemical combustion; furthermore both deflagration and detonation are possible. Additionally, maximum explosion pressures of particulate explosions are generally similar to maximum explosion pressures of gas/vapor explosions. Thus (for deflagrations) typically 5–10 times the original pressure (Eq. 2), and for detonations roughly 20 times the initial pressure. As previously noted, this similarity is caused by the fact that the maximum adiabatic flame temperatures of common combustible particulates burning in air are usually similar to those of combustible gases/vapors, i.e., usually 1,500 to 3,000 K.

#### 4.2.2 Differences: Combustion Mechanism of Particulate Explosions

The most fundamental difference between gas/vapor explosions and particulate explosions lies in their respective explosion mechanisms. Gas/vapor explosions occur homogeneously—within one phase, the gaseous phase. Mechanistically, gas/vapor explosions thus occur in a pre-mixed mixture of molecules (e.g., methane molecules and oxygen molecules) which react with one another at a molecular level.

Relative to gas/vapor explosions, the mechanism of particulate explosions is more complex. Particulate combustion occurs heterogeneously (i.e., involving at least two distinctly different phases, a solid phase (solid (powder)) and/or liquid phase (e.g., mist)) and a gaseous phase (normally air). The complexity of the mechanism of particulate explosions is caused by many possible steps occurring sequentially in time:

1. Heating of the unreacted particles due to radiant heat from the approaching flame and/or conductive/convective heating via hot unburned gases.
2. Heating of the particle surface and, via heat conduction,
heating of the particle interior (particle volume).

3. Depending on the temperature reached by heating and the volatility of the particles (e.g. melting and boiling points), either no, partial or complete vaporization of the particles before the flame reaches them.

4. For relatively volatile substances (e.g. diesel fuel, polyethylene), complete vaporization and subsequent ignition and combustion of the resulting vapors which have been pre-mixed into the gaseous phase. This is essentially a gas explosion.

5. For partially vaporized particles, ignition of the combustible vapors formed (e.g. aluminum vapor boiling off molten aluminum particles) followed by ignition of the particles and further combustion at their surface. For such burning particles, diffusion of oxygen to the combusting surface zone and diffusion of combustion products (e.g. carbon dioxide, water vapor) into the bulk gaseous phase.

6. For substances of very high sublimation, melting and/or boiling points (e.g. graphite, tungsten) combustion exclusively on the surface of the particles. Various phase transformations depending on the melting and boiling points of oxides formed relative to the adiabatic flame temperature of the particles.

7. Eventually: further combustion on the surface of the charred remains of out-gassed organic particles (e.g. coal). Reaction rate controlled by diffusion to, from, and within the particle.

Mechanistically, of all these steps, gas/vapor explosions involve only step 4. Due to all this, the three-zone burning model has been developed, Dahoe et al. for a dust explosion.

Diffusion is the rate-determining step of the heterogeneous combustion mechanism process pictured in Fig. 2: oxygen molecules must diffuse in from the bulk gaseous phase to the particle surface, and reaction products from the burning particles must diffuse out into the bulk gaseous phase. Diffusion usually occurs much more slowly than the rate of chemical reaction, whose rate tends to increase exponentially with temperature.

The complex mechanism of particulate combustion is influenced by many chemical and physical parameters such as: chemical composition; particle size (distribution); phase(s) of the particulates involved (solid and/or liquid); for liquids, volatility (vapor pressure as function of temperature (e.g. boiling point)); for solids, idem, including sublimation, melting, and boiling point; surface structure/ specific surface area; heat conductivity and heat capacity; for substances forming liquid or solid oxides (e.g. coal, many metals, such as aluminum, magnesium, iron), melting and boiling points of the oxides; turbulence (affects rate of mass transfer (e.g. diffusion versus mixing via convection); flame temperature (K) and thermal intensity (kW/m²) of the combustion process (affects rate and mechanism of heat transfer).

Fig. 2 illustrates the sequential steps of a mechanism proposed for the ignition and combustion process occurring
4.2.3 Particle size and particle size distribution: smaller particles = greater hazard

Reducing particle size tends to increase the particulate explosion hazard, as expressed by both explosion severity and explosion sensitivity indexes. Figs. 3 and 4 show examples of the huge effect of the particle size on, respectively, LEL and MIE (explosion sensitivity); Fig. 5 shows the effect of particle size on maximum pressure and rate of pressure rise (explosion severity).

Given the decisive effects of particle size on the particulate explosion hazard it is surprising that many, especially older (ca. pre-2000), studies presenting explosion behavior as a function of the particle size are neither clear as to how the particle size is defined nor how it is measured. Already in 1980, Ballal noted this hiatus, commenting: “Clearly, from the point of view of fundamental combustion studies, it is the Sauter mean diameter (SMD), particle size
distribution, and equivalence ratio that are of great importance.” Yet even in Eckhoff’s 2003 text\(^3\), presently perhaps the best single general source on dust explosions, the Sauter mean diameter is not mentioned\(^3\). Föster explicitly discusses the importance of how the particle size is measured and expressed, including the Sauter diameter\(^3\). Experimental results that do not clearly state how the particle size is expressed should be viewed with circumspection.

Particulates with the same average particle size often have different particle size distributions, which can result in significantly different particulate explosion hazards. For example, a powder having a broad particle size distribution may exhibit high explosion sensitivity and severity, whereas the same powder—with exactly the same chemical composition, but with a much more narrow particle size distribution around the same median size—may (at standard test conditions) not explode at all. The reason is that the first powder contains a significant fine fraction which is much more sensitive to ignition than the coarse fraction. These fines are easily ignited, and the ensuing combustion is sufficiently energetic to ignite the coarser fraction. Particle size distributions should therefore not be characterized by median size or an undefined mean size, but by a well-chosen mean size, such as the Sauter mean diameter. During size measurements, the size of so-called equivalent spheres is determined which is dependent on diameter. We return to this question when discussing nanoparticles in Section 7, Current and future research.

4.2.4 Effects of turbulence

By turbulence we mean the highly irregular motion of fluids (here gas) in which instantaneous velocities (i.e. speed and direction of fluid motion) exhibit rapid, irregular, and apparently random fluctuations. Superimposed on the net velocity of the fluid are separate small pockets of fluid called eddies or vortexes, whose size and (rotational) velocity similarly exhibit rapid, irregular, and apparently random fluctuations. Turbulence is a prime example of so-called complex behavior: i.e. behavior in a system in which a seemingly negligible change in a part of the system can greatly change the whole system’s behavior, making accurate and precise prediction impossible. Complex behavior is not deterministic; it is stochastic (i.e. probabilistic).

Turbulence is essential for the occurrence of particulate explosions, being necessary to disperse particulates, mix them with air, and keep them suspended. Additionally, turbulence has a complex effect on the dust explosion hazard. On the one hand, increased turbulence reduces the hazard by reducing explosion sensitivity (e.g. increasing MIT, MIE, LEL, etc.)\(^3\). This effect is due to the fact that at the limits of ignition (i.e. at the conditions of MIT, MIE, LEL, etc.), increased turbulence hampers ignition by dispersing ignition energy. The physical reason for this is that increased turbulence mixes more cold fluid into the just-barely ignitable kernel of air plus particulates, and this quenching effect prevents ignition.

