1
Introduction

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1.1
Problem Description

In industry and transportation silos serve as containers for storing bulk materials or dusts. Volumes of silos range from a few cubic meters as supply silos in process chains to some thousand cubic meters for storing fuels, grain or sugar, for example. Recently, in Europe some coal storage silos have been erected storing up to 50 000 tons of coal.

Many silos are of cylindrical shape but there are also silos with rectangular cross section or those formed by the intermediate space between adjacent cylindrical silo cells. As will be explained below, silo size and shape affect fire appearance and fighting.

Silo batteries – an arrangement of up to 100 or more single silo cells on one site – offer storage capacities for dozens of thousands of tons of material.

About 80% of bulk materials are flammable, among them those which are stored in large masses like grain or other crops. Hence, in the case of a fire the release of an enormous amount of energy has to be expected, which endangers the static integrity of the structure and makes fire fighting extremely difficult. In addition, huge emissions of smoke and flue gases impede the access to the fire site and harm the environment.

Besides the fire itself the hazard of an explosion has to be taken into account when flammable bulk materials are stored in silos. Fine particles may be contained in the bulk material or are produced by abrasion during handling. When these fine particles are dispersed in air as may happen during filling or emptying the silo, eventually an explosive dust cloud is formed in the interior of the silo. If an ignition source of sufficient energy is then in place a dust explosion is likely to occur.

Another explosion hazard results from flammable gases. Under the action of a heat source many organic bulk materials undergo thermal decomposition (pyrolization) whereby flammable gases like carbon monoxide, methane, propane

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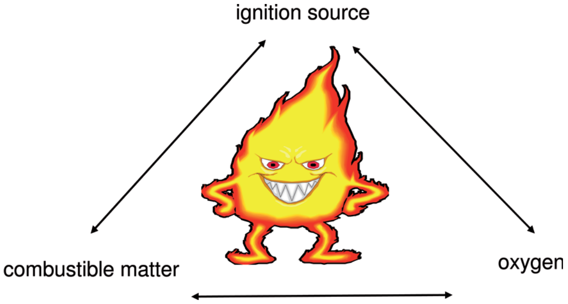


Figure 1.1 The fire triangle.

or hydrogen are produced. If these gases mix with air an explosible gas cloud may be generated.

To start a fire three pre-requisites are necessary: a flammable material has to be brought together with an oxidizer (in most cases the oxygen contained in the ambient air) and an ignition source has to act on the mixture. This relation is described by the well-known fire triangle, Figure 1.1.

In silos where flammable bulk materials are stored, the first two pre-requisites are present permanently. The reason why not all of these silos go up in flames is the absence of an effective ignition source. Ignition sources are characterized by their energy and their duration of action. Not every ignition source is able to ignite any flammable material or mixture. There is a strong relation between the efficiency of an ignition source and the ability of the material to act as a receptor of the ignition energy. The ignition sensitivity of a material depends on its chemical structure and on physical properties like particle size, porosity and moisture content.

The physical and chemical properties of materials which are relevant for the fire behavior will be described later in the present chapter. Chapter 2 deals with different mechanisms of ignition of solid materials in detail, among them self-ignition of bulk materials, which has been revealed to be the cause of a large number of silo fires in the past.

In a hazard analysis five different factors have to be considered:

- hazards connected to the bulk material handled,
- hazards connected to the process equipment,
- hazards connected to the mode of operation and maintenance,
- the velocity of the fire spread,
- the losses expected in the case of a fire or an explosion.

The assessment of these factors leads to a concept for prevention of and protection against fires and explosions. Both technical and operational measures are possible; in many applications different measures of these two types are combined. Risk assessment is described in detail in Chapter 3, especially the analysis of hazardous properties of bulk materials. How to take appropriate preventive and protective measures to minimize the hazard of a fire or an explosion in silos is explained in Chapter 4. Some technical solutions for fire detection, alarming and subsequent fire suppression which are currently available on the market are presented in Chapter 5.

Chapter 6 contains a number of case studies of silo fires from which many valuable lessons could be learned. In the cases mentioned it turned out that there are some significant differences to, for example, fires in buildings which require different fire fighting strategies and expert knowledge.

Chapter 7 is intended to give some guidance for fire fighting in different situations fire fighters may encounter when called to a silo fire site. This is demonstrated using a further case study, however focused more on fire fighting than on the causes of the fire and the chain of events.

In Chapter 8 special precautions are highlighted for the case when inerting is the measure of choice for fire extinction.

