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Minimising fire risks at chemical storage facilities

Basis for the guidelines for safety engineers

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ABSTRACT

The report addresses fire safety engineering problems of chemical storage facilities. The methodology of the guidelines is based on the ISO/TC 92/SC4 *Fire Safety Engineering* -documents. The basic elements of fire safety design of a chemical warehouse are described: construction design, model fires and fire simulation, storage and packaging, preventive and protective systems, building location and safety distances. Concerning the design of the warehouse construction, the following items are discussed: compartmentation and structures, escape routes, smoke ventilation and retention of spills and fire fighting water. Design fires and fire development are discussed with an emphasis on the fire simulation models. The influence of the storage layout and packaging on the fire spread and the consequences of fire are discussed, including the effects of the size and separation of the stacks, the physical properties of the packaging and the nature of the stored materials, as well the mechanisms in which packaging can contribute to the fire. The discussion on the preventive and protective systems includes treatise on alarms and fire detection, sprinklers and other automated means of extinction. Also some conclusions derived from the TOXFIRE project on the influence of extinction on chemical fires are presented. An assessment of safety of the chemical storage facilities includes a brief discussion on the warehouse location, orientation and site access. The question of safety distances is handled in more details by presenting a four-step procedure as a guide to assess low risk distances. The ingredients of this procedure are 1) the survival fraction, 2) toxicity values, 3) fire scenario, dispersion and weather situation and, 4) the exposure time.

PREFACE

In many countries, there are a large number of chemical plants and storage facilities that handle and store substantial amounts of hazardous substances, *e.g.* pesticides. Chemical fires constitute one of the most important hazards from these activities: they can give rise to serious damage to the environment and population and cause extensive economical losses. Today only limited documentation is available concerning the assessment of the fire safety at chemical plants and chemical storage facilities.

The present report is a guidelines document aimed at providing fire safety engineers with the basic information needed in fire safety questions of chemical storage facilities. This study is part of the CEC-project titled *Guidelines for Management of Fires in Chemical Warehouses* (TOXFIRE) which was initiated in order to remedy some of the problems related to chemical fires. The work has been sponsored by the CEC ENVIRONMENT programme (contract no. EV5V-CT93-0275), Finnish Academy, Technology Development Centre of Finland, Ministry of the Environment and Palotutkimusraati (the Finnish Board of Fire Research).

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1 INTRODUCTION

1.1 THE TOXFIRE PROJECT

In many countries, there are a large number of chemical plants and storage facilities that handle and store substantial amounts of hazardous substances, *e.g.* pesticides. Chemical fires constitute one of the most important hazards from these activities. Today only limited documentation is available concerning the assessment of the potential consequences from fires at chemical plants and chemical storage facilities.

The project *Guidelines for Management of Fires in Chemical Warehouses* (TOXFIRE) was initiated in order to remedy some of these problems. The project is financially supported by the CEC ENVIRONMENT programme (contract no. EV5V-CT93-0275). The project was carried out during a three-year period (1993-1996) by an international consortium which included the following partners:

- Risø National Laboratory, Denmark (co-ordinator),
- NERI - The Danish National Environmental Research Institute, Denmark,
- South Bank University, United Kingdom,
- VTT Building Technology, Finland,
- VTT Manufacturing Technology, Finland,
- Lund University, Sweden,
- SP - The Swedish National Testing and Research Institute, Sweden,
- FOA - The Swedish National Defence Research Establishment, Sweden.

Based on a number of characteristics the substances are classified according to ignitability, heat release, burning rate, smoke evolution, combustion products and the influence of the packaging materials on the combustion products. The source characteristics are described by parameters obtained by carrying out combustion experiments on various scales and by studying the effects of scaling. In addition, the fire scenarios are characterised by the degree of ventilation, the packaging materials, the stacking of the materials and the response of the building. Also the suppression is an important parameter, *i.e.* active and passive suppression and the fire brigade tactics. The consequences to humans as well as the environment are assessed. Finally, existing modelling methods used for risk assessment are studied, along with the handling and prevention of the accidents.

Based on these investigations, the basis for two sets of guideline documents in relation to fires in chemical warehouses has been developed: guidelines for the safety engineers and guidelines for the fire brigades. In parallel also a quick decision system to be used by the fire chief in case of chemical fire was developed. A common introduction for these outcomes of the TOXFIRE project, providing a condensed summary of the project, is given in a separate report [Rasmussen 1996].

The present report is the safety-engineering guidelines documentation of the TOXIRE project. It comprises basic information needed in fire safety engineering evaluation or design of a chemical storage facility. The data presented have mainly been obtained from three sources of information. Firstly, the knowledge acquired from the results of the TOXFIRE project, secondly, many of the basic facts on fire safety have been derived from the ISO/TC 92/SC 4 *Fire Safety Engineering* - documents and thirdly, specific data on chemical warehouse safety have been obtained from the GIFAP report *Guidelines for Safe Warehousing of Pesticides*.

The text is a compilation of contributions of several specialists from the research organisations which participated the TOXFIRE project. Especially, chapter 3 is completely written by Dr Roderick McIntosh from SBU and section 5.2 by Dr Lena Karlsson from FOA. The treatise on computer fire simulation is based on material prepared by a number of international experts in ISO/TC 92/SC 4/WG 2, chaired by Prof. Matti Kokkala from VTT.

1.2 ELEMENTS OF FIRE SAFETY IN CHEMICAL WAREHOUSES

Generally, the characteristics of a building with respect to its fire safety may divided into three categories [ISO/WD 13388]: 1. fabric and structure of the building and 2. fire safety systems of the building. 3. the building orientation. The items discussed in these categories include

1. - overall size and shape of the building and storey heights
   - positions and sizes of windows and other areas of low fire resistance in the external envelope
   - location of fire separating elements (*e.g.* walls, doors, shutters, floors and roofs)
   - location of load bearing elements of construction and their fire resistance (*e.g.* beams and columns)
   - location and dimensions of vertical and horizontal shafts and ducts and fire resistance of enclosing elements
   - nature of construction (*e.g.* materials forming the frame, walls, partitions, floors, suspended ceilings and roof)
   - thermal properties of lining materials, *i.e.* thermal conductivity, specific heat and density
   - configuration of hidden voids (*e.g.* voids associated with hollow walls, floors and floors, suspended ceilings and raised floors)
   - location of main entrance(s) and normal circulation routes

- location and width of stairways and other spaces used for normal circulation within the building
- location and height of fire-fighting stairways, fire-fighting lifts and protected lobbies
- location of exit routes and fire resistance of enclosing elements

2. - availability of fire-fighting water inside and outside the building
   - number and location of external fire hydrants
   - number of fire appliances used in first attendance
   - equipment carried on fire appliances
   - access points for fire appliances
   - travel distance and route to fire site from fire brigade
   - zones covered by fire detection and alarm systems
   - positions of fire alarm call points
   - zones covered by automatic sprinklers
   - location and vent area of manual and automatic smoke vents
   - zones covered by pressurisation systems

3. - location of the building relative to the site boundary, other buildings and to other fire hazards
   - orientation of the building.

Concerning chemical warehouses, additional items to be taken into account include

4. - the properties of the stored products (*e.g.* solid/liquid, flammability, toxicity, oxidising propensity/explosivity, corrosive properties)
   - hazard potential to the environment, *i.e.* to human, vegetation, soil, water
   - retention of fire-fighting water and cleaning of other extinguishing media such as foams and powders
   - security of the warehouse
   - safety distances.

The above lists enumerate a large variety of items which are connected to the fire safety of the warehouse. If each of them could be optimised, the outcome would be a system of ultimate safety regarding fire hazards. Yet realisation of such an optimal facility is far beyond the resources available and, in practise design solutions are results based on compromises between the different aspects of the performance requirements of the system. The tool in making the compromises is risk analysis. It enables one to derive *quantitative* figures which the decision-making process can be based on.

In fire risk analysis, first a list of conceivable event sequences or scenarios is developed which then is augmented with quantitative descriptions of the events and their probabilities. With the increasing computational power of modern computers, more and more complicated systems can be analysed in this way. The major obstacle in the quantitative analysis is the availability of quantified knowledge of the subprocesses.

This fact is particularly pertinent in the case of chemical warehouses. Although the research efforts in the field of chemical warehouse safety, such as the TOXFIRE project, have considerably alleviated this problem, the present status of knowledge is too deficient for a full quantitative risk analysis of the consequences of a chemical warehouse fires. Thus, in this document the question of quantitative risk assessment is not dealt with. Rather, the features of fire safety questions associated with chemical storage facilities are addressed on a qualitative level.

This document is structured following the above general classification augmented with special items regarding warehousing of toxic chemicals. The aspects of construction of the warehouse and assessing its fire safety are addressed in chapter 2. Chapter 3 is concerned with safe ways to organise the storage and the influence of packaging materials on the fire safety. Detection methods and systems for automated fire fighting are discussed in chapter 4. The issue of the hazards of the warehouse to its surroundings is addressed in chapter 5. Besides the text-chapter material, intended to provide a condensed and lucid treatment, there are several Appendices focusing on relevant technical details.

2 CONSTRUCTION DESIGN AND FIRE HAZARD ASSESSMENT

2.1 CONSTRUCTION DESIGN

2.1.1 Compartmentation and structures

The warehouse building should be divided in to compartments by internal walls. The principal characteristic of chemical warehouses guiding the compartmentation design is that the fire loads are readily high. The detailed requirements for the compartmentation follow national legislation.