On the other hand, for an already ignited, highly energy-rich particle-air mixture (e.g. an already ignited polyethylene-air mixture in the middle of its explosive range), increased turbulence vastly increases the hazard by increasing explosion severity (i.e. especially by increasing flame speed, \(S_f\) and thus \((dP/dt)_{max}\) and the \(K_{50}\) factor). Reasons for this effect are firstly, that greater turbulence tends to increase the surface area of the flame of a burning mixture. Turbulent eddies cause an initially flat (two-dimensional) flame to transform into a (severely) ‘wrinkled’ three-dimensional flame, thus greatly increasing the flame’s surface area. Since the flame’s surface is the area on which energy is being released (W/m\(^2\)), an increase in surface area increases the total rate of energy release. That turbulence increases the explosion severity applies not only for dust and mist explosions, but also for gaseous

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**Fig. 5**\(^3\) Effect of median particle size by mass on explosion severity: maximum rate of pressure rise of powdered polyethylene as a function of particle size. (Section 4.2.4, which discusses the importance of turbulence, explains why ethylene gas is also included here.)
explosions occurring in energy-rich mixtures, as illustrated in Fig. 5, illustrates the effect of turbulence on deflagrations of ethylene gas. Turbulence is the mechanism that can accelerate the flame speeds of deflagrations from ca. 10 to hundreds of meters per second and even cause deflagrations to transit into detonations.

A second reason is that turbulence also tends to decrease the slowing effect of diffusion, diffusion being a factor inherently reducing the rate of combustion of multi-phase (i.e. heterogeneous) mixtures. One can consider each particle to be enveloped in a thin laminar ‘film’ of a given thickness, through which diffusion takes place. Increased turbulence reduces the thickness of this laminar film, thereby reducing the time it takes for diffusion through the film to occur. When diffusion is the rate-determining step, faster diffusion speeds up the rate of energy release, thus increasing the severity of the explosion. (However, at a high turbulence intensity, this effect can be counteracted by flame quenching and extinction due to a high cooling rate.)

Through turbulence, a particulate explosion can become self-feeding: i.e. a small explosion starting somewhere in a plant grows due to the settled/deposited dust (or a liquid film) on floors and machinery being stirred up by the pressure waves and turbulence generated before the flame arrives. Explosions can in such cases propagate from one plant or installation to another—with devastating effects. Many disastrous dust explosions of this kind—in which a primary explosion generates and ignites one or more secondary explosions—are known. Dust deposits of only a few millimeters thickness or less, usually caused by bad house-keeping (and thus ultimately poor management), are sufficient to raise dust concentrations into the explosive range (i.e. above the LEL).

Additionally, inside a process installation a small, incipient explosion can, as it propagates through piping connecting vessels within the installation, generate increasing turbulence. It is this self-generated turbulence that can cause flame speeds to accelerate dramatically. In the extreme case, flame acceleration accelerates the flame speed from values typical of a deflagration, i.e. ca. 10 m/s, to supersonic velocities: a detonation. This feared phenomenon is called a deflagration-to-detonation-transition: DDT.

Another dangerous phenomenon associated with turbulence as an explosion propagates between interconnected vessels is pressure piling. Effects pressure piling causes in a secondary vessel are pressure increase, temperature rise (due to this compression), turbulence caused by the flow into the secondary vessel from a primary vessel, and possibly also flame-jet ignition as the explosion propagates from the primary to the secondary vessel. These factors can result in vastly increased explosion pressures and rates of pressure rise in secondary vessels. It is for these reasons that the propagation of incipient explosions must be prevented (e.g. via compartmentalization; see Table 4).

Theoretically, turbulent flow can be analytically predicted using Newton’s Laws of motion applied three-dimensionally (i.e. Navier-Stokes equations). In practice, however, turbulence is ‘too complex’ for analytical solution. This is frustrating, considering the importance of predicting the behavior of turbulent systems, such as the turbulent flow of all types (e.g. around automobiles, ships, aircraft), combustion of fuel in engines (e.g. diesels, jet turbines), and explosive combustion. The great breakthrough in calculating turbulent behavior was the development of Computational Fluid Dynamics (CFD), made possible by the advent of (super-)computers. A great breakthrough in directly measuring turbulence before and during particle explosions, e.g. in testing equipment, was the development and application of Laser Doppler Anemometry.

Computational Fluid Dynamics (CFD) has led to breakthroughs in modeling and thus predicting gas/vapor explosions, and more recently, particulate explosions. We return to CFD in Section 7, Current and future research.

4.3 Combined chemical and physical effects

4.3.1 Effects of humidity

Chemical composition determines not only combustibility, but also whether and to what degree a particulate is hydrophilic (‘water-loving’) or hydrophobic (‘water-hating’). Hydrophilic powders tend to adsorb/absorb air moisture, thus forming a layer of water molecules on the particle surface. This layer causes particles to stick together (agglomerate), which can strongly increase the virtual particle size and thus reduce the specific surface area. The specific surface area plays an important role in chemical kinetics and adsorption/absorption kinetics and therefore strongly influences the explosion hazard. In particular the Minimum Ignition Energy of hydrophilic powders is often strongly reduced by reducing the concentration of adsorbed/absorbed water. In particular, MIE values may decrease by a factor of 100 or even more.

Additionally, a layer of adsorbed water tends to increase the electrical conductivity of powders, thereby reducing the tendency to generate and retain a static electrical charge, thus reducing the hazard of ignition by static electricity.

4.3.2 Upper explosion limit, explosive range, volumetric explosion energy

Mixtures of combustible gases and vapors with air generally have sharply defined explosion limits (LEL and UEL values) and thus sharply defined explosive ranges (UEL – LEL). Additionally, the UEL values of gases and vapors at ambient pressure and temperature are typically roughly two times the stoichiometric concentration.

By contrast, particulates have less sharply delineated explosion limits; in particular, the upper explosion limits...
(UELs) of particulates are poorly defined for two reasons. Firstly, a particulate-air mixture initially above the UEL-concentration will, through deposition caused by gravity, eventually enter the explosive range. For this reason the UEL value for a particulate usually has little practical significance and can even be dangerous by engendering false confidence.

Secondly, while a gas/vapor explosion takes place between molecules, a particulate explosion involves the surface of the particles. As the mass concentration of the powder in a powder-air mixture increases to (far) above the theoretical (mass-based) stoichiometric concentration, the powder particles simply burn to a thinner depth. Thus, while gas/vapor explosions generally show a sharp maximum explosion severity at roughly the stoichiometric concentration, and explosion severities fall sharply past this concentration, the dust explosion severity is generally reached (far) above the (mass-based) stoichiometric concentration and, additionally, it falls off slowly (often far) above the stoichiometric concentration. Fig. 6 illustrates this effect graphically, contrasting the sharply defined explosion severity of methane in air compared with the much flatter behavior of polyethylene powder in air, as a function of concentration.