Chapter 9 introduces briefly computational methods for the prediction of self-ignition and fire propagation scenarios considering a computational model of the real silo configuration as an example of advanced methods for fire hazard assessment.

1.2
Influence of Material Properties on Fire

Bulk materials are characterized by a number of physical and chemical properties. Some of these properties have strong relevance for ignition sensitivity and fire spread. There are different mechanisms of how bulk materials react in a fire. Firstly, organic materials when exposed to heat may decompose and release gases some of which are combustible themselves and burn in a gas-phase reaction. Secondly, the solid material itself or the solid residues of the decomposition reaction burn by oxidation at the surface of the solid particles.

It is obvious that at least the reaction rate of the combustion step largely depends on the free surface area the particles offer to the oxygen molecules to be absorbed. Hence, the volume fraction of the voids within the bulk good is of importance for the fire behavior. Oxygen penetrates into or between the voids by diffusion or if the voids are large enough by convection. The characteristic length scale of this type of mass transfer is the free path length between the voids, which depends on the particle diameter.

Furthermore, for most bulk goods each individual particle has pores which allow oxygen to penetrate into the particle and then to react with the solid. The pores may be of such a size that free motion of the oxygen molecules is no longer possible. This type of diffusion is called Knudsen diffusion. The characteristic length in this case is the pore diameter.

1.2.1
Particle Size Distribution, Particle Shape and Internal Surface Area

Particles in an arbitrary deposit of bulk material may have different sizes and shapes.

Fractions of freshly mined coal for example range from up to several tens of centimeters to a few millimeters depending on the brittleness of the coal and on the mining method. In addition, significant amounts of dust particles with diameters in the range of micrometers may be present, for example due to the excavation procedure or due to abrasion during transportation. For such a material the particle diameters cover several orders of magnitude.

Other products like grain consist of particles within a comparatively narrow range of particle sizes of a few millimeters. However, a small but non-negligible portion of fine dust usually exists.

The traditional method to measure particle diameters is sieving. Mostly vibratory sieves are used, where the particles fall successively through a cascade of sieves of decreasing mesh sizes. By weighing the masses of particles remaining on the different sieves the particle size fractions can be determined within the range given by the mesh width of the different sieves. As a result of interpolation between the discrete mesh widths one obtains a curve as plotted in Figure 1.2.

An example of such a vibratory sieve is shown in Figure 1.3.

A more recent way of particle analysis is the laser diffraction method. In this method the particles are dispersed either in a liquid or in a gas flow and a laser beam passes through the suspension. The interaction of the laser beam with the surface of a particle causes a bending of the light waves. This effect depends on the curvature of the particle surface and can be measured by a detector.

Both methods work best when the particles are of spherical shape. In this case the particle size is defined unambiguously by the particle diameter. Normally bulk goods will, however, not be of spherical shape. This is the main source of error in particle size analysis. Figure 1.4 shows electron microscope scans of dust particles of three different Chinese black coals and a German lignite coal.

A key quantity to characterize the susceptibility of a bulk good to react is the internal surface area. This quantity strongly corresponds to the particle porosity

