

Approaches towards a generic methodology for storage of hazardous energy carriers and waste products

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Energy carriers – either conventional or ‘new’ ones – have to be provided in large amounts to meet the requirements of permanent availability and reliable supply of electricity. Depending on their state of aggregation, energy carriers are either stored in large masses (if solid or liquid) or at elevated pressures (if gaseous). Both impose the hazard of large-scale fire, in the latter case additionally the danger of explosion or unintended release. Very similar hazards occur for wastes. Solid wastes are present in large masses and only a small part is recycled. Most of the solid wastes are used in energy conversion. The main gaseous waste is CO₂. During capturing also the hazard of unintended release exists. In this article, existing approaches for safe storage and fire prevention are discussed and a generic methodology is outlined. This methodology consists of the following steps:

- gaining knowledge about the behaviour of the material stored (reactivity, thermal stability, etc.),
- assessing the environmental conditions for the storage site (neighbourhood, safety distances, etc.),
- assessment of prospective consequences of an incident and
- development of individual loss prevention conceptions.

All steps require both experimental testing and theoretical considerations about accident scenarios as integral parts of the methodology.

Keywords: storage; hazardous materials; energy carriers

1. Introduction

Carriers of primary energy have to be stored in large masses to assure reliable supply chains for energy conversion. Not only consumers expect stable availability of electricity or heat, but industry and infrastructure need unrestricted access to energy

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resources to prevent stand-still of production lines and traffic means and the economic losses connected to it.

Moreover, for some technologies breakdown of energy supply can create a technological risk due to failure of emergency systems.

The present study outlines a methodology for the assessment of hazards – first of all technical hazards – which are connected to storage of usually large amounts of energy carriers. In addition, storage of wastes from energy conversion or of wastes which is used as fuels (refuse-derived fuel, RDF) are also addressed.

Different examples of storage processes are investigated to analyse the hazards connected to the storage processes and to derive a generic model of hazard assessment.

According to the materials stored special consideration is given to

- the thermodynamic state of aggregation,
- the chemical reactivity and
- the toxic potential.

According to the technical conditions of storage, special consideration is given to

- the thermodynamic properties of storage (pressure and temperature),
- the interaction with the containment,
- the sensitivity of the environment,
- the precautions taken to prevent incidents and
- the emergency response in case of incidents.

Hazards connected to the large-scale storage of liquids and gases – not only fuels but also chemicals – have been addressed in the comprehensive book of Mannan (2005), namely in Chapter 22. Some hazards occurring during storage compared to processing of material are summarised in Table 1.

Special hazards occur during underground storage of hazardous materials:

- restricted or no access to the storage site (e.g. for emergency operations, repair, etc.),
- unknown and uncontrollable pathways for reaction products and
- unknown behaviour of rock strata under thermal load (in case of unintended heat release from the stored products).

2. Sample cases

2.1. *Hydrogen*

Established technologies for storing of hydrogen are:

The hazards exhibited in Table 1 are by far not complete, but only intended to illustrate special hazards connected to storage processes.

- Compressed gaseous hydrogen in a hydrogen pressure tank.
- Liquid hydrogen in a (LH₂) cryogenic hydrogen tank.
- Slush hydrogen in a cryogenic hydrogen tank.

Table 1. Hazards connected with storage of materials compared to processing.

State of aggregation	Processing	Storage
Gaseous	• Elevated pressures and temperatures • Ignition sources inherent in the process (e.g. hot surfaces, mechanical and electrical sparks) • Transient changes of state	• Elevated pressures • High energy density • Unintended releases • Formation of explosible clouds • Runaway reactions
	• Ignition sources inherent in the process (e.g. hot surfaces) • Rapid phase change • Elevated pressures and temperatures	• Unintended release • Rapid phase change • BLEVE • High energy density • Soot and smoke formation
	• Ignition sources inherent in the process (e.g. hot surfaces, friction and hot spots) • Elevated temperatures (e.g. in dryers)	• High energy density • Self-ignition • Soot and smoke formation (at circumstances toxic)
Liquid		
Solid		

Large quantities of gaseous hydrogen are stored in underground caverns, salt domes, depleted oil/gas fields, aquifers, excavated rock caverns (porous rock structures) or mines. Usually, the storages contain gaseous H_2 compressed up to 200 bar. There also exist extremely large storage facilities (of about $15,000\text{ m}^3$) which contain hydrogen tanks pressurised only to 12–16 bar.

Compressed hydrogen in hydrogen tanks at 350 and 700 bar is used for mobile storage in hydrogen vehicles. Hydrogen tanks (cartridges or canisters) are made of composite material because of hydrogen embrittlement. Hydrogen tanks compressed at 700 bar were demonstrated in 2001.

The LH2 tank contains H_2 under cryogenic temperature of 20.4 K (-252.8°C).