Combustible construction materials or ones able to contribute to the spread of fire should be avoided in storages housing toxic materials. For the framework, re-inforced concrete is preferable to unprotected steel frames. Load bearing steel members should be protected against heat, *e.g.* by a sprayed insulation.

To provide protection for external fire risks the external walls should be of solid construction with non-combustible cladding systems. For insulation non-combustible materials such as mineral wool should be used.

Internal division walls intended to prevent fire spread between compartments should have a good fire resistance, *e.g.* 90 min or more. Materials complying to this prerequisite and providing sufficient structural strength and solidity include concrete and solid brick. Openings for electrical cables, *etc.* should not be made on the fire-resistant walls. Doors in the these walls must have equal fire resistance as the wall itself. In case of fire, the doors should close automatically.

2.1.2 Escape routes

The basic requirement for escape routes is that a person can gain access to a place of safety from every location in the building [ISO/WD 13394].

In large warehouses, exit routes for emergency purposes other than the main entrances should be available [GIFAP 1988]. Recommended locations between these exits is such that for anyone inside the warehouse, the distance to the emergency exit should not exceed 30 m. They should be clearly marked and should not be blocked at any time of operation of the warehouse.

2.1.3 Smoke ventilation

To ensure adequate smoke and heat relief in case of fire the roof of the warehouse should provide ventilation opening with an area of at least 2 % of the floor area. The ventilation panels must be open in case of a fire which stipulates that they should be permanently open or become actuated automatically.

2.1.4 Retention of spills and fire-fighting water

In many chemical warehouse fire incidents the principal damage has been the pollution of water-ways located in the vicinity of the warehouse [Wäckerlig 1987]. To avoid this, the storage facility must have equipment to retain any spills and fire-fighting water.

The volume of the contaminated water may readily be large, up to several cubic meters per ton of burning chemical. An estimate of the order of magnitude of the water flux requirement $\dot{m}''_{water}$ (kg/(s·m^2)) may be obtained considering the rate of heat production per unit area of the stored products $\dot{Q}''$ (W/m^2):

$$\dot{m}''_{water} \approx \dot{Q}'' \big/ \Delta H_v \tag{2.1}$$

where $\Delta H_v \approx 2.2\ \mathrm{MJ/kg}$ is the latent heat of vaporisation of water. A typical value for $\dot{Q}''$ is ca. 500–1000 kW/m^2 yielding a value of 0.2–0.5 kg/(s·m^2) for the water flux. Expressed in units of millimeter per minute, commonly used in sprinkler regulations, these values correspond to water flux densities of *ca.* 10–30 mm/min. Thus a water layer with thickness of several centimeters may readily be produced in a few minutes. Hence, a storage vessel, specifically intended for containment of the fire-fighting water is often required.

The costs involved in building the container can be reduced by decreasing the amount of water needed in fire extinction. One efficient way to achieve such a reduction is to minimise the fire size at the time of the fire brigade arrival by installing alarm and automatic suppression systems in the warehouse. A further reduction in the water requirement can be achieved if a water mist system is used instead of a conventional sprinkler system [Mawhinney 1993]. In extreme cases with very large fires, minimising the environmental impact of the incident may even make it advisable to let the warehouse burn freely and concentrate the fire-fighting efforts to the protection of the surroundings.

The drainage system of the warehouse should not expose the public drainage system to danger of contamination even in the case of fire.

2.2 DESIGN FIRES

In assessing the fire safety of a building, the essential task is proper characterisation of the potential fires.

Typical fire scenarios include, *e.g.*, burning of a single item, fire in a room corner, fires of cables or ducts, which may all occur in chemical warehouses. The distinctive feature of chemical warehouse fires is the properties of the stored goods which may vary widely: hazards of some compounds may arise from their explosive ignition and burning, while for some other compounds the fire risks may be related to their immense toxicity which may, in the case of a fire, be spread in an uncontrolled way. Although a comprehensive inventory of all possible fire scenarios for the virtually endless variety of industrial chemicals is impossible, some non-specific guidelines may well be derived based on general fire safety principles and specific empirical findings such as those obtained in the TOXFIRE project.

A design fire is an idealisation of the real fire development. It should reproduce the essential features of the real fire which vary depending on the actual situation. Typically, the fundamental characteristics of the fire include the heat release rate, the heat of combustion of the fuel, smoke production and, in the case of chemical warehouse fires, the toxicity of the fire effluents.

The design fire depicts the time evolution of the fire parameters. The phases covered are usually

- ignition
- the growth period *i.e.* from ignition to flashover or full fuel involvement
- the period of fully developed burning *i.e.* post-flashover fire or post propagation period of increasing fire severity
- the decay period *i.e.* interval of declining burning until the ambient conditions are re-established.

Fire engineering interest is mainly focused to the growth period or to the period of fully developed fire. In the former case, the main concern is usually saving human lives, but this phase is also of importance since passive or active actions taking place during it may significantly mitigate the fire propagation or even stop it. In the latter case, the attention is paid especially to the structural considerations.

The growth period of a fire is frequently described by the t^2 model. It relates the heat release rate of the fire $\dot{Q}_{\mathrm{fire}}$ to the time t elapsed after the ignition at time t_0 as

$$\dot{Q}_{\mathrm{fire}} = \alpha\left(t - t_0\right)^2 . \tag{2.2}$$

The parameter α specifies the growth rate which may be divided into four classes, slow, medium, fast and ultra-fast. The α values customarily assigned to the different fire growth rates are [Evans 1988]: slow $\alpha = 0.003$ kW/s^2, medium $\alpha = 0.01$ kW/s^2, fast $\alpha = 0.05$ kW/s^2 and ultra-fast $\alpha = 0.1$ kW/s^2. An example on the applicability of the t^2 model has been given in Fig. 2.1 where the model has been applied to a pool fire of a hydrocarbon mixture fuel: increase in the heat release rate is reproduced by the model with $\alpha = 0.04$ kW/s^2, *e.g.* development of burning of the particular fuel may be characterised as "fast". We would like to emphasise, however, that the t^2 model predicts best growth of small fires, such as that shown in Fig. 2.1 [Babrauskas 1996].

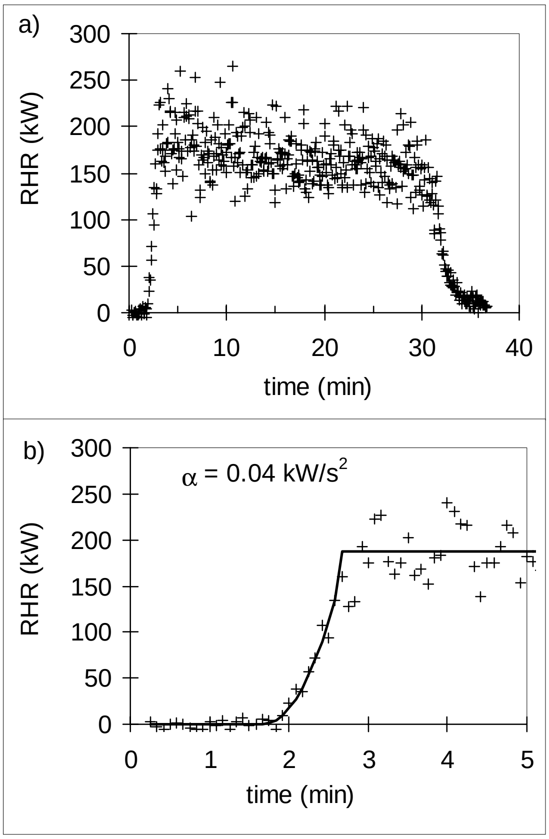

Figure 2.1. An example of the applicability of the t^2 *fire growth model to a fire in an isolated 0.5* m^2 *pool of hydrocarbon mixture fuel: the whole burning period (a) and the growth phase (b). The solid curve in (b) delineates the rate of heat release (RHR) according to the* t^2 *model with the parameter* $\alpha = 0.04$ *kW/s*^{2}*. After the growth period the burning is fuel controlled.*

While Eq. (2.2) with given α values provides exact figures describing the fire growth it is essential to bear in mind that there are several factors which actually control the growth, *e.g.* the size and arrangement of the combustible materials, the size of the compartment, properties of the compartment barriers and ventilation conditions, the first being the foremost in importance.

The growth period of the fire ceases when the fuel supply reaches its maximum (*e.g.* a pool of fuel with limited area, see Fig. 2.1a) or when the supply of oxygen can not be increased any further. The subsequent fire development is either fuel or ventilation controlled. If the fire space has been equipped with an automatic suppression system, after its actuation the fire development is controlled by its efficiency.

If the fuel supply and ventilation are sufficient, the fire may grow to involve all combustible materials in the compartment, *i.e.* a flashover occurs. Thereafter the fire grows until it becomes limited by the ventilation conditions.

The flashover is a result of the high heat fluxes generated by the fire. They arise from the fire plume, from flames under the ceiling, from the hot surfaces in the upper part of the compartment and hot combustion products trapped under the ceiling [Drysdale 1985, p. 284]. For a particular fire scenario, development to flashover depends on, *e.g.* the compartment size, dimensions and number of ventilation openings and the thermal properties and thickness of the compartment boundaries.