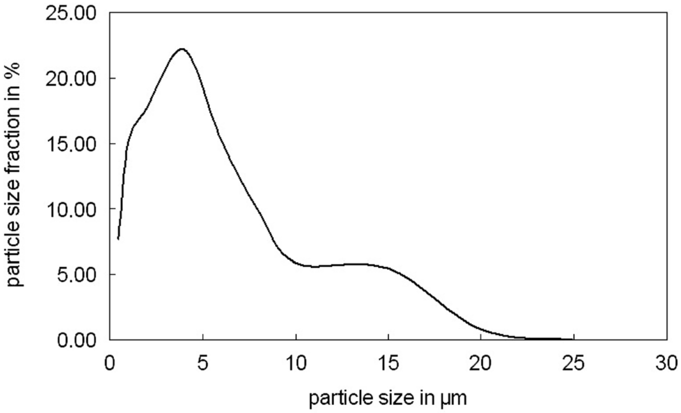
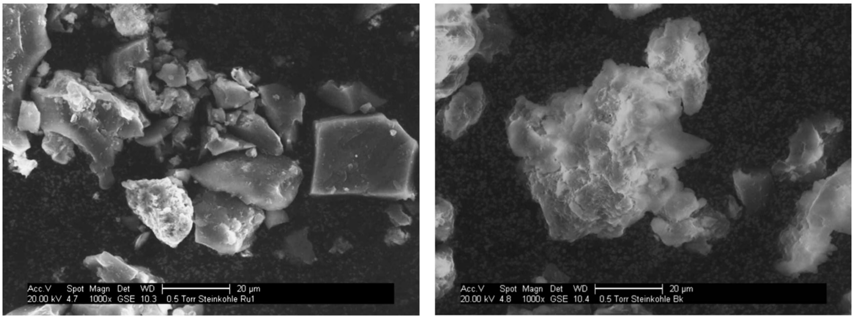
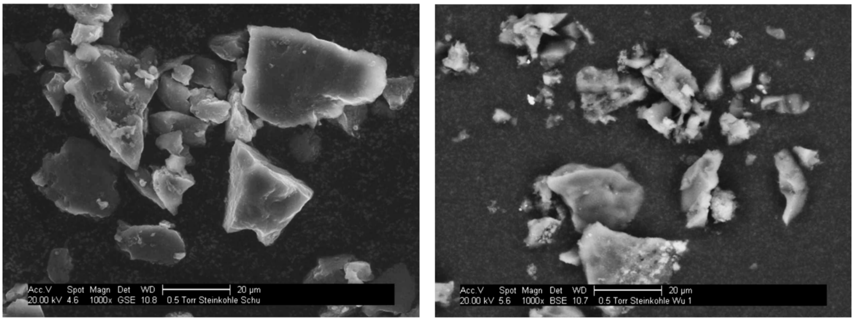


Figure 1.2 Result of the particle analysis of a fine dust.

Figure 1.3 Vibratory sieve for particle size analysis of particulate matter (Courtesy of Retsch GmbH).



black coal (Ruquigo) lignite coal (Germany)



black coal (Shi Zhua Shan) black coal (Wuda)

Figure 1.4 Electron microscope scans of cut-to-pieces particulate material.

described in Section 1.2.3, below. The internal surface area of a particle is the totality of all surfaces the particle offers to an adsorbate including those of each individual pore.

In powder technology it is more common to work with the specific surface area, which is the internal surface area divided by the mass of the particle. The unit of the specific surface area is therefore m^2/g.

In general, a particle is the more reactive the larger its specific surface area. The specific surface area can be measured by the BET method, where BET stands for the developers of this method: Brunauer, Emerett and Teller. In this method after evacuating the sample of particles one measures the amount of a gas which can be adsorbed in a monomolecular layer on the particle surface. Mostly nitrogen at a temperature slightly above its boiling point (77 K) is used as an adsorbate.

1.2.2
Bulk Porosity and Bulk Density

The bulk porosity is the ratio of the volume of the voids in an accumulation of bulk material to the entire volume of this accumulation. The voids are filled with gas so that the porosity may be described according to Equation (1.1)

$$\varepsilon = \frac{V_g}{V_g + V_s} \tag{1.1}$$

where V_g is the volume taken up by the gas phase and V_s the volume occupied by the solid particles. The latter one is the sum of the volumes of individual particles.

For bulk goods loosely heaped up porosities have to be expected in a range between about 0.3 and 0.8 depending on the kind of material. Compaction of the heap reduces the porosity.

The bulk density – sometimes also called the apparent density – is closely related to the porosity. It is defined as

$$\rho_b = \varepsilon \cdot \rho_g + (1-\varepsilon) \cdot \rho_s \tag{1.2}$$

where ρ_g is the density of the gas filling the voids and ρ_s is the density of the solid particles forming the heap. The bulk density of a bulk good can be measured more easily than the bulk porosity. A widely accepted method is described in the standard ISO 171 [1].

The porosity can then be calculated from the bulk density, the gas density and the particle density

$$\varepsilon = \frac{\rho_s - \rho_b}{\rho_s - \rho_g} \approx \frac{\rho_s - \rho_b}{\rho_s} \tag{1.3}$$

Provided that the gas pressure, temperature and composition are known, the gas density can be obtained from the equation of state for a perfect gas

$$\rho_g = \frac{p \cdot M}{R \cdot T} \tag{1.4}$$

with p as the pressure and T as the temperature on the Kelvin scale. M is the molecular mass of the gas and R is the universal gas constant.

The particle density can be measured as described in Section 1.2.4, below.

1.2.3
Porosity of Individual Particles

Solid particles of coal, wood, grain, cotton and many other products have internal pores. The pore diameters range from a few micrometers (macropores) to a few nanometers (micropores). Some of these pores are open to the particle surface; others may be completely embedded in the solid material (blind pores). Figure 1.5 shows a sketch of the pore structure of a solid particle.