Energy content increases with substance amount. Common gases typically have a density of roughly 1 kg/m³ (at STP). Solids and liquids generally have a much higher density, typically 1,000 kg/m³ or more, thus at least about 1,000 greater than gases. Therefore a typical powder-air mixture often contains more energy per unit volume (i.e. volumetric energy content, J/m³) than a gaseous mixture. This greater amount of energy manifests itself in that a particulate explosion lasts longer in time than gas explosions. Important to note is that, for these reasons, explosions of aerosols (dusts, mists) also tend to cause more fire damage than explosions of gases.

Furthermore, since particulate explosions can occur at concentrations far above stoichiometric concentrations, a particulate explosion occurring in and rupturing closed equipment within a factory can emit large quantities of hot unburned material. Upon contact with air this hot unburned material can explode, resulting in a second explosion occurring inside the factory.

4.4 Hybrid mixtures

Hybrid mixtures are mixtures of combustible solid particles and air containing a combustible gas and/or vapor. Minimum ignition energies (MIEs) of typical flammable gas/vapor mixtures (e.g. methane in air, gasoline vapor in air), which are mixtures of individual molecules, are often very low (e.g. MIE values typically between 0.1 to 1 mJ; by comparison a human body can generate a static electric spark of 10 mJ); such low MIE values of gases/vapors lead to a large ignition hazard. Many common powders, however, have MIEs at least an order of magnitude higher than flammable gases/vapors, i.e. above 10 mJ. The insidious hazard of hybrid mixtures, first clearly discussed by Bartknecht already in 1980 and illustrated in Figs. 7 and 8, is that the presence of even low concentrations of flammable gases/vapors (e.g. originating from traces of evaporated solvents) can greatly increase the explosion sensitivity by reducing LEL values and drastically reducing MIE values; idem for the explosion severity, in particular the rate of pressure rise. Mixtures of combustible solid particles and air containing a combustible gas and/or vapor (hybrid mixtures) thus combine the worst hazards of dust explosions and gas explosions: the high explosion sensitivity of gas explosions, the high energy density of dust explosions, the high rate of pressure rise of gas/vapor
explosions, and explosion pressures as high as those of gas/vapor explosions.

We discuss recent research on hybrid explosions in Section 7, Current and Future Research.

5. Knowledge of the explosion behavior of particulates applied in fuel air explosive (FAE) weapon technology

5.1 General

So far we have reviewed scientific and technological knowledge with the goal of identifying and reducing particulate fire and explosion hazards. But such science can also be used for military goals, and additionally, understanding the technology can lead to safety improvements.

As noted, the most powerful explosives are detonations. Detonations of explosive solids such as TNT occur at supersonic velocities (flame speeds between 5,000 to almost 10,000 m/s) and produce extraordinarily high maximum explosion pressures (between 200,000 to nearly 500,000 baro). However, from a military standpoint, conventional high-explosives such as TNT have some inherent limitations. Firstly, while the maximum explosion pressures generated are enormous, they decrease rapidly with distance, since the TNT explosion is by approximation a ‘point source’. Thus the destructive effect is restricted to a relatively small area and volume. Secondly, the extraordinarily high pressures developed are actually much too high for a number of military purposes. Thirdly, conventional explosives such as TNT contain oxygen within their molecule. This oxygen is necessary to sustain the detonation process, but it also makes up a substantial part of the weight of the explosive. But oxygen is freely available in air. By using atmospheric oxygen, rather than having oxygen within the explosive itself, the destructive effect of a given mass of explosive can be substantially increased.

From a military standpoint, a useful explosive device (e.g. bomb) would have the following properties (Table 3).

Table 3 Possible general requirements for a particle-based bomb as shown feasible in open sources

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Generate a maximum pressure wave of approximately 15 to 20 bar overpressure, as such pressures are 100% lethal to humans, obliterate conventional buildings, destroy communication antennae, and severely damage and/or overturn vehicles.</td>
</tr>
<tr>
<td>2.</td>
<td>Generate this overpressure over a large surface area and large pie-like volume. Generate and maintain this pressure for a sufficiently long time duration (Δt), giving it more time to do damage (i.e. by creating a larger explosion impulse, ( \int P , dt ) (Eqs. 5–6)). Additionally, create a flame with the highest possible temperature to generate more lethality and damage.</td>
</tr>
<tr>
<td>3.</td>
<td>Produce the above-mentioned effects with a device of minimum volume and weight (e.g. by using the oxygen available in air).</td>
</tr>
<tr>
<td>4.</td>
<td>When used within an enclosed area such as bunkers or caves, consume the oxygen in the air, and by the nature of the combustion process sustaining the explosion, generate toxic gases such as carbon monoxide to poison those not killed by blast. Additionally, due to the rapid cooling of the hot explosion gases within the enclosed area, subsequently create a significant underpressure that can fatally damage lungs (i.e. create a partial vacuum, also called rarefaction).</td>
</tr>
<tr>
<td>5.</td>
<td>Be cheap to produce and safe to store and to transport.</td>
</tr>
</tbody>
</table>
charges bursts open the container and disperses the fuel into a cloud of fine particulates (droplets and/or dust) that mix with atmospheric oxygen. This cloud flows around objects and penetrates into structures. The second charge then detonates the entire fuel-air cloud, which has a substantial volume and is thus certainly not a ‘point source’. The detonation, which occurs throughout the whole cloud, generates a blast wave of ca. 20 bar overpressure within the cloud which completely destroys unreinforced buildings and kills 100% of exposed people (e.g. soldiers in foxholes). Outside the fuel-air cloud the explosion blast wave attenuates, but since overpressures of even some tenths of a bar can cause severe damage, the ‘death-and-destruction diameter’ of an FAE (i.e. inside and outside the fuel-air cloud) can be very large relative to normal bombs; e.g., for a 500 kg bomb ca. 100 m, thus an area of ca. 8,000 square meters. For obtaining a blast and flame, FAEs are the most powerful non-nuclear bombs. It was once thought that they might even be used to simulate nuclear explosions. (We add, however, that in addition to offensive use, FAEs are important defensively. Through their low detonation pressure and long explosion duration, FAEs are used to clear minefields, thus obviating the need for manual clearance.)

A problem with FAEs is that their initiation to detonation is quite difficult, requiring an ignition energy typically up to a million times greater than that needed to ignite a deflagration. Additionally, to ensure complete detonation in the entire fuel-air cloud, the particle concentration must vary little around an optimum value. (This fact can also help to increase civil safety by designing measures that reduce the chance of accidental detonations.)

The nature of FAEs is such that up-to-date information continually appears in (in the authors’ opinion) relatively reliable websites such as Wikipedia, IMAS (International Mine Action Standards), and Global Security.

### 6. Preventing and mitigating particulate explosion hazards

An abundance of literature exists describing course, prevention and mitigation of particulate explosions, including not only scientific and technological aspects, but also relevant standards, norms, legislation, and proper management (e.g. see Appendix). Here we divide prevention/mitigation into four categories:

1. Good management
2. Reducing the hazard of the particulate itself
3. Reducing the hazard of the system producing the particulate
4. Combinations of Points 1 to 3

### 6.1 Reducing hazard through good management

It is now known that poor management is the root cause of the overwhelming majority of industrial fires and explosions, as shown by countless investigations. Not the lack of knowledge, but unawareness or not properly applying it. It is for this reason that comprehensive safety management systems have been developed over the last three decades. Indeed, Points 2 to 4 above follow from good management. It is beyond our scope to discuss this extensive topic; here we merely cite two representative publications and discuss this point a bit further in 6.4.