2.3 FIRE SIMULATION MODELS

If the above mentioned parameters are known the likelihood of flashover may be estimated. The techniques available for this purpose range from sophisticated computer models to simple analytical models. The former ones are either the field models based on computational fluid dynamics or the less complicated zone models. The latter are based on correlation formulae derived from empirical findings, and though robust, may be used to obtain at least order-of-magnitude estimations.

2.3.1 Analytical models

Analytical fire simulation models are amenable for hand calculations [as a general reference see, *e.g.* SFPE 1995]. They vary in complexity from simple relations addressing properties of isolated fires [*e.g.* Babrauskas 1986] to models which take into account the properties of the fire enclosure [*e.g.* Beyler 1986].

As an example, some models used to predict flashover [Babrauskas 1980, McCaffrey *et al.* 1981, Thomas 1981] are outlined in Appendix 2. Predictions of these approaches applied to the two reference warehouses described in Appendix 5, are depicted in Fig. 2.2 which shows the dependence of the flashover time on the growth parameter α of the t^2 model. It may be seen that, *e.g.* in a case of a fast growing t^2 fire ($\alpha = 0.05$ kW/s^2), the estimated times to flashover onset are shorter than 10 minutes for both warehouses.

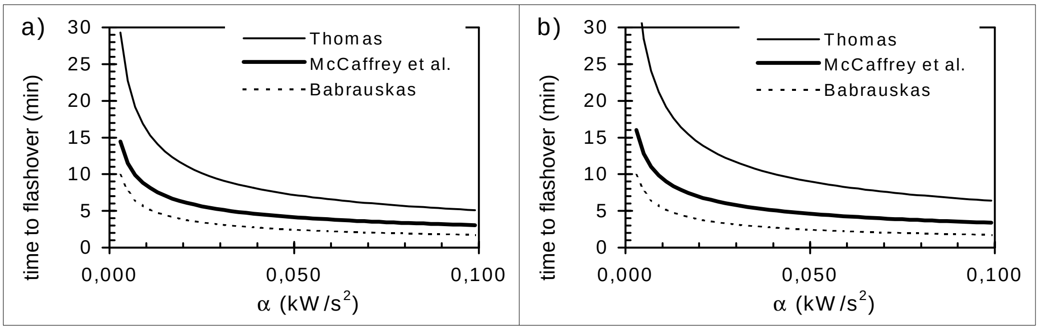

Figure 2.2. An example of the analytical fire simulation models: estimates for the time to flashover in the two reference warehouses, the smaller warehouse (a) and the larger one (b). The reference warehouses are described in Appendix 5 and in ref. [Särdqvist 1996].

2.3.2 Zone models [ISO/WD 13390]

Zone models are used for fairly simple predictions of the development of a fire in an enclosure taking into account the actual fireload, the geometry of the enclosure, including effect of openings, and the thermal feed-back from the enclosing structures.

In zone models, the enclosure is divided into a limited number of volumes. Normally the room is divided into two volumes with an upper hot layer and a lower cold layer during the development of the fire. When the fire becomes fully developed, the model usually will change into one zone. Each zone is treated as a homogeneous volume, meaning that all variables, *e.g.* the temperature, reflect the mean value for each volume. As the number of zones are limited, the equations of the zone models can be solved by personal computers.

Basically, the zone models solve the equations of mass and energy as a function of time. If there are openings in the room to other rooms or the surroundings, interchanges with these are also considered. The general theory behind the models is described, *e.g.* in ref. [Quintiere 1987].

The required input data varies among zone models. They will at least require a description of

- the building geometry, *i.e.* floor area, ceiling area, room height, position and size of openings leading to other compartments or to the surroundings
- the building materials used, *i.e.* specific heat capacity, density and heat conductivity for each material. In addition, surface characteristics, such as heat transfer coefficients and effective emissivity are often required.

- the design fire given as the rate of heat release (RHR) and the locations of the fire. RHR can be defined in many ways, the simplest being defining the RHR as a function of time based on some mathematical formulas, *e.g.* the t^2-fire growth. Many models also allow the user to specify a range of data points for the RHR based on full-scale experiments.

Some models also allow the user to specify heat detectors, smoke detectors, installation of smoke ventilation, installation of mechanical ventilation, *etc.*

Based on the input data given by the user, the zone model will then be able to predict

- compartment smoke filling as a function of time, *i.e.* the depth of the hot smoke layer

- average smoke layer temperatures as a function of time

- velocity, mass and heat flow out of the openings.

Some models also calculate the average smoke densities and oxygen depletion.

Zone models are suitable for predictions of smoke fillings and the development of a fire in a room including time to flashover. The results can also be used for detection and activations, but one should check which values are being used as this can differ from model to model. If only the values from the upper zone of a single room are used, this can lead to very conservative results.

For structural responses, the results from zone models can be used but the designer must be exactly aware of how the gas temperature is derived and if it is appropriate to use this temperature on the given structural element. Because the upper layer temperature is an average temperature in the whole upper part of the room, the maximum temperatures and the consequent thermal exposures may be much higher locally.

The zone models that are publicly available today do not include validated algorithms for predictions of reaction to fire, *e.g.* spread of flame on lining materials.

Designers need to carefully examine whether the two zone assumption will be appropriate for a particular design situation. The two zone assumption may not be appropriate for situations where

- buoyancy is low

- there are high inlet velocities through openings

- high wall jet velocities occur

- the fire grows so rapidly that mixing does not occur in the upper layer

- significant upper layer cooling occurs due to heat loss to the fabric of the structure (walls and ceiling)
- fire suppression is causing significant mixing in the enclosure
- there are effects of fire/wall proximity that could invalidate the axisymmetric assumption for entrainment from all directions.

These effects may be expressed as limitations on zone models related to

- enclosure length/width/height ratios
- enclosure height and floor area considerations
- maximum or minimum fire size or heat release rate (relevant to the dimensions of the enclosure)
- effects of building air handling systems and vent airflows
- numerical accuracy and uncertainty of results
- verification of experimental results

2.3.3 Field models [ISO/WD 13390, Cox 1995]

Field modelling is the term used for the application of Computational Fluid Dynamics (CFD) to the simulation of the growth and spread of fire. In contrast with zone modelling, little or no a priori simplifications about the heat and mass transfer processes that occur during the fire are made. In the field models, the spatial dependencies and temporal development of the quantities of interest are predicted by a set of equations representing the fundamental equations of conservation of the mass, momentum, energy and chemical species. This set of equations is solved numerically taking into account the boundary and initial conditions that represent the particular fire scenario under consideration.

To date, the most successful application of the technique has been simulation of the movement of the gaseous products of combustion (smoke) throughout enclosures. The method enables a range of problems that a zonal approach could not tackle to be encompassed. For example, the influence of pre-fire temperature gradients throughout the air in an enclosure can be included, as can the influence of external wind pressures on the movement of smoke within a building or other enclosure. Although in principle the method can be used to study the whole range of fire processes including fire growth and spread, such techniques are still in the research phase and are not yet developed to the point where they can be used in practical fire safety engineering studies.

The primary outputs from field models are a series of time histories for each of the variables solved, *i.e.* gas velocities, gas temperatures, fuel, oxidant and combustion product concentrations together with pressures - at each elementary control volume throughout the calculation domain. In addition, mass fluxes through ventilation openings as well as convective and radiative heat fluxes across the face of solid boundaries are also provided.

Secondary variables can be deduced from primary ones by the use of further assumptions. Smoke obscuration in each control volume, for example, can be deduced from the local combustion product concentration, as can the concentration of individual chemical species. However, deductions of these secondary variables are heavily dependent on the assumptions made and are in the spirit of the zonal modelling approach. The validity of these assumptions must always be kept under review.

Since Computational Fluid Dynamics is a particularly complex undertaking, its practitioners tend to be highly skilled but often also highly specialised, possibly knowing little of fire science and engineering. Therefore, in its application to fire problems, it is particularly important that a multi-disciplinary team oversees the project to ensure that the problem is properly posed and that the results produced make practical sense. This applies also to the use of zone models.

The responsibilities of the fire engineer can be summarised as follows:

- To simplify the problem down to its essential features. The presence of design features may influence some aspects of a problem but not others, *e.g.* structural beams which may significantly affect detection times but not smoke filling times.

- To specify the way that the fire source is to be treated. Decide in discussion with the CFD practitioner whether the fire is to be treated simply as a heat source of known volume or area or whether a combustion sub-model is essential

- To 'shadow' the CFD simulations with simple calculations to determine whether the results properly represent the problem.

3 STORAGE AND PACKAGING

3.1 STORAGE LAYOUT

The layout of a warehouse can affect fire spread mechanisms and the consequences of fire. The size of stacks and the separation gap between the stacks can have a great effect on the damage caused and toxic gases released. An adequate thermal barrier provides an acceptable alternative to a large separation between the stacks. For strong oxidants and other dangerous substances, dedicated storage buildings are recommended.

The Health and Safety Executive's Chemical Safety Series (refs. [HMSO 1985]–[HMSO 1991]) contains guidelines for the storage of certain substances. Sodium chlorate and other strong oxidants should be stored in a separate area from other materials in stacks containing a maximum of 25 tonnes and either a separation between stacks of at least 3 metres, or a thermal barrier (*e.g.* a brick wall). In addition, the store should be sited at least 10 m from other buildings or combustible materials (including grassland, brambles etc.), and the factory boundary. A substantial barrier (*e.g.* a double brick wall) can be used as an alternative.