For the behavior of the particle in a fire only the open pores are of interest since they allow oxygen to be adsorbed at the surface of the particle.

Particle porosity can be measured using special equipment. Different porosimeters are available to measure the sizes of macropores, mesopores or micropores. The sizes of macropores are measured by injecting liquid mercury into the pores of particles which previously have been evacuated. As there is a correlation between the pore size and the injection pressure, a stepwise increase of the injection pressure gives the pore size distribution of the solid.

The sizes of mesopores and micropores are measured using gas adsorption techniques. In this case nitrogen or carbon dioxide is injected into the pores instead of mercury.

The particle porosity strongly influences the ignitability and the burnout rate of solid particles. The higher the porosity the larger the surface the particle offers to oxygen molecules to react. Therefore, particles with high porosity ignite more readily than those with low porosity. In addition, the burnout takes place much faster when the porosity is higher.

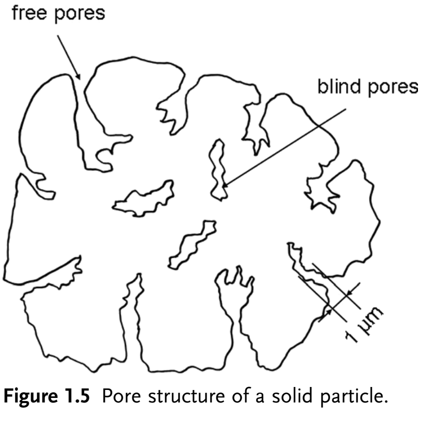


Figure 1.5 Pore structure of a solid particle.

1.2.4

Particle Density

The particle density is the mass of the particle divided by the volume of the particle. This quantity can be measured using a so-called pycnometer. In the simplest case a sample of particles of which the mass is known is immersed in a liquid and the extrusion of the volume of the liquid is measured. For very precise measurements and if the porosity of the particles is high, a gaseous fluid, say helium, is used instead of a liquid and the pores are evacuated before the measurement.

1.2.5

Humidity

Humidity plays a key role in the susceptibility of flammable bulk goods to ignite; however, different and partly counteracting effects have to be considered. Experiments by Krause and Schmidt [2] have shown that samples of wood chips or crushed lignite coal with volumes between 6 and 13 L could not be ignited by an embedded heated coil when the mass fraction of water was 40% or higher.

Below this content of water smoldering fires could be initiated within the bulk goods. The propagation of these smoldering fires was of course delayed compared to dry samples due to the evaporation of the water.

Hence, there seems to be some kind of limit of the water content above which fire propagation is not possible because the heat provided by an ignition source or produced by a beginning exothermic reaction is completely absorbed by the water. Below this limit the influence of the water on ignition of bulk goods may be either impedimental or promotive. The impedimental effect is simply the absorption of heat from the ignition source or from a beginning exothermic reaction to heat up and evaporate the water.

A promotive effect of water on the ignition of bulk goods may be observed, for example, when freshly harvested plants are stored; for example, hay, alfalfa, forage and so on. Some silo fires happened because moist goods were stored. A case study describing this effect is contained in Chapter 6 of this book. Therefore, in the case of organic material it is important to reject material with a humidity higher than 16% in mass for storage.

As experience shows, at a mass fraction of water above 16% in mass fermentation starts within the stored material raising the temperature to a level as high as 70 °C. Together with the oxygen contained in the air filling the void volumes of the stored material the elevated temperature forms a favorable starting condition for self-ignition. More details about the mechanism of self-ignition will be given in Chapter 2.

Another promotive effect of water occurs when comparatively dry bulk goods are wetted (without being soaked through). When the water is adsorbed at the surface of the solid particles the heat of adsorption is released. This leads to a temperature rise in the heap of the bulk goods which may be a pre-condition for a self-ignition. Indeed, practitioners from the mining industry have reported that for example coal deposits when exposed to rain after a longer period of dry weather start to smolder.

A similar effect can be observed when the humidity of the air striking above the surface of the deposit is increased. Here, in addition to the heat of adsorption, the heat of condensation is also released and contributes to a temperature increase within the bulk material. Experimental evidence of these phenomena has been gained by Lohrer [3].

A rough but simple method to measure the humidity of a bulk good is drying a sample of the material in a vacuum dryer. The mass fraction of water is simply the difference between the initial mass of the sample and the mass after drying. The drying temperature has to be chosen in such a way that thermal decomposition of the material does not occur. The drying is finished when between two successive weighings no alterations of the mass are observed.