### 6.2 Reducing the hazard of the particulate itself

Most technical methods to reduce particulate hazards follow logically from the basics described in previous sections, being simply negations of causative or exacerbating factors; e.g. since smaller particles increase the hazard, increase the size of particles. Most of these methods are thus ‘scientifically trivial’—but nevertheless effective: e.g. “increasing particle size”, “increasing particle humidity”, “preventing hybrid mixtures”, etc. Such measures have been known for decades and are described in detail in literature (e.g. see Appendix).

### 6.3 Reducing the hazard by improving the system in which the particulate is produced, stored, transported

The hazard is reduced by firstly preventing explosions from occurring and secondly, mitigating their effects should an explosion nevertheless occur. Prevention is achieved largely by, where possible, eliminating sources of fuel (e.g. practicing ‘good housekeeping’) and eliminating possible ignition sources such as (static) electrical and mechanical sparks and hot spots. The indexes listed in Table 2, which relate to ignition, logically suggest possible preventive measures: e.g. keeping particulate concentrations below LEL; through inertization, reducing oxygen concentrations ideally to below LOC; maintaining all surface temperatures below MIT; etc. Protective measures relate to hindering the propagation of an explosion. We briefly summarize a number of these measures in Table 4. Our discussion is necessarily superficial; in addition to extensive description in textbooks (see Appendix), excellent reviews of prevention and mitigation also exist.

### 6.4 Combinations of Points 1 to 3: Inherently Safer Design (ISD), Layers of Defense Approach (LOPA), ‘Holistic’ Approaches—components of ‘Loss Prevention’

Over the past decades, new design methodologies called...
Inherently Safer Design (ISD) and Layers of Protection Analysis (LOPA) have been developed that systematically avoid or at least mitigate chemical hazards like fire and explosion. Inherently Safer Design (ISD) is based on the logical negation of basic factors causing and exacerbating a hazard\textsuperscript{58). ISD uses keywords such as: Reduce, Substitute, Attenuate, and Simplify. Layers of Protection Analysis, whose starting point in the ideal case is Inherently Safer Design, is based on designing successive rings of ‘protective layers’ (“Layers of Protection”) around a process\textsuperscript{59). Each layer offers protection and/or mitigation in the event of disturbances and failure of a preceding layer. ISD and LOPA are examples of the systematic, comprehensive, and science-based discipline known as Loss Prevention\textsuperscript{60), which has been developing since the 1980s. The ISD- and LOPA-concepts date from approximately the end of the 20th century, but apparently only during this last decade have they been specifically applied to controlling dust explosion hazards\textsuperscript{61) and, most recently, explosion hazards of nano-particles\textsuperscript{62). Incorporating the ISD and LOPA design methodologies into computer-based ‘Expert Systems’, which also include explosion indexes (\textit{Tables 1 and 2}) for the materials used and produced, represents a formidable new tools for achieving safety through basic process design\textsuperscript{63). Perhaps even more promising are ‘holistic’ approaches to process safety. These include systematic technical approaches (e.g. ISD, LOPA, Quantitative Risk Analysis (QRA)), but expand considerably to include broad social-economic factors affecting top management such as the ‘emergent’ (i.e. ‘complex’) nature of society. A key goal is to find a proper balance between the pressure to increase profitability and (the costs of) adequate safety, and to provide top management with effective tools\textsuperscript{64).}

7. Current and future research

7.1 General

A plethora of knowledge already exists concerning the fire and explosion hazards of particulates and their effective control. Once again we emphasize that awareness, dissemination, and proper application of existing knowledge, i.e. the key responsibilities of management, are sufficient to prevent the overwhelming majority of industrial incidents.

Nevertheless research continues, with interesting and useful results. Particulate explosion falls within the much larger field of particle combustion, which is of major importance because a significant part of total world energy generation occurs through particulate combustion (e.g. diesels, jet engines, coal-based electric power generation). Up-to-date reviews of state-of-the-art particle combustion science and technology of this type therefore regularly appear in textbooks\textsuperscript{65). Combustion science also relates to achieving advanced (military) goals such as powering hypersonic aircraft using detonation-based engines, possibly fueled by aluminum nanoparticles\textsuperscript{66).}

Here we concentrate on the particulate research relating to industrial hazards. Many excellent reviews of particulate fire and explosion hazards have appeared over the years\textsuperscript{67). A general line of progress in research has been firstly, an increasing knowledge and insight into particulate explosion behavior and explosion mechanisms and better quantitative description and prediction. Secondly, stimulated through further development of CFD, better modeling, enabling more accurate prediction of fire and explosion ignition and propagation and the design of more cost-effective preventive and protective measures. Below we summarize some interesting areas in which progress and, for particulate explosion modeling, certain breakthroughs have been made.

We divide our discussion into particles themselves (nanoparticles and hybrid mixtures) and systems containing particles.

7.2 Effects of reducing particle size towards the size of molecules: Nanoparticles

Spherical nanoparticles are defined as those having a diameter of less than 100 nm (0.1 micron); non-spherical nanoparticles are defined as those having at least two dimensions smaller than 100 nm. Due to their special properties, the production and use of nanoparticles is strongly increasing. Interest in health and safety aspects of
nanoparticulates has grown recently because of their ability to penetrate into the deepest parts of the lung\textsuperscript{68} and their suspected heightened explosion hazards\textsuperscript{69}.

In discussing the effects of reduced particle size it is useful to distinguish between different groups of materials that may exist in the nano range such as:

1. Natural organic materials (e.g. grain, linen, sugar, etc.)
2. Synthetic organic materials (e.g. plastics, pigments, pharmaceuticals, etc.)
3. Carbon, coal and peat
4. Stable reactive substances such as reactive metals (e.g. Al, Mg, Si, Ti, etc)
5. Unstable reactive substances such as high explosives (e.g. TNT, HMX, CL-20)
6. Unstable mixtures composed of different powdered substances (e.g. gunpowder)

(Note that ‘Stable reactive substances’ and ‘Unstable reactive substances’ are defined in Section 4.1.)

In a thorough review, Eckhoff\textsuperscript{70} compares the explosion behavior of nano- versus micron-sized particles and presents a number of general conclusions:

1. For all commonly used powders (Groups 1 to 4), the explosion hazards, as expressed by the explosion severity (our Table 1) and explosion sensitivity indexes (our Table 2), increase strongly as the particle size decreases from mm values to the lower end of the micron range (roughly 1 to 10 microns (see our Figs. 3–5)).
2. Nearly all experimental data on nanoparticle explosion hazards are available only in the upper-end of the nano range, i.e. around 100 nm or not much lower (usually $\gg$ 10 nm; lowest values found were 15 nm\textsuperscript{71}).
3. Explosion sensitivity, particularly as expressed in the MIE value, continues to increase as particle size decreases down into the (higher end) of the nano range; i.e. MIE values continue to decrease with decreasing particle size into the nano range.
4. By contrast, explosion severity, as expressed by $P_{\text{max}}$ and $K_{\text{Si}}$ values, appears not to increase as particle size decreases from the micron range into the (high) nano range.