The recommendations for ammonium nitrate and ammonium nitrate based fertilisers again incorporate a dedicated storage facility. Products containing more than 28% nitrogen should be stored in stacks of no more than 300 tonnes. For products containing less than 28% nitrogen, stacks may be up to 2000 tonnes. Where dedicated storage is not possible the stacks should be a maximum of 3 m wide and 2 m high. The gap around the stacks should be at least 1 m., and there should be a 1 m gap between the top of the stack and the roof/ceiling or any suspended lighting. Storage of ammonium nitrate should be away from other possible sources of heat and fire, such as combustible materials or heating pipes. Due to the corrosive nature of ammonium nitrate, galvanised structures or jointing should be avoided, and any thermal barriers should be preferably made of concrete. Also, light fittings should be impermeable to the dust from the fertiliser.

Chemicals which react together should generally not be stored together. For example, cyanides will react with many acids to form hydrogen cyanide. In a fire it can be difficult to prevent compounds coming into contact with each other. Good packaging can reduce the danger, but the chemicals should still not be stored in close proximity.

Spontaneously combustible materials should be separated from other combustible materials by a suitable gap (5 m or more) or a screen which will prevent the transmission of heat for at least 30 minutes. Effective alternative means of shielding the materials may be acceptable. At least a 5 m separation should similarly be allowed for the protection of packaging by corrosive materials which may attack it, and the subsequent risk of fire.

The effect of separation can be demonstrated using an amended version of the SBU computer model. Table 3.1 gives results where the temperature of the first stack is set constant at 1273 K (1000°C), representing a burning stack. Sodium chlorate is the stored material, and the temperature of the gas phase is specific to the vessel dimensions used. The temperature of the solid is therefore the more important variable.

Table 3.1. Demonstration of the influence of separation.

	2 m separation		**3 m separation**		**5 m separation**		**10 m separation**	
time (min)	**Tgas**	**Tsolid**	**Tgas**	**Tsolid**	**Tgas**	**Tsolid**	**Tgas**	**Tsolid**
10	752	650	724	564	669	471	562	383
20	750	761	730	668	690	557	608	437
30	733	814	718	726	687	610	616	475
40	711	844	698	761	676	646	615	497

The time taken for reaction to commence in the outermost node nearest the fire is shown in Table 3.2. It shows that at 5 m, reaction takes more than 30 minutes to begin. If this is the safety criterion, then this can be assumed as a safe distance. The recommended distance is 3 m, and it can be seen that this will permit reaction after 830 seconds. With a lower flame temperature, this may prove to be a safe distance.

Table 3.2. The time taken for the reaction to commence in the outermost node nearest the fire.

Separation distance (m)	**Time reaction commences (sec)**
2	490
3	830
5	1840
10	no reaction within 40 minutes

3.2 EFFECT OF PACKAGING ON WAREHOUSE FIRE SPREAD

The effect of packaging on fire spread through a warehouse is dependent on the physical properties of the packaging and the nature of the materials being stored. Typical packaging materials are steel, glass or plastic containers, paper or synthetic sacks, and cardboard boxes. Often more than one type can be present, *e.g.* glass or polythene bottles contained within cardboard boxes.

Packaging can affect the fire spread in several ways :

1. If it is readily combustible, it will aid fire spread.
2. If its integrity fails, through melting, buckling or overpressurisation, it can expose the stored material to the flame.
3. The thermal conductivity of the packaging can insulate the stored material from much of the heat source, reducing the rate of fire spread.
4. It can contaminate the stored material, affecting the rate of heat output from the burning material.

Typical package materials and their likely effects on fire spread are given below.

3.2.1 Plastic containers

Plastic containers are used widely in chemical storage. Dependent on the actual plastic, the containers will exhibit different behaviour. Thermosetting plastics will fail by decomposing at high temperatures, and tend to pyrolyse rather than combust, giving a slower fire spread rate. They also provide reasonable insulation, reducing the rate of temperature rise of the stored material. The more common thermoplastics will melt at relatively low temperatures, and also tend to be readily combustible. Although they will provide reasonable insulation, this is often academic, as the plastic will melt at relatively low temperatures. Storage of liquids in such containers could result in the liquid leaking and flowing outward toward the flame. This would be especially hazardous with flammable liquids.

3.2.2 Metal containers

Metal containers are often used to store larger quantities of chemicals. The metal provides very poor thermal insulation to the stored mass, and the temperature will rise at almost the same rate as the metal. Metal vessels will however provide good integrity; they give good strength and will not melt.

3.2.3 Paper or cardboard boxes and sacks

Paper or synthetic sacks are likely to lose integrity when exposed to flames, allowing the stored material to escape and flow. Aluminised paper sacks will give slightly greater protection when exposed to fire.

Cardboard boxes are often used to contain smaller packages and aid in storage. These boxes are readily combustible when exposed to flame, but may provide thermal insulation for a short period if they can be prevented from burning. Once alight, the effect of the fire becomes dependent on the internal storage within the box.

3.2.4 Thermal insulation

The use of insulated storage vessels can shield the stored mass from the high temperature of the flames. Adequate insulation should prevent the material from reaching the point where it pyrolyses or combusts. Since the insulation can only protect the material from a limited fire exposure, the thickness of the insulation should be based on an exposure time preventing the material from reaching the hazardous temperatures.

3.2.5 Example of stored material – sodium chlorate

Sodium chlorate is generally packaged in metal drums, with a polythene liner. The drums may be reusable, and may rust with age. The polythene liner is to prevent the chemical coming in contact with contaminants. In a fire, the polythene will melt, allowing the chemical to contact with the internal wall of the drum. The effects of polythene and rust on sodium chlorate have been studied by the HSE [Thomson *et al.* 1985], and it has been shown that the rust will reduce both the onset temperature of runaway and the melting point. The polythene causes a more vigorous reaction. The combined effect can cause an additional hazard.

An alternative, where the material is packaged at the production stage, is to have the sodium chlorate packed in polythene sacks, shrink-wrapped to a pallet. Wooden pallets should not normally be used, as the sodium chlorate can permeate the wood, creating a hazard. However, they can be used in this case, if the pallet wood is new.

Data on the protection offered by insulation, where the entire cylinder or stack is exposed to the flame (*i.e.* total engulfment by the flame), obtained using the SBU model, is available [McIntosh & Nolan 1997]. Differing grades and thicknesses of insulation are compared over a period of exposure.

4 PREVENTIVE AND PROTECTIVE SYSTEMS

4.1 ALARMS AND FIRE DETECTION

Every warehouse storing toxic chemicals must have a system to alarm the fire brigade. At its simplest, this means a manual alarm via push buttons or telephone. However, any larger chemical storage facilities should be equipped with automatic alarm systems based on self-acting fire detection ensuring rapid fire brigade response also when the warehouse is unoccupied.

The crucial point in automatic fire detection and the potential functions activated by the sensor is the time. This time lag from the fire ignition until the actuated utility is fully operational consists of: 1) the time delay before any changes occur in the observable physical quantity (usually heat or smoke) at the sensing device location, 2) the time it takes for the sensor element to actuate (*e.g.* reach pre-set temperature or sufficient smoke density) and, 3) the activation time, *i.e.* the time delay between the sensor actuation and the initiation of the triggered action (such as opening of the smoke vents or air displacement in sprinkler piping). Each of these factors is discussed in Appendix 3.

Automatic fire detection may be based on observation of heat, thermal radiation, combustion gases or smoke generated by the fire. Of the detection devices the ones acting on the principles of heat or smoke detection are the most commonly used.

Thermal fire detection devices are widely used because they are very simple in construction, are not vulnerable to failures in supplies of electricity and may be used in dusty or hot environments. They are cheap and fulfil the minimum requirements of fire detection. Thermal detectors have a rather slow response: they can react only when the fire has grown large enough to generate a substantial amount of heat, and also their intrinsic temporal response is rather long, ranging up to several minutes.

Smoke detectors are based either on the influence of smoke particles on ion mobility or on optical detection principles utilising the light absorbing or scattering ability of smoke. These devices accommodate more sophisticated components than thermal sensors and hence, are more susceptible to electrical disturbances or environmental factors. They also require regular maintenance and cost more than thermal detectors. Compared to the thermal devices the sensitivity of smoke detectors is considerably higher and their response to fire faster.

In chemical warehouses accommodating products of very high hazard potential due to *e.g.* their extreme toxicity or high propensity to ignite, early detection of fire is imperative. Thus, instead of the rather slow thermal detectors, the more rapidly acting detectors based on smoke or gas sensing should be used.

4.2 SPRINKLERS AND OTHER AUTOMATED MEANS OF EXTINCTION

In large chemical warehouses installation of automatic fire fighting systems is advisable. Such systems control the fire and may even extinguish[†] it thus making the fire brigade fire-fighting efforts notably faster and efficient. This alleviates considerably the hazards involved with the fire and also reduces the direct and indirect financial losses caused by the fire. For example, the reduced need for fire-fighting water may greatly mitigate the costs associated with the post-fire cleansing of the environment.

The techniques of fire suppression may be classified according to the extinguishing agent employed as 1) water suppression, 2) gaseous suppression, 3) foam suppression[‡] and, 4) powder suppression. Improvements to the traditional extinguishing methods are offered, *e.g.* by techniques using water mist and aerosols. A more detailed discussion of the suppression methods is presented in Appendix 4.