A more precise method to measure the humidity of solid materials is titration. A detailed description of this method is given for example in [4].

1.3
Chemical Properties of Bulk Goods

1.3.1
Chemical Structure

Besides the physical properties mentioned in Section 1.2 the behavior of bulk goods in a fire is also influenced by their chemical properties. The main fire (and explosion) hazard results from the ability of these materials to react with oxygen connected with the release of heat. There are different laboratory tests to assess the flammability of materials, which are described in Chapter 3.

Most of the bulk goods stored in silos and revealed to be flammable are of organic nature. This also includes coal which originates from organic matter, but which is sometimes considered to be a mineral. The chemical structure of coal is not completely understood until now and in addition may vary depending on the origin. However, according to Wang *et al.* [5] there is some evidence that coal contains so-called functional groups originating from carbohydrates and these functional groups mainly influence the behavior during oxidation.

Other exceptions are, for example, some metal powders like aluminum, brass or others, carbon black which is nearly 100% carbon and activated carbon which usually consists of more than 95% carbon.

A chemical species which has bonded the maximum possible number of oxygen atoms cannot burn. An example for such a material is sand, which mainly consists of silicon dioxide. A silicon atom has four free electrons in its outer shell. Each oxygen atom can bond two of them such that the silicon dioxide molecule is stable. The same applies to a carbon atom, which also has four free electrons. Therefore, carbon dioxide is also non-combustible. Both sand and carbon dioxide are well known as extinguishing agents.

In contrast to this, in carbon monoxide two free electrons remain and hence a molecule of carbon monoxide can react with an oxygen atom to form carbon dioxide.

It is well known that carbon monoxide is an explosible gas (and in addition a very toxic one).

More complex molecules contain so-called functional groups. Functional groups are fragments of other molecules which are bonded to the first one. For example, 2-butanone (methyl ethyl ketone), which is a product of wood fires, has an ethyl group which is a fragment of an ethane molecule. The bondings of functional groups are sometimes comparatively weak and therefore easy to destroy. During such a process heat is released, which leads to a temperature rise in the material.

1.3.2
Heat of Formation and Calorific Value

Any molecule of a chemical species is composed of different chemical elements. The elements are linked to each other by a chemical bond. Some chemical reactions consume external energy, for example in the form of heat, to synthesize a molecule (endothermic reaction). This energy is then stored in the molecule as heat of formation. The total heat of formation of the products is higher than that of the reactants.

When such a molecule is broken up by some other chemical reaction the heat of formation is released again and increases the temperature of the reactive system (exothermic reaction).

Other molecules evolve spontaneously when the reactants are activated by a small portion of energy (the so-called activation energy). Spontaneous reactions are always connected with a release of energy. This means that the total heat of formation of the products is always lower than the total heat of formation of the reactants. The difference is the heat of reaction.

The unit of the heat of formation is J/mol. Chemical elements and molecules of monatomic gases by definition have a heat of formation of zero. Since during the formation of some molecules out of their elements heat is released, these molecules have a negative heat of formation. For example, the heat of formation of water at standard conditions (atmospheric pressure, 25 °C temperature) is -286 J/mol, that of carbon monoxide is -111 J/mol and that of carbon dioxide is -394 J/mol. If carbon monoxide reacts with oxygen to form carbon dioxide the heat of reaction is $\Delta H_{\mathrm{R}} = 111\,\mathrm{J/mol} - (-394\,\mathrm{J/mol}) = 283\,\mathrm{J/mol}$.

It needs no explanation that fires are always dominated by exothermic reactions (despite some intermediate reactions in the flame that may be endothermic). A quantity that describes how much heat can be released when a certain amount of reactant is burnt is the gross calorific value. The gross calorific value is the ratio of the heat energy released during combustion of a fuel to its mass. For example, the quality of fossil fuels can be ranked according to their gross calorific value.

Some flammable solids like coal, wood, cellulose, grain and others contain a fraction of hydrogen. During combustion the hydrogen reacts with oxygen and forms water vapor. The latent heat of the water vapor reduces the energy which can be extracted from the combustion. Therefore, the net calorific value is the gross calorific value diminished by the latent heat of vaporization.

In fire safety often the fire load is used to estimate the heat release of a fire. This is the gross calorific value multiplied with the total mass of material stored and divided by the ground area on which the material is stored. For storage of bulk materials, however, it is more appropriate to use the volume of the storage facility instead of the ground area.

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