Point 1 above follows logically from the fact that specific surface area increases as particle size decreases (e.g. wooden logs do not explode, but finely powdered sawdust does; the finer the sawdust, the greater the explosion hazard).

Concerning Points 2 and 4 above, Eckhoff notes inherent physics-based limitations in creating true nanoparticles and dispersing them into stable clouds of true nanoparticles\textsuperscript{72}. Coagulative forces such as van der Waals’ forces increase significantly as particle size decreases from the micron into the nanometer range. Thus nanoparticles inherently tend to coagulate into conglomerates of multi-particles. Also due to strong coagulative forces, it is difficult to disperse nanoparticles as nanoparticles, and even once dispersed into a cloud, true nanoparticles will, through collisions, tend to rapidly (e.g. before ignition occurs) coagulate into larger, micron-sized conglomerate particles.

With this explanation in mind, Eckhoff explains the apparent anomaly of Point 3 (explosion sensitivity, expressed as MID) by theorizing that the electric spark, inherent to the MIE testing procedure, may be powerful enough to cause eventually formed conglomerates to break up into true nanoparticles.

Concerning Group 4 powders mentioned above (Stable reactive metals such as aluminum), Eckhoff briefly mentions another factor affecting explosion severity and sensitivity: the degree to which reactive metal particles are covered with an oxide layer. An oxide layer is completely non-reactive and is a heat sink, thus tending to inert the powder. Obviously the finer the particles, the greater the relative mass of even a thin oxide layer and thus the greater the reduction of explosion hazard\textsuperscript{73}. This phenomenon was widely known already decades ago, since the production of fine powders of reactive metals.

Nanoparticles of reactive metals form a special case as more explosion research has been done on them than on any other type of nano-particulates. This is due to their widespread (military) use—past, present, and future—as components of pyrotechnics, rocket propellants, and (fuel-air) explosives. It has long been known, for example, that if sufficiently fine and sufficiently pure (e.g. free of oxide film), many metals are so reactive that if suddenly dispersed in air they will spontaneously—without any external ignition source—burn/explode; i.e. they are pyrophoric\textsuperscript{74}. Being pyrophoric, their MIE is zero and their MIT is below ambient temperature. Whether pyrophoricity occurs in practice depends on a heat balance involving factors like exothermicity of the oxidation reaction, particle size, thickness of oxide layer, and boiling points of metal and oxide relative to adiabatic flame temperature\textsuperscript{25,76}. The pyrophoric nature of fine powders of reactive metal, especially those in the nano range, complicates testing procedures to determine explosion indexes, requiring modification of standard dust explosion testing equipment and procedures for explosion severity\textsuperscript{77} and explosion sensitivity\textsuperscript{78}.

Experimental measurements, complemented with theoretical studies, suggest some very interesting particle combustion and explosion phenomena unique to sub-micron/nano-sized particles. The following figures illustrate some of this behavior.

For powders that do not readily volatilize such as carbon and metals with high melting points, Fig. 9 illustrates the change in reaction mechanism as the particle size decreases from the low mm range to below roughly about 1–10 µm: the combustion mechanism changes from being diffusion-controlled in the region of large particles to being
chemical-kinetically controlled in the region of increasingly smaller particles. As previously noted in Section 4.2.2, gas/vapor explosions, which occur between molecules, are chemical-kinetically controlled and dust explosions of large particles are diffusion-controlled. But as particle size decreases and begins to approach that of gas molecules, it is to be expected that powder explosions will progressively become more like gas/vapor explosions.

Huang et al. (Fig. 10) also illustrate the transition from diffusion control to chemical-kinetic control of the reaction rate as particle size decreases from the micron range into the nanometer range (Bidabadi et al. present nearly identical results and conclusions.) As already noted, a fundamental property of the flame of a given mixture of a combustible substance in air at given conditions is its laminar burning velocity, $S_L$. Also as mentioned before, hydrocarbon fuels in air exhibit laminar burning velocities of tens of centimeters per second or somewhat higher. Highly reactive combustible gases such as hydrogen and acetylene have laminar burning velocities in air typically in the meters-per-second range. Reactive combustible particulates in the micron range have laminar burning velocities in air that are typically approximately a factor of ten smaller.

This same line of reasoning—nanosized particles in the homogeneous, chemical-kinetically controlled regime, and micron-sized particles in the heterogeneous, diffusion controlled regime—can also be applied to the ignition of fine metallic particles (i.e. their MIE and MIT), as is shown in Fig. 11 for the Minimum Ignition Energy (MIE) of powdered aluminum (chemical-kinetically controlled at small particle sizes and diffusion controlled at larger sizes).

Concerning Group 5 powders (unstable substances such as high explosives), it appears that reducing particle size from the micro to the nano range increases (military) usefulness by increasing explosive power while reducing sensitivity to ignition (the latter as expressed by impact sensitivity). This was found for one of the most powerful explosives known, CL-20, as well as the explosives TATB and HMX (all these explosives are more powerful...
Concerning Group 6 powders (unstable mixtures such as gunpowder), it is reported that, at least for flash powder used in fireworks, reducing particle size from the micro to the (upper) nano range increases explosive power but in contrast to results reported above for a number of high explosives, also increases ignition sensitivity (as expressed by impact sensitivity)\(^9\).

We conclude this section by commenting that more research needs to be done in the lower regions of nano-sized particulates (i.e. \(< 100\) nm) to be certain about the explosion behavior of particles closely approaching molecular size. It would seem reasonable to these authors (SML and HJP) to assume for the time being that for such particles, their explosion indexes as expressed in Tables 1 and 2 will increasingly resemble those of gases/vapors with a similar basic molecular structure, as chemical kinetics starts to control the rate of overall reaction. But this must be experimentally verified, because pyrolysis and diffusion rates in the case of organic dusts and the breaching of oxidized surfaces of metal particles can stretch reaction times. Such effects will mitigate explosion index values.

### 7.3 Hybrid mixtures

Recent research largely validates but also complements Bartknecht’s basic findings (e.g. Figs. 7–8) by providing additional information\(^9\) and a more fundamental description of relevant explosion phenomena, linking hybrid mixture behavior with modern safety analysis methods, modeling hybrid explosion behavior, and even modifying industrial standards. Dufaud et al.\(^8\) comment on how better knowledge of hybrid explosion behavior is used to modify an important industrial norm (NFPA 68; venting of deflagrations). Dufaud et al.\(^9\) study effects of pyrolysis gases/vapors evolving during dust explosions of organic powders and develop a predictive model. Garcia-Agrada et al.\(^1\) develop an insightful way of graphically presenting hybrid explosion behavior in terms of measured \(K_{St}\) values and 5 combustion regimes: non-explosive, dust-driven, gas/vapour-driven, gas-gas/vapour-driven, and ‘synergistically’ driven. Denkevits performed unique experiments, namely combining a highly reactive gas, hydrogen, with a much less reactive substance (tungsten)\(^2\), or a very much less reactive element, pure carbon (graphite)\(^3\), both pure carbon and tungsten are, for practical purposes, non-volatile. Previous researchers had combined flammable gases/vapors with powders that volatilize (i.e. most organic materials). Especially interesting are the results with graphite, which show that a hybrid explosion with a highly reactive substance (hydrogen) and a combustible substance of low reactivity (e.g. graphite) can occur in two distinct stages: initial fast explosion of the reactive substance, followed by a second, relatively slow explosion of the inactive substance, ignited by the initial explosion. On the subject of approaching hybrid explosion hazards with new methods, using polyethylene production as an example, Abuswer et al.\(^5\) combine controlling the hazard (and risk) of hybrid dust explosions with Inherent Safer Design (ISD, described in Section 6.3), Quantitative Risk Analysis (QRA, e.g. employing Fault Tree Analysis), and CFD modeling using DESC (described below in Section 7.5).