The most frequently employed techniques in automatic systems are those using water or gases. However, for flammable liquids, installation of fixed foam or powder extinguishing systems may in some cases be necessary since for such fires conventional water extinction systems may be unsuitable and gas systems may be too slow or inefficient. It should be noted that with the development of the modern water-mist extinction techniques, the applicability of water systems for putting out liquid fires is continually improving.

All automatic systems cause false alarms. However, the probability of their occurrence may be drastically reduced by proper installation and maintenance. Also, tests on the system should be performed before its routine use.

4.3 INFLUENCE OF EXTINCTION ON CHEMICAL FIRES: CONCLUSIONS FROM THE TOXFIRE PROJECT

In the TOXFIRE project, the influence of extinction on quantities of chemical compounds released by fires was investigated in micro, small, medium and large scale fire tests [Jørgensen & Smith-Hansen 1995, Markert 1996, Hietaniemi *et al.* 1996, Andersson *et al.* 1996 , Månsson *et al.* 1996]. Information on the chemicals studied in the TOXFIRE project is included in Appendix 1.

The fire effluents explored cover a rather wide selection of toxic combustion products ranging from the simple gases such as CO, HCN, HCl, SO_2 and nitrogen oxides to more complex compounds such as benzene, chlorobenzenes,

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[†] For simplicity, in this text actions of sprinklers and such appliances are referred to as suppression or extinction even though it may be that the actual purpose of the system is to control the fire rather than to put it out.

[‡] Conceptually, systems utilising foam (*i.e.* mixture of water and foam-forming chemicals) and those using pure water (sprinklers and water-mist systems) may be grouped together into a category of water-based extinction systems.

naphthatalenes, *etc*. Also the amount of the unburned parent compound in the exhaust gases, often referred to as the "survival fraction", was determined. The extinction method used was water spraying.

According to the results of the small-scale experiments, the effects of water extinction may be diverse. On one hand, with the polymer samples (esp. nylon) extinction leads to increased toxicity of the combustion gases via elevated production of CO, HCN and nitrogen oxides. On the other hand, extinction may have a cleansing influence on the exhaust gases: for example, in extinction tests of the tetramethylthiuram monosulphide and 4-chloro-3-nitrobenzoic acid samples, less high-molecular compounds were found in the fire effluents than in the corresponding tests without extinction.

The increased abundance of the toxic gases like CO decreases the safety of people in the vicinity of the fire, in particular fire fighters. The decreased amount of high molecular weight compounds, especially the survival fraction, suggests that water extinction diminishes the hazards involved with dispersion of airborne toxic materials from chemical warehouse fires. However, the result emphasises that fire fighting in a chemical warehouse has a high propensity to pollute water and soil in the neighbourhood of the warehouse.

5 LOCATION AND SAFETY DISTANCES

5.1 LOCATION, ORIENTATION AND SITE ACCESS

When establishing a new storage preference should be given to locations in areas dedicated to industrial activities; however, proximity to food production or storing facilities should be avoided. A chemical warehouse should not be placed in the vicinity of hospitals, schools or other similar institutions. Also, proximity to housings, shopping areas or any other regions of dense population should be avoided. If possible, in placing the warehouse the prevailing wind direction should be taken into consideration so that the possible airborne fire effluents would be carried to least harmful regions.

The warehouse should be placed at least at a 10 m distance from surrounding buildings or other properties.

Access of emergency vehicles to the warehouse should be provided from at least one side, but preferably from two sides. Any potential restrictions to the site access should be inspected and provisions to eliminate their affects in the case of an emergency should be planned in advance.

5.2 ASSESSMENT OF SAFETY DISTANCES

5.2.1 General

Toxic effects are a function of dose. When a substance is administered as a well defined amount, *e.g.* oral or intravenous, the dose is expressed as amount substance per kilo body weight, usually mg/kg. A value frequently used to describe the acute toxicity of a substance is the dose that is supposed to result in a 50 % lethality, LD_{50} (Lethal Dose 50 %). With exposure to gases and/or aerosols, the toxic effect is expressed as a function of concentrations in air, mg/m^3 or ppm. A value analogue to LD_{50} is consequently LC_{50} (Lethal Concentration 50 %). Dosage is however a function of exposure time as well. The exposure time must thus be stated for every LC value given.

Dose can be defined for other levels of probability as well, *e.g.* LC_{05}. LC_{05} values are frequently used as low risk levels even though the statistical definition of LC_{05} is the concentration that causes lethal injury to 5 % of the exposed population. In this report, LC_{05}, exposure time, pesticide survival fraction, and an applicable dispersion model, will be used as tools to estimate low risk distances. For further discussion concerning the LC_{05} value as a suitable low risk value see [Karlsson 1996].

5.2.2 A four-step procedure to assess low risk distances

1) Pesticide survival fraction

By the survival fraction we mean the portion of the substance that does not undergo decomposition in the fire. The survival fraction varies with the pesticide formula, physical and chemical properties, degree of ventilation, combustion temperature, *etc*. The influence of the compound properties may be clearly seen in the results of the TOXFIRE project, quoted in Appendix 1: the survival fraction varies from negligibly low percentages to values as high as 16 %. Partial burning of certain pesticides could result in the formation of oxidation products far more lethal than the parent product [Magnusson 1996] and considerations has to be taken to possible additive, synergistic and antagonistic toxic effects [Lilliehöök 1996].

In the following example we assume survival fractions of 100 and 10 % .

2) LC_{05} values

If possible, LC-values (human) are collected from the literature. When such data are missing, the LC-values are transformed from animal values. If animal values are transformed to human values, consideration has to be taken to individual variations in a normal human population, variations that do not exist in laboratory animals. Low risk assessments based on transformed data are applicable to healthy adults only. The casualties in a human population are increasing with the proportion of children, elderly people, and people with various diseases, and the assessment has to be compensated according to this.

The example corresponds to a fictitious, very toxic pesticide, *Fictivion*. The LC-values, following single exposure, are listed in Table 5.1.

Table 5.1. The LC-values of a fictitious, very toxic pesticide, Fictivion.

LC_{50} (rat, 4h)	**LC_{05} (human, 30 min/work)**	**LC_{05} (human, 5 min/work)**
10 mg/m^3	0.45 mg/m^3	1.1 mg/m^3

3) Fire scenario, dispersion, and weather situation

The amount of stored chemicals will obviously influence the size of the warehouse and thus the size of the fire. For these examples, however, only one fire scenario has been studied, which means that the amount of released toxic substance per unit time has a constant value (of 1 kg/s). The chosen fire scenario corresponds to "the small warehouse, scenario 2" in [Särdqvist 1996]. The amount of stored chemicals will thus limit the exposure time rather than the source strength.

The dispersion of the smoke cloud is dependent on the wind speed, wind direction and the stratification. When calculating the resulting concentrations, a Gaussian plume model is used: for details see [Winter & Johansson 1996]. In the example, the wind speed is assumed to be 5 m/s with neutral stratification, a common weather condition for mid-latitudes. Since the wind direction is very difficult to forecast, only the maximum distance, to which the concentration is higher than the LC_{05} value, is considered.

4) Exposure time

The exposure time is the period when humans are exposed to the substance. In the example, the exposure time corresponds to the time the specific fire is developing smoke. We assume 5 and 30 minutes respectively. The exposure time can here be affected by automatic alarms, sprinkler systems, plant design, amounts of stored chemicals, *etc.*

5) Assessment of low risk distances

From LC_{05}, exposure time, pesticide survival fraction, and with an adequate dispersion model, the low risk distance, concerning danger of lethal injury, can be estimated.

Staying closer to the fire than the low risk distance would thus require adequate personal protection. Unprotected people must be instructed in advance to take appropriate actions, following the alarm. Those instructions could be; listen to the radio for further information, stay indoors, shut windows, doors, ventilation, and if necessary be prepared to evacuate.

If such actions, concerning the public safety, are not considered sufficient or practicable, the stock of very toxic contents has to be limited to an amount that does not imply hazards of lethal injuries to the public. This limitation of the amount of stored chemicals cannot be calculated unless both the exposure time and the source strength is allowed to vary. The tool for such calculations is not yet available.

Table 5.2. An example summarising the four-step procedure to assess low risk distances of the fictive pesticide, Fictivion.

Survival fraction	**Exposure time (min)**	**Amount (kg)**	**LC_{05} (mg/m^3)**	**Maximal radius, low risk distance (km)**
100 %	30	1800	0.45	2.9
100 %	5	300	1.1	2.0
10 %	30	1800	0.45	0.6
10 %	5	300	1.1	0.4

5.2.3 Comments on the assessment of safety distances

In the above, a simple theoretical model of a very complex reality is discussed. The largest uncertainty in the model is probably the source strength, *i.e.* the fire scenario. As already stated, the amount of stored chemicals does not influence the size of the fire and furthermore, variations in the intensity of the fire are not considered at all. The presented work can be looked upon as an example of how complicated problems may be handled, and the results should therefore be viewed as rough estimates.

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APPENDIX 1

EXPERIMENTAL DATA ON HAZARDS ASSOCIATED WITH CHEMICAL FIRES

Risks associated with fires involving toxic chemicals have been investigated experimentally in the COMBUSTION and TOXFIRE projects. The results of these projects have been summarised in their final reports [Smith-Hansen 1994, Petersen & Markert 1996] and in the separate reports addressing the outcomes of each experimental effort [see refs. in Smith-Hansen 1994 and Petersen & Markert 1997].

Several chemical compounds were studied in the these projects; they are listed in Table A1.1. The substances were chosen to be representatives of typical classes of toxic chemicals.

The experiments covered a wide range of test methods with different scale fires: micro-scale tests in the DIN 53436 furnace [Smith-Hansen & Jørgensen 1992, Jørgensen & Smith-Hansen 1995, Markert 1996], small-scale tests in a cone calorimeter [Mikkola & Kallonen 1994, Hietaniemi *et al.* 1996], medium-scale tests in a 1/3-Scale Room Furnace [Andersson *et al.* 1994, Andersson *et al.* 1996] and large-scale experiments indoors [Månsson *et al.* 1994, Månsson *et al.* 1996] and outdoors [Nolan 1994].

In the experiments, the combustion characteristics and yields of combustion products of the substances were determined. In Table A1.2 important results concerning the fire hazards of the compounds are presented, that is: 1) assessment on the ease of ignition, 2) maximum value of heat release rate per unit sample area, 3) the effective heat of combustion, needed in fire load estimation and 4) smoke production (specific smoke production area). The data presented are values deduced from the small-scale cone calorimeter experiments in well-ventilated conditions with an external irradiation of 50 kW/m^2 [Hietaniemi *et al.* 1996].

Table A.1. Chemicals studied in the COMBUSTION and TOXFIRE projects.

Substance	**Formula**	**Name in short or abbreviation**	**Category**	**Method of study**
ammonium nitrate	NH_4NO_3		fertiliser	micro, small
O,O-dimethyl-S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl) methyl]-phosphorodithioate	$C_{10}H_{12}N_3O_3PS_2$	Azinphos methyl	organophos-phorous insecticide	micro, medium
O,O-dimethyl-O-p-nitrophenyl phosphorothioate	$C_8H_{10}NO_5PS$	Parathion methyl	organophos-phorous insecticide	micro, small, medium
2-methyl-4-chlorophenoxyacetic acid		MCPA	chlorophen-oxyherbicide	micro, small
tetramethylthiuram monosulfide	$C_6H_{12}N_2S_3$	TMTM	industrial chemical containing N and S atoms	micro, small, medium, large
O,O-dimethyl-S-(N-methylcarbamoylmethyl)-phosphorodithioate	$C_5H_{12}NO_3PS_2$	Dimethoate	organophosporous insecticide	micro, small, medium
4-chloro-3-nitrobenzoic acid	$C_7H_4ClNO_4$	CNBA	industrial chemical containing N and Cl atoms	micro, small, medium, large
chlorobenzene	C_6H_5Cl	CB	liquid solvent	micro, small, medium, large
2,6-dichlorobenzonitrile	$C_7H_3Cl_2N$	Dichlobenil	herbicide with the cyano group	micro, small
hexachlorocyclohexane	$C_6H_6Cl_6$	Lindane	heavily chlorinated insecticide	micro, small

Table A.2. Data related to fire hazards of some chemical compounds. Method of study: cone calorimeter at 50 kW/m^2.

Substance	**Ease of ignition**[1)]	**Max. RHR**[2)] **(kW/m^2)**	**$\Delta H_{c,eff}$**[3)] **(MJ/kg)**	**Smoke production**[4)] **(m^2/kg)**	**Survival fraction**[5)] **(%)**
Lindane[6)]	0	–	–	–	2
DMMP	3	1400	17	200	0.1
DCBN	2	200	6	600	16
CNBA	2	250	5	2200	0.2
TMTM	3	1300	23	negligible	negligible
CB	4	550	14	1700	4
Nylon	1	1200	31	350	–
PP	2	1600	43	450	–

Notes:

1) An estimate of the ignitability of the substance based on the time of ignition observed in the cone calorimeter tests. Notation used: 0 – no ignition, 1 – slow ignition, 2 – medium rate ignition, 3 – fast ignition and 4 – very fast ignition.

2) Rate of heat release per unit sample area measured in the cone calorimeter tests. The sample was exposed to an external heat radiation of 50 kW/m^2.

3) The effective heat of combustion determined from the cone calorimeter experiments, includes, *e.g.*, the fire retarding effect of the chlorine emitted by the chlorine containing compounds.

4) Smoke production is expressed as the specific smoke production area, evaluated as $\int k\dot{V}_{\mathrm{exhaust}}\mathrm{d}t \big/ \Delta m_{\mathrm{sample}}$, where k is the extinction coefficient, $\dot{V}_{\mathrm{exhaust}}$ is the exhaust gas flow rate and $\Delta m_{\mathrm{sample}}$ is the mass lost from the sample during the test. Values quoted correspond to burning in an environment with sufficiently oxygen and the external heat radiation of $\dot{q}'' =$ 50 kW/m^2.

5) The term survival fraction signifies the portion of the parent (fuel) compound which escapes the fire as such, without decomposition and oxidation.

6) Lindane did not burn in the cone calorimeter tests.

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APPENDIX 2

EXAMPLE OF ANALYTICAL FIRE SIMULATION MODELS: ESTIMATION OF THE TIME OF FLASHOVER

In this Appendix, we outline some analytical models which may be used to predict occurrence of flashover. The models are based on correlation formulae derived from experimental data and give a simple expression for the critical heat release rate, $\dot{Q}_{\text{critical}}$, required to induce flashover in a compartment. Combined, *e.g.*, with the t^2-fire growth model, one may estimate the instant t_{critical} at which the flashover occurs using

$$t_{\text{critical}} = \sqrt{\dot{Q}_{\text{critical}} / \alpha} \; . \tag{A2.1}$$

Predictions for the times of flashover onset, obtained using the three models described below, in the two example warehouses, are shown in Fig. 2.2.

A simple expression for $\dot{Q}_{\text{critical}}$ is given by Babrauskas [Babrauskas 1980]:

$$\frac{\dot{Q}_{\text{critical}}}{\text{kW}} = 750 \cdot \left(\frac{A_{vent}}{\text{m}^2}\right) \sqrt{\left(\frac{H_{vent}}{\text{m}}\right)} , \tag{A2.2}$$

where A_{vent} and H_{vent} represent the area and height (mean values evaluated in an appropriate way) of the ventilation openings. The expression

$$\frac{\dot{Q}_{\text{critical}}}{\text{kW}} = 7.8 \left(\frac{A_{\text{total}}}{\text{m}^2}\right) \left[1 + 48.5 \frac{\left(\frac{A_0}{\text{m}^2}\right)\sqrt{\left(\frac{H_{vent}}{\text{m}}\right)}}{\left(\frac{A_{\text{total}}}{\text{m}^2}\right)}\right] = 7.8 \left(\frac{A_{\text{total}}}{\text{m}^2}\right) \left[1 + 48.5 \left(\frac{\Omega}{\text{m}^{1/2}}\right)\right] \tag{A2.3}$$

introduced by Thomas [Thomas 1981], incorporates also the influence of the internal surface area of the compartment, A_{total}. The second equality in Eq. (A2.3) introduces the ventilation factor Ω, frequently used to characterise ventilation in compartments,

$$\Omega = A_{\text{vent}} \sqrt{H_{\text{vent}}} / A_{\text{total}} \; . \tag{A2.4}$$

The model developed by McCaffrey *et al.* [McCaffrey *et al.* 1981] embodies the influence of the compartment properties in more detail. The relation between $\dot{Q}_{\text{critical}}$ and the driving force, the temperature of the hot gas layer T_{HGL}, may be expressed in following form:

$$\dot{Q}_{\text{critical}} = \sqrt{\dot{Q}_1 \dot{Q}_2} \left(\frac{T_{\text{HGL}} - T_0}{480 \ {}^\circ\text{C}}\right)^{3/2} . \tag{A2.5}$$

The prerequisite of flashover is commonly expressed as a condition that the hot gas layer temperature rises 500 °C above the ambient temperature, $T_{\text{HGL}} - T_0 = 500$ °C.

In Eq. (A2.5) the influence of the compartment properties has been incorporated into the two heat rate parameters $\dot{Q}_1$ and $\dot{Q}_2$, related to the ventilation conditions and to the thermal properties of the enclosure, respectively:

$$\dot{Q}_1 = c_p \rho_0 T_0 A_{\text{vent}} \sqrt{gH_{\text{vent}}} = c_p \rho_0 T_0 \sqrt{g} A_{\text{total}} \Omega \qquad \text{(A2.6)}$$

and

$$\dot{Q}_2 = h_k A_{\text{total}} T_0 \qquad \text{(A2.7)}$$

The parameter h_k is an effective heat-transfer coefficient which includes the properties (thickness D, thermal conductivity k_b, specific heat c_b and density ρ_b) of the enclosure boundaries:

$$h_k = \frac{k_b}{\Lambda}. \qquad \text{(A2.8)}$$

The parameter Λ depends on whether the characteristic time of burning, t, is shorter or longer than the thermal penetration time $t_p = \frac{1}{4} D^2 \rho_b c_b / k_b$ of the boundary: if $t < t_p$, $\Lambda = \sqrt{(tk_b)/\rho_b c_b}$ and if $t > t_p$, $\Lambda = D$. The other quantities are: c_p – gas heat capacity, ρ_0 and T_0 – ambient atmosphere density and temperature.

Naturally, the models are best applicable to situations resembling those used in the tests providing the empirical foundations of the approach, *i.e.* relatively small compartments with a regular shape (not elongated, *etc.*) with the fire growth not exceedingly fast.