### 7.4 Predicting values of particulate hazard severity (Table 1) and sensitivity (Table 2) indexes

Reyes et al. predict dust severity indexes (\(P_{max}\) and \(K_{St}\)) using Quantitative Structure Property Relations (QSPRs) relations\(^4\). Such an approach (also commonly called Quantitative Structure Activity Relations: QSARs) is used with increasing success to predict a whole host of the physical, chemical, and even physiological-medical (e.g. anti-carcinogenic) effects of substances, thus obviating, or at least greatly reducing, the need for (expensive) testing. We caution, however, that even \(P_{max}\), which theoretically is a chemical thermodynamic entity and thus invariant, can depend strongly on how it is measured (e.g. degree of turbulence)\(^5\). The reason is that at higher heat loss, maximum temperatures are lower, resulting in slower kinetics, which in turn hampers reaching the equilibrium reaction product composition and thus the adiabatic flame temperature.

### 7.5 Modeling the propagation of particulate explosions using computational fluid dynamics (CFD)

Particle technology engineers are used to applying Discrete Element Modeling (DEM) when they want to study particle flow in various situations. As regards dust dispersion, even a combination of DEM and Computational Fluid Dynamics (CFD) proves very useful, as shown by Hilton and Cleary\(^6\). However, so far computer capabilities fall short of depicting model heating, gasification and combustion around discrete elements; only a code based on differencing a continuum is capable of modeling flow and flame (reactive gas dynamics). Norwegian Gexcon, a spin-off of Bergen University, obtained over a period of at least 20 years considerable experience in modeling vapor cloud explosions by developing the CFD-code FLACS (Flame Acceleration Simulator). For instance, applying this code, Gexcon was able to successfully simulate the surprisingly high pressures which occurred in the explosion of a gasoline components cloud resulting from an overflowing storage tank at the Buncefield site near London in 2005\(^7\). The FLACS code simulates the flame speed-overpressure dynamics of an exploding cloud by solving the Navier-Stokes conservation flow equations, the gas equation of state, a sub-grid scale turbulence model.
and the combustion energy release rate. The latter is dependent on the turbulent intensity which an advancing flame faces. This turbulence is generated by the flow ahead of the flame, pushed forward by the expansion of hot gases behind the front and the interaction and friction of the flow with obstacles and congestion in the environment. This phenomenon of turbulence in the unburnt gas by which the expanding hot reaction products accelerates the flame is called a feedback mechanism. The results of runs of the code have been extensively validated against explosion test results at various scales.

Already in 1996, Van Wingerden98) of Gexcon clearly listed the necessity and possibility of applying Computational Fluid Dynamics (CFD) for creating an overall model of propagating dust explosions within a contained space such as a process plant, and using this model to optimally design safeguarding measures. In analogy to vapor cloud explosion modeling, the Norwegian-based Gexcon company initiated in 2003 a multi-partner European research project DESC, an acronym which stands for Dust Explosion Simulation Code99). Additional problems with dust explosions are, however, that flame propagation occurs with an even more complex mechanism than in gas explosions and that the flame in a dust explosion is also “feeding itself” by whirling up settled dust. This dust dispersion part is still not fully developed and further experimental work is being carried out in shock tubes to investigate all relevant parameters, with the aim of being able to more reliably model the dust concentration and turbulence intensity into which the explosive flame propagates. More advanced codes apply large-eddy simulation but are limited with respect to the space dimensions they can cover. Nevertheless, compared to the capabilities of CFD to successfully model gas explosion behavior, at this moment CFD modeling for particulate explosions is still in its infancy. In his 2010 lecture, Skjold presents a detailed and frank evaluation of the state of CFD explosion modeling, the Norwegian-based Gexcon company recently published an interesting application of DESC in a cube by applying a shadow-graph technique, for which the methane serves to stabilize the flame. The dust concentration is varied over quite a wide range. The experimental results were compared to calculated ones based on a straightforward onedimensional heat balance deflagration model and applying a devolatilization rate model of coal particles as a function of temperature. The devolatilization also acts as a heat sink. The model yields a devolatilization zone thickness and a burning velocity. This approach is rather promising; it can also be applied on controlled turbulent intensity flames as shown by Rockwell and Rangwala104), and can be expected to be applied on a variety of dust-fuel-air systems.

Di Benedetto and Russo105) tackled the aspect of combustion after the devolatilization stage of organic dusts, which is very important to the burning velocity of the dust-air mixture, and hence to the $K_{\text{st}}$ value. By applying devolatilization test results from various sources, carried out by thermogravimetry with attached chromatographic analysis of the pyrolysis gas produced, the composition as well as the rate of formation of flammable gas at various temperature levels was obtained from a number of dusts, namely cornstarch, polyethylene, and cellulose. The authors then used the CHEMKIN Premix module to calculate the laminar burning velocity given the gas composition and the known GRI-Mech 3.4 kinetic combustion mechanism. In addition, they applied a relation between the pressure increase in a closed vessel, its radius, and the ratio of specific heats developed by Dahoe and De Goey106) to calculate the rate of pressure rise. Subsequently, they derived the $K_{\text{st}}$ value or deflagration index from the rate of pressure rise and the cube root of the vessel volume. Although the results did not cover the experimental values very accurately, the trends of the effect of concentration with the $K_{\text{st}}$ value fitted the experimental ones surprisingly well. To obtain the best fit, the pyrolysis composition to be used in the model must be determined at the highest temperature and heating rate of the thermogravimetric apparatus. Low-temperature gasification kinetics differ from higher-temperature ones. The missing link is now the relation between the burning velocity and turbulent intensity. As mentioned above by the work of Rockwell and Rangwala, there is some progress also in this direction, albeit slow.