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APPENDIX 3

OPERATION TIMES OF FIRE DETECTION SYSTEMS

One of the most essential factors considering the alarm and automatic extinction devices is the time it takes for the system to start its operation. This time lag is determined by: 1) the time delay before any changes occur in the observable physical quantity (usually heat or smoke) at the sensing device location, 2) the time it takes for the sensor element to actuate (*e.g.* reach a pre-set temperature or sufficient smoke density) and, 3) the activation time, *i.e.* the time delay between the sensor actuation and the initiation of the triggered action (such as opening of the smoke vents or air displacement in sprinkler piping).

A3.1 INITIAL DELAY TIME

With thermal or smoke detectors, there may be a significant time lag before any changes occur at the sensor location in the physical quantity (heat rise or smoke density increase) triggering the sensor. This delay time t_d depends on the properties of the fire (heat release rate, smoke production), on the warehouse construction (size, shape, ventilation, smoke vents, *etc.*) and sensor arrangements.

As an example of t_d for heat detectors, combining several of these factors, let us consider the expression (A3.1), deduced empirically by Heskestad and Delichatsios [Heskestad & Delichatsios 1978]

$$t_\mathrm{d} = 0.95\left(\frac{H^{4/5}}{(A\alpha)^{1/5}}\right)\left(1 + r/H\right) \tag{A3.1}$$

where $A = g/(c_0 T_0 \rho_0) \approx 0.028$ m^2/kg incorporates the initial temperature T_0 (K), specific heat c_0 (kJ/(kg·K)) and density ρ_0 (kg/m^3) of air and influence of buoyancy via the gravitational acceleration g. The warehouse construction and sensor arrangement are presented by the room height H and detector distance from the fire axis r. The factor α determines the fire growth rate relating the heat release rate of the fire $\dot{Q}_\mathrm{fire}$ to the time elapsed after the ignition at time t_0 as

$$\dot{Q}_\mathrm{fire} = \alpha\left(t - t_0\right)^2 . \tag{A3.2}$$

In small compartments, t_d can be neglected, but in large spaces it may be notable, approaching the sensor response time.

A3.2 SENSOR RESPONSE TIME

The time it takes for the sensor element to reach its actuation level depends on response time of the sensor element. For a thermal or smoke sensor, the temporal response can be[†] characterised by a time constant τ, governing the rate of change in the value x_{sensor} of the control variable x at the sensor according to the following first-order differential equation

$$\frac{\mathrm{d}x_{\text{sensor}}}{\mathrm{d}t} = \frac{x_{gas} - x_{\text{sensor}}}{\tau} \tag{A3.3}$$

where x_{gas} describes the value of x for the gas. For thermal detectors, x is temperature, and for smoke sensors, x denotes the smoke density. The value of gas temperature or smoke density depends on the fire characteristics (heat generation rate and speed of fire growth, see Appendix 1) of the burning material and also on the fire environment. For thermal detectors, the time constant τ depends on, *e.g.* sensor material, geometry and the gas flow velocity u at the sensor, $\tau \propto u^{1/2}$. For smoke sensors, the time constant is inversely proportional to u, $\tau \propto u^{-1}$ [Björkman *et al.* 1992]. For thermal sensors, the time constant is stated most frequently as the RTI value, $\mathrm{RTI} = \tau u^{1/2}$, which may be employed with a known or estimated value of the flow velocity u.

The problem of response of thermal detection systems, and the closely related issue of fire induced flow beneath ceilings, has been elaborated in several publications. The approaches range from development and use of empirical correlation formula based on properties of stationary fire plumes [Alpert 1972] to models necessitating the use of computers [Alpert 1985]. In large compartments, it may be necessary to consider the time development of the fire explicitly and incorporate the time delay t_{d} (Eq. (A3.1)) into the calculations [Heskestad & Delichatsios 1978, Beyler 1984].

The formulae relate the properties of the fire (heat release rate Q_{fire}, growth speed α) and geometry of the room and sensor locations (room height H and detector distance from the fire axis r) to the gas temperature T_{g} and flow velocity u, and further, via Eq. (A3.3) to the detector temperature T_{d}. Most often, the sensor actuation is depicted by a pre-set temperature limit T_{act}, a typical value of which is 57 °C, but functioning of a temperature-rise sensor may also be predicted by determining the time at which the detector temperature derivative reaches a fixed critical level: $\mathrm{d}T_{\text{d}}/\mathrm{d}t = (\mathrm{d}T/\mathrm{d}t)_{\text{critical}}$.

In Fig. A3.1 results of such calculations, corresponding to slow ($\alpha = 0.003$ kW/s^2), medium speed ($\alpha = 0.01$ kW/s^2), fast ($\alpha = 0.1$ kW/s^2) and very fast ($\alpha = 0.1$ kW/s^2) growth of the t^2-model fire, are shown. The corresponding response times with an actuating temperature of 60 °C are given in Table A3.1. The crucial point is how much before the development of flashover the sensor triggers. Estimates of the time of flashover may be read from Fig. 2.2: the predictions of the model of McCaffrey *et al.* are given in Table A3.1.

[†] The model is presented in its simplest form. More refined formulations for thermal sensors take into account the thermal conductivity of the sensor. In Eq. (A3.3) this would lead to replacement of x_{sensor} on the right-hand side by $(1 + C/\sqrt{u})x_{\text{sensor}}$ where C is the known as the conductivity factor of the sensor.

Besides sensing devices, the methods quoted above are applicable to predict temporal response of other self-actuating devices such as automatically collapsing smoke vents.

Table A3.1. Estimates for the times of detection and times of flashover in the two reference warehouses.

	SMALL WAREHOUSE		**LARGE WAREHOUSE**	
α (kW/s^2)	**detection time (minutes)**	**time of flashover (minutes)**	**detection time (minutes)**	**time of flashover (minutes)**
0.003	4.5	14.5	6.0	16.0
0.01	2.5	8.5	3.5	9.5
0.05	1.5	4.0	2.0	4.5
0.1	1.0	3.0	1.5	3.5

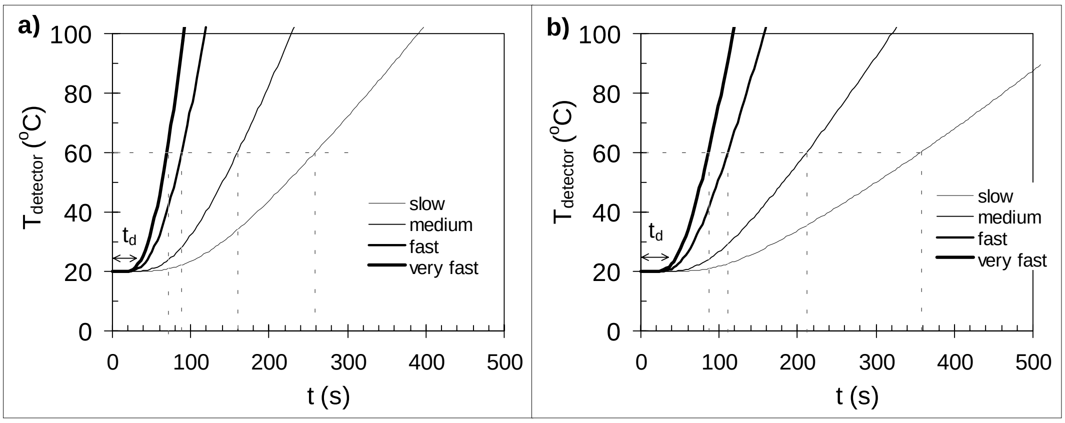

Figure A3.1. Examples of thermal detector response times in the two reference warehouses: the smaller warehouse with room height H = 4 m (a), and the larger warehouse with room height H = 6 m (b). The detector spacing is assumed to such that r = 1 m. The temperature curves correspond to slow (α = 0.003 kW/s^2), medium speed (α = 0.01 kW/s^2), fast (α = 0.05 kW/s^2) and very fast (α = 0.1 kW/s^2) fire growth rates. Also the delay time t_d is shown.

A3.3 ACTIVATION TIME

The activation time is the time interval from detection of the fire by the sensing element until the actuated utility, *e.g.* suppression system or smoke control assembly, is fully operational. It consists of a potential delay after the detection and the actual time required to activate the system. Factors influencing the activation time in some suppression systems include:

1) Wet pipe sprinkler systems:
   The activation time is negligible.

2) Dry pipe sprinkler or suppression device systems:
   The activation time is the time required to expel the system air.

3) Gaseous flooding systems:
   The activation time is the time required to establish the specific concentration of the suppression agent in the relevant volume.

4) Foam systems:
   The activation time includes the period required to expel the system air and the time needed to generate the required foam agent concentration.

5) Powder systems:
   The activation time includes the period required to expel the free air.

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APPENDIX 4

FIRE EXTINGUISHING TECHNIQUES

The fire extinguishing techniques may be classified according to the extinguishing agent employed as: 1) water systems, 2) gaseous systems, 3) foam systems[†] and, 4) powder systems. Improvements to the traditional suppression methods are offered, *e.g.* by techniques using water mist and aerosols.

A4.1 WATER SUPPRESSION

Operation of water as an extinguishing agent is based on the following mechanisms: heat absorption in the liquid phase (cooling), inerting effect (making the atmosphere inflammable) of the gas-phase water, influence of momentum of the water droplets and blocking of heat radiation by the droplets. The principal mechanism is cooling deriving its power from the high latent heat of vaporisation of water. It may affect fire via the flames, the fuel surface and through prewetting the surrounding non-ignited regions.