An interesting further step is modeling the effect of particle size on dust explosion indices. Di Benedetto et al.107) performed a study of the effect of particle size on the deflagration index. As explained above, devolatilization can

which dust particles float statically in position by an up-going flow of air, as in a fluidized bed102). A recent and more successful series of experiments measuring the laminar burning velocity of coal dust-methane-air mixtures has been performed by Xie et al.103) The measurement takes place on the principle of obtaining a steady-state flame fed by a continuous flow of fuel-air and observing the flame cone by applying a shadow-graph technique, for which special equipment had to be developed.
be measured by performing thermogravimetric experiments over a certain range of temperatures. In this study it was also modeled. This was done as a two-step kinetic rate process: first step is the formation of a molten phase, while the second step is a pyrolysis (cracking) and volatilization. Mass and energy balances in differential form were derived for the conversions under influence of convected and radiant heat. The volatilization depends on the dimensionless Biot number, $Bi$, being the ratio of the time constant of heat conducting into the particle and that of the external heat transfer. Two cases were considered: one in which the external heat transfer dominated ($Bi << 1$) and the other in which internal heat transfer controls ($Bi >> 1$). For the first case, the dimensionless Damköhler number, $Da$, is considered, being the ratio of the external heat transfer time constant and the characteristic pyrolysis conversion time. Next, two regimes are distinguished: regime I in which the external heat transfer controls the pyrolysis ($Bi << 1$ and $Da >> 1$), and a second (II) where the pyrolysis is the slowest ($Bi << 1$ and $Da << 1$). For the second case ($Bi >> 1$), the dimensionless Thiele number, $Th$, is applicable, being the ratio between conducted heat time constant and the characteristic pyrolysis time. This results in a third and fourth regime (III and IV) with pyrolysis controlled rate ($Bi >> 1$ and $Th << 1$) and conversion controlled by internal conduction ($Bi >> 1$ and $Th >> 1$), respectively. Particle size appears in the nominator of both $Bi$ and $Th$ number. A third dimensionless number, $Pc$, is defined as the ratio between the time constants of pyrolysis and combustion. This ratio is equal to the quotient of the product of density and laminar burning velocity, and the product of particle size and flame thickness. If $Pc$ is larger than unity and if pyrolysis is controlled by conversion kinetics (regimes II and III), the pyrolysis reaction rate controls the explosion. Alternatively, at a $Pc$ smaller than one, the combustion of volatiles controls. In the case of regime I, the product of $Da$/$Pc$ should be evaluated, and in the case of regime IV $Tr$/$Pc$. Depending on the particle size, one or the other regime dominates. When the particle size is smaller than a certain critical value depending on the dust material, heating and devolatilization rates are relatively high ($Pc$, $Da$/$Pc$ and $Th$/$Pc$ << 1) and combustion kinetics determine flame propagation which can be considered to produce a maximum $K_{af}$ value. The other regimes can be defined by evaluating the dimensionless numbers. On this basis, simulations were performed which gave further insight. For instance, the simulations yielded for the four regimes the ratio of maximum volatiles production rate at any particle size and at a particle size near zero as a function of particle size. The model was applied to polyethylene dust. The particle size was varied between 10 and 900 microns. Compared with experimental results of the $K_{af}$ values, the simulated ones were in fair agreement. More dust types should be investigated.

Finally, Di Benedetto et al. accomplished a CFD study to simulate the dust dispersion in the 20-liter explosion vessel. The dust concentration variation in time and space after its injection into this vessel, being the standard test equipment used by many, is still unknown. This is important, because the 20-liter vessel is supposed to produce the same results as a 1-m³ vessel and for that purpose, the ignition delay time and pressure difference ratio which determine the pre-ignition turbulence and dust dispersion have been carefully selected. How large the margin is, is uncertain. Measuring of the turbulence level with a laser velocimeter (also named Laser Doppler Anemometer) as in the case of gas is not possible with dust. The dust concentration selected was 250 g/m³, the dust density 2100 kg/m³, so that it appeared possible to apply an Eulerian approach to the time-averaged Navier-Stokes equations for the gas phase and a Lagrangian one for the dust particles. A solution was obtained with the ANSYS Fluent code. The solid-phase flow was simulated by means of the (Lagrangian) Discrete Phase Model. It appears that multiple vortex structures develop which push the dust towards the walls. Hence the concentration is far from uniform. The turbulence level at the center near the ignition is rather high. Further studies will be needed to investigate the effect of particle size distribution and of other particle characteristics.

8. Summary and Conclusions

Particulate hazards include fire and explosion. The key difference between fire and explosion is that the rates of physical and chemical processes occurring during explosions are much faster than those occurring during fires because during a fire, fuel and air are clearly separated, while in explosions fuel is ‘pre-mixed’ with air. Particulate explosions, like particulate fires, produce flames, intense heat, and high temperatures, but unlike fire, particulate explosions produce a ‘blast’, a destructive pressure or shock wave, and sometimes also high-velocity fragments caused by bursting equipment. It is essential to be aware that:

**ALL COMBUSTIBLE POWDERS AND MISTS CAN EXPLODE**

Characteristics of explosions are the propagation velocity (called flame speed, $S_f$), maximum pressure; $P_{max}$, maximum rate of pressure rise, $(dP/dt)_{max}$; time duration of the explosion, $Δt$; and the integral of explosion overpressure over time, $\int P dt$, called explosion impulse, $I_{exp}$. Most particulate explosions occur as a deflagration, which is simply a very rapid burning. Deflagrations propagate at less than the speed of sound and produce pressure waves which have finite $(dP/dt)_{max}$ values. Typical $P_{max}$ values for particulate deflagrations at optimum composition are ca. 5–10 times the initial pressure, and flame speeds ($S_f$ values) are typically around 10 m/s. Under certain circumstances of
The most important physical property affecting fire and explosion occurring (deflagration of detonation), caused by explosions. Such indexes include the type of energy (MIT and MIE), and Limiting Oxygen Concentration (LEL and UEL), Minimum Explosion Temperature and concentration). Examples are: Lower and Upper Explosion Limits (NFPA). Extensive analysis of industrial accidents shows that it is not lack of knowledge that is the most general cause of accidents, but rather unawareness and/or improper application of such knowledge, thus management failure. Therefore, while we outline the basics of prevention and protection, we stress that the generic cause of most particulate fires and explosions is poor management. To tackle this problem, modern safety management systems are evolving. Such management systems are being combined with new design methods such as Inherently Safer Design (ISD) and Layers of Defense Analysis.
While an abundance of knowledge (data, theory) exists, research on the fire and explosion hazards of particulates nevertheless continues, with interesting and useful results. One important area is nanoparticles, whose production and use are increasing rapidly. Research so far shows that reducing the particle size down from the mm range to the micron range (1000 nm) strongly increases both the explosion severity and explosion sensitivity. Further reduction into the (high) nanometer range shows a continuing explosion sensitivity increase (i.e. lower MIE), but no further increase in explosion severity (i.e. \( P_{\text{max}} \) and \( K_{\text{st}} \) values remain constant, or even increase slightly with further particle size reduction). We note, however, that nearly all research has been restricted to the high end of nanoparticle size; i.e. to particles around 100 nm or somewhat smaller (\( \geq 15 \) nm). Creating smaller nanoparticles and dispersing them into clouds is hampered by strong cohesive forces (e.g. van der Waals’ forces). Research on reactive metallic nanoparticles is further complicated by their tendency to spontaneously oxidize or even exhibit pyrophoric behavior. Nevertheless, it is clear that as the particle size decreases from the micron range into the nanometer range, the mechanism of particulate explosions increasingly resembles the mechanism of gas/vapor explosions; i.e. the reaction rate is less controlled by diffusion and more by chemical kinetics. Various researchers theorize and extrapolate or calculate that in the extreme case, when particulates approach the size of individual molecules, their explosion mechanism will become identical with that of gases and vapors, namely controlled exclusively by chemical kinetics. At these low nanodiameters, the fundamental explosion parameters such as laminar burning velocity and sensitivity and explosion severity indexes will increasingly resemble those of gases and vapors (e.g. indexes of smaller and smaller (nano-sized) polyethylene particles increasingly resembling those of ethylene gas; aluminum (a stable but reactive metal) nanoparticles, although chemically very different, having a laminar burning velocity increasingly close to that of acetylene (a highly reactive gas)).

Another important area of research is acquiring a deeper understanding of particulate fire and explosion reaction mechanisms, and through such knowledge being able to better quantitatively describe and predict fire and explosion behavior. Making use of Computational Fluid Dynamics (CFD), powerful models are being developed to predict the course of (particulate) explosions (e.g. \( S_t, P_{\text{max}}, \Delta t, (dP/dt)_{\text{max}} \) these as functions of time, location, and initial conditions), both inside and outside installations. Such models enable more cost-effective safety design and operation. Present CFD modeling of dust explosion behavior, however, still requires further development to reach the reliability presently achieved for modeling gas/vapor explosions.

### Symbols and Abbreviations

- AIT: Auto-Ignition Temperature (usually Minimum Auto-Ignition Temperature)
- bara: bar absolute pressure
- baro: bar overpressure
- CCPS: Center for Chemical Process Safety (USA)
- DDT: Deflagration-Detonation Transition
- DIN: Deutsches Institut für Normung (German Institute for Standardization)
- ISD: Inherently Safer Design
- LEL: Lower Explosion Limit (= LFL: Lower Flammability Limit)
- LOC: Limiting Oxygen Concentration (below which explosion is not possible)
- LOPA: Layer of Protection Analysis
- MESG: Maximum Experimental Safe Gap
- MIE: Minimum Ignition Energy
- MIT: Minimum Ignition Temperature
- NFPA: National Fire Protection Association (USA)
- PVC: Polyvinylchloride
- SMD: Sauter Mean Diameter \( (D_{3,2}) \)
- STP: Standard Temperature and Pressure
- TNT: TriNitroToluene
- UEL: Upper Explosion Limit (= UFL: Upper Flammability Limit)
- Δt: Time duration of explosion
- Δt: Time
- \( T \): Temperature
- \( V \): Volume of a vessel

### Appendix. Some recommended literature sources


2) While dust explosion hazards are extensively studied, much less is available for mist explosions. Examples are: Gant, S. M. and Scholten, R. M. (1999), “Explosion theory for dummies”, NPT Process Technieck, 2, pp. 19–24. Derivation is based on assumptions that flame thickness is small relative to vessel diameter and that flame speed is independent of temperature and pressure.


6) Dahoe et al. (1996, 2003) derive more realistic—and considerably more complex—equations describing flame speed effects on pressure rise and K factor for thick dust flames,
11) Using such indexes (Tables 1 and 2), in combination with chemical thermodynamic data and data from practice (e.g., accidents), the National Fire Protection Agency (NFPA) ranks hazards of powders in terms of Health, Fire, and Instability. See Center for Chemical Process Safety, (2005), “Guidelines for Safe Handling of Powders and Bulk Solids”.
12) On the basis of a number of simplifying assumptions, and using only secondary school chemistry and physics, Lemkowitz and Scholten correctly derive, in terms of trends, how changes in ambient temperature, pressure, and flow (turbulence) affect nearly all important fire and explosion indexes: Lemkowitz, S. M. and Scholten, R. M. (1999), op cit.
17) Powdered ammonium nitrate, mixed with an inert compound such as calcium carbonate to reduce its explosion hazard (‘phlegmatizing’ it), is a widely used fertilizer. In spite phlegmatizing inerts, a number of serious explosions of large piles of powdered ammonium nitrate have nevertheless occurred.
19) The above source also lists common water-reactive substances (Table 3.4, page 50) as also does ‘Common Water Reactive Chemicals’, http://www.esd.uga.edu/chem/pub/waterreactivemat.pdf.
21) In some cases, such as explosions of finely divided metals (e.g., powdered aluminum), even three phases can be simultaneously present: a solid phase (solid aluminum oxide), a liquid phase (molten aluminum), and a gaseous phase (air, even vaporized aluminum).
versity of Technology, 2000, 297 pages (ISBN: 90-90-

42) Modified from Pellmont, G. (1979), “Explosions- und Zünd-Verhalten von Hybriden Gemischen aus brennbaren Stäuben und Brenngasen”, PhD thesis, No. 6498, ETH Zürich. Figure 7 here is taken from Eckhoff, R. K. (2003), op cit, Figure 1.60, p. 52. Modified from Bartknecht, W., (1981), “Explosions—Course, Prevention, Protection”, Springer-Verlag, Fig. 1-5.4, p. 51. Figure 8 here is taken from Eckhoff, R. K. (2003), op cit, Figure 1.65, p. 55.


46) Direct ignition of detonations of gaseous fuel-air mixtures requires high energies, typically (more than) a million times greater than those required to ignite deflagrations.
60) For an overview of Loss Prevention, see, for example, Mann, Ref. 15 in the Appendix.


69) Safety and health issues are central in the Nanosafe: Safe Production and Use of Nanomaterials. International conferences held biannually in Grenoble, France in 2008, 2010, and 2012. Noticeable is that while in 2008 and 2010 fire and explosion safety issues were discussed in many lectures, since then these issues seem relatively clear, in comparison with health issues, which in 2012 still received much atte-


Author's short biography

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Saul Lemkowitz studied chemical engineering (B.Sc.) at Rutgers University in the United States. After working at Allied Chemical Europe in The Netherlands, he studied chemical engineering at Delft University of Technology (M.Sc. Ph.D.). He remained at Delft University, as an associate professor of loss prevention and sustainability, researching dust explosions and teaching explosion safety (later together with Prof. Hans Pasman). For almost 30 years he has also taught explosion safety to industry. While being formally retired, Dr. Lemkowitz still actively teaches at Delft University and to industry and publishes articles.

Hans J. Pasman

Dr. Ir. Hans J. Pasman is a research professor at Mary Kay O’Connor Process Safety Center of the Department of Chemical Engineering of Texas A&M University and emeritus professor chemical risk management of the Delft University of Technology in the Netherlands. He has also been a member of the Dutch Council of Hazardous Substances until this council was disbanded in 2012. Graduated in chemical technology at Delft University of Technology in 1961, and finishing a doctor’s thesis in 1964 while employed by Shell, he joined the Dutch organisation for applied research, TNO, in 1965, performing research in reactive materials, gas, dust and energetic material explosions, investigation of industrial accidents and risk analysis, while also managing part of the organization. He has been a member of the Working Party on Loss Prevention and Safety Promotion in the Process Industries since 1972, and has been chairman of the International Group on Unstable Substances for 10 years, of the European Study Group on Risk Analysis (1980–1985), of a NATO Group on Explosives (1982–1992), and chairman of the EFCE Working Party on Loss Prevention (1986–2004). In this latter capacity, he was instrumental in founding the European Process Safety Centre in 1992. He is active in writing and reviewing process safety articles and has obtained numerous awards.