Water extinction systems operate by delivering pressurised water through nozzles. In conventional sprinkler systems, the droplets produced are *ca.* 1000–2000 μm in diameter whereas in water-mist systems the droplets are smaller, with the size distribution concentrated below 400 μm, which radically increases the cooling ability of the water spray [Mawhinney 1993]. Due to the increased efficiency, the total amount of water required in the mist systems is considerably smaller than that needed in conventional sprinkler systems: the typical water deposition fluxes from sprinklers varies between 3 and 15 $l/(min \cdot m^2)$, whereas in water-mist systems it typically is *ca.* 1 $l/(min \cdot m^2)$. For fire suppression in chemical storage facilities this is a very appealing feature. The major drawback of water mist systems is that they use more elaborated techniques and, consequently, are more expensive than the conventional sprinkler systems.

A4.2 GASEOUS SUPPRESSION AGENTS

Gaseous fire extinguishing media operate either through the mechanism of inerting or through chemical suppression of the combustion chain reactions.

The fire suppression gases belonging to the first category are carbon dioxide CO_2, nitrogen N_2 and argon Ar, and their mixtures. They make the fire atmosphere inert by cooling the flame gases below a temperature (~ 1550 K), below which sustained combustion is no longer possible. Suppression based on cooling by inert

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[†] Conceptually systems utilising foam (i.e. mixture of water and foam-forming chemicals) and those using pure water (sprinklers and water-mist systems) may be grouped together into a category of water-based extinction systems.

gases is augmented by the associated reduction in the oxygen concentration which diminishes the reactivity of the flames.

To cool the flames below the critical temperature requires large amounts of gas suppressants, the typical required volumetric concentrations being at least 30 % for CO_2 and *ca.* 50 % for N_2 and Ar. The oxygen concentration of the atmosphere decreases correspondingly, readily approaching 10 % which is untenable for humans. Hence, before the inerting gases are applied the space must be evacuated.

The large amounts of suppressants require lengthy discharge times, 1–2 minutes or longer. With the requirement of evacuation, this means that the activation time of the gaseous suppression systems in long, *ca.* 3–5 minutes. Also the ability of the gases to cool the solid structures in the fire space is low and thus, their concentration has to be maintained rather long to prevent re-ignition of the hot surfaces.

The fire fighting gases which act through the chemical suppression mechanism are extremely efficient, in particular the fire-fighting halogenated hydrocarbons or Halons such as CF_3Br and CF_2ClBr called the Halon 1301 and Halon 1211, respectively. However, these compounds destroy the ozone in the stratosphere extremely efficiently and hence, their use as suppressants will be denied (it has already been partially banned). Halons exhibit also a strong potency to enhance the greenhouse effect (Global-Warming Potency, GWP). Several replacing agents for Halons have been introduced, such as $CF_3CHF\ CF_3$ (FM-200), which have only a small tendency to decompose ozone. However, basically, these compounds are hydrocarbons with halogen atoms and hence, potentially hazardous to stratosphere, *e.g* due to their rather large GWP values.

A4.3 FIRE SUPPRESSION FOAMS

Foams are primarily used to fight fires involving flammable liquids. Foams are applied directly on the burning object, most frequently from mobile devices. In the cases where large amounts of flammable liquids are stored, transported or used, also permanently installed foam systems are used.

Foams suppress fires in three ways: firstly by forming a fire resistant blanket which blocks off the access of oxygen to the fuel. Secondly, this covering impedes the release of the flammable vapours. Thirdly, foams possess cooling capacity associated with their water content. Usually, foams are classified according to their ability to expand using an (volumetric) expansion ratio, *i.e.* the ratio between the finished foam and the foam solution. For low expansion foams, the expansion ratio is below 20, and for high expansion foams above 200.

There are several different types of foam concentrates available; the proper selection of the foam depends on the hazard type. The commonly used fire-fighting foam concentrates together with some properties are listed below [Cash 1995].

1. Protein foam concentrates (P)
    - aqueous solutions of hydrolysed proteins;
2. Fluoroprotein foam concentrates (FP)
    - protein foam concentrates with added fluorinated surface active agents,
    - resistant to contamination of hydrocarbon liquids;
3. Film-forming fluoroprotein foam concentrates (FFFP)
    - protein foam concentrates with added fluorinated surface active agents,
    - resistant to contamination of hydrocarbon liquids,
    - film-forming on some hydrocarbon liquid fuels;
4. Synthetic foam concentrates (S)
    - solutions of hydrocarbon surface active agents;
5. Aqueous film-forming foam concentrates (AFFF)
    - based on hydrocarbon and fluorinated hydrocarbon surface active agents,
    - film-forming on some hydrocarbon liquid fuels;
6. Alcohol resistant foam concentrates (AR)
    - foams for use on foam-destructive liquids, derived from any of the above mentioned foam types.

A4.4 POWDER SUPPRESSION AGENTS

Powder fire suppression media are mainly used in portable extinguishing devices, but are also employed in fixed suppression systems. The powders are usually propelled by nitrogen. Their benefits are good suppression power and non-toxicity, but the major disadvantage is their staining effect.

Powders may be classified into B-powders used for fires involving liquids and to AB-powders applicable to fires with solids or liquids. The fire-fighting powders are basically salts: typical B-powders are, *e.g.* sodium or potassium bicarbonate ($NaHCO_3$, $KHCO_3$) and commonly used AB-powders are, *e.g.* ammonium phosphate or ammonium sulphate ($NH_4H_2PO_4$, $(NH_4)_2SO_4$).

The extinguishing effect of powders is based on the properties of their principal components, salts, which act via three mechanisms: 1) cooling, 2) chemical inhibition of the combustion chain reactions and 3) locally lowering the O_2 concentration. Powders have also a tendency to form films on burning solids which blocks access of oxygen to the hot surface.

A novel technique in powder-based fire suppression is the use of extinguishing aerosols. These aerosols are created by burning suitable pyrotechnical materials which first vaporise and then condense forming small particles. The aerosols are salts like powder suppression media and derive their function from the same mechanisms. However, due to the substantially smaller particle size, aerosols utilise these mechanisms more efficiently than the conventional fire-fighting powders – analogous to water mist being more effective than conventional sprinkler sprays.

In case of a fire, the aerosol formation may initiate automatically or be triggered electrically. The major benefit of aerosols extinction is that no vessels, pipelines or other permanent installations are required. It has been suggested that the extinction power of 4 kg of aerosol precursor fuel would correspond to that of 150 kg of CO_2. The activation time of aerosol extinction is lengthy as the aerosol production process is relatively slow.

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APPENDIX 5

REFERENCE WAREHOUSES

To render the discussion in the guideline documents of the TOXFIRE project more concrete, two warehouses were chosen as reference objects. In the present report, these warehouses are addressed in the context of the fire simulation models outlined in the Appendices 2 and 3; in the guideline document addressing the fire-brigade actions, referencing is more frequent [Särdqvist 1996].

The reference warehouses vary considerably: one is a rather small building constructed a hundred years ago as a model farm while the other, a rather large building designed for storing pesticides, is less than ten years old.

The smaller warehouse is built in two floors with a loft. The building area is 53 m×22 m. The ground-floor walls are made of brick and stone and the upper story is of wooden construction. The compartment floor is made of steel beams with brick arches. The largest compartment in the 1st floor is used as the example room in Appendices 2 and 3. Its area is 53 m×22 m and height 4 m. If the doors and windows are closed, the ventilation opening area may be estimated to be 0.5 m×2 m (width × height) while the total area of doors and windows is *ca.* 1 m×5 m plus 0.5 m×2 m.

The building area of the larger storage building is *ca.* 60 m×100 m. The floor area of the largest compartment, used as the example room in Appendices 2 and 3, is 20 m×30 m and its height equals 6 m. The ventilation opening area may be estimated to be 2.5 m×3 m.

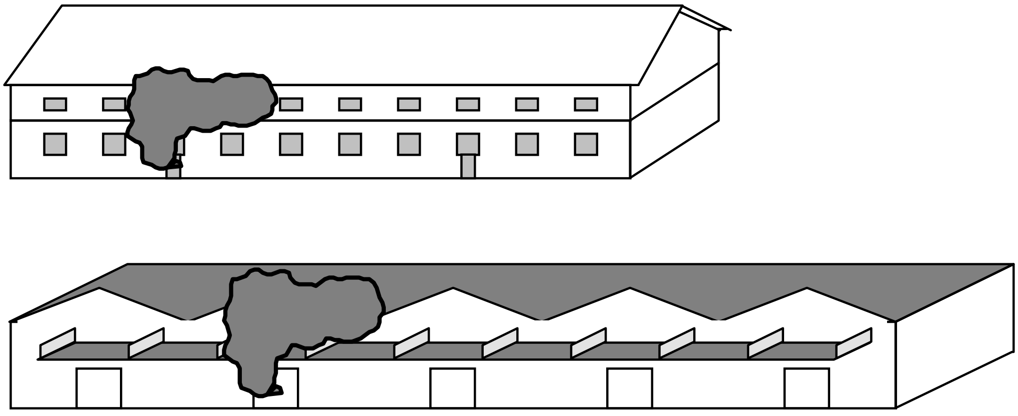

Figure A5.1 The reference warehouses: the upper building is the smaller warehouse with an area of 53 m × 22 m and the lower one the larger warehouse of an area of ca. 60 m × 100 m. The fires depicted correspond to fires limited to a single compartment. [Särdqvist 1996]

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