A combination of LH2 and solid hydrogen at the triple point with a lower temperature and a higher density than LH2 is known as slush hydrogen. It is formed by cooling down the LH2 to nearly the melting point 14.01 K (-259.14°C) by increasing density by 16–20% compared to LH2. It is proposed as a rocket fuel instead of LH2 in order to increase the amount of fuel in the tank.

From the standpoint of safe storage, the categories of hazards have to be considered for hydrogen according to Table 2.

2.2. Underground storage of wastes

This example was previously reported by Lerena and Krause (2009). Construction wastes containing a large fraction of asbestos were stored in an underground facility in France.

Figure 1 shows an example of such a storage (not the one where the incident occurred).

Though asbestos is nearly non-reactive, the wastes contained residues of reactive material which were not recognised when the storage was erected. Consequently, the stored material underwent exothermic reactions ending in self-ignition and a subsequent fire.

The fire was first noticed when a foul odour and liquid slurry emanated from the storage site.

Extinction works lasted for two months applying water as extinguishing agent. The weaknesses of the safety concept in this incident were:

Table 2. Categories of hazards for hydrogen storage.

Chemical reactivity	• Readily ignitable ($\text{MIE}^a < 1\text{ mJ}$) • Ignites with any ignition source • Wide explosible range (between 4 and 75 vol%)
Thermodynamic storage conditions	• Elevated pressures (gas storage) • Rapid phase change (in case of leakage at cryogenic storage)
Interaction with containment	• Embrittlement • Possible failure of safety installations

^aMinimum ignition energy.



Figure 1. Example of underground storage of wastes (courtesy of BMG Engineering).

- The material was considered as non-reactive. Therefore, insufficient fire precautions were taken.
- No testing was undertaken for the thermal stability of the stored material. Testing was considered to be difficult due to the asbestos.
- The emergency procedures were not sufficiently elaborated.
- The fact that asbestos-containing waste may contain combustible or self-heating materials went unnoticed.

The consequences of the fire and the lessons learnt from it were:

- The activity of the storage was stopped.
- The sector where the fire occurred was closed.
- The risks related to the thermal instability and combustibility were known but forgotten.
- Improved preventive procedures to avoid storing combustible and self-heating materials were considered to be developed.
- Emergency procedures to intervene if, however, a fire occurs have to be defined.

2.3. Underground storage of coal

Despite a rapid increase in use of ‘alternative’ energy carriers, the by far largest portion of primary energy provided for electricity and heat energy production on global scale comes from coal. Considering the increasing request for electricity in some parts of the world, this will only gradually change in the near future.

For the reason of reduction of air pollution, a tendency emerged to store coal rather in containments than in open heaps. These containments are e.g. silos with a capacity of up to 100,000 tons erected above ground.

Compared to storage in open heaps, a number of new risks emerge:

- The volume-to-surface ratio V/S of the bulk is increased. V/S is the decisive geometrical parameter for self-ignition of coal storages. The general trend is, the higher V/S the higher is the hazard of self-ignition.
- Signs of a fire (smoke and elevated concentrations of fire gases) will be noticed possibly later outside the enclosure.
- Fire fighting is much more complicated and cost-intensive, since in contrast to open heaps, it is not possible to simply extract burning material.

Sipilä and Auerkari (2010) recently reported about coal storage in underground caverns of a total capacity of 250,000 tons distributed over four individual storage sections. This case study is not discussed in detail here since there exists a special paper under the above reference.

However, a few conclusions from this case should be mentioned:

- The reactive potential and influencing parameters of the coal stored have to be known or tested (volatility, calorific properties, humidity, grain size distribution, onset temperature, etc.).
- The conditions of storage have to be settled (packing density, ingress of air, first in-first out loading/unloading, monitoring, preventive measures, etc.)
- Methods of hazard reduction, which were taken after the incident:
 - (a) improved air tightness to reduce self-heating,
 - (b) control of coal grades (to some extent),
 - (c) monitoring for conveyors and other equipment,
 - (d) improved monitoring (temperature and gases),
 - (e) improved extinguishing.
- Not all hazards were foreseen before appearing, at least until it was attempted to discharge once frozen coal from the silo to discharge from the silo.

Figure 2 shows a hot spot generated by an auto-ignition process in the stored coal identified with thermal camera imaging.

2.4. Above ground storage of combustible wastes and recycling materials

Industrial and municipal wastes are stored in large masses over long periods of time.

Waste deposits of more than a 100,000 tons of material are not seldom.

During long-term storage, these deposits undergo complex chemical conversion. Some of the undergoing reactions are exothermal and gradually increase the temperature inside the deposit possibly resulting in a so-called runaway reaction which is an uncontrolled increase in temperature and often the starting point of a fire.

Waste deposits usually have the form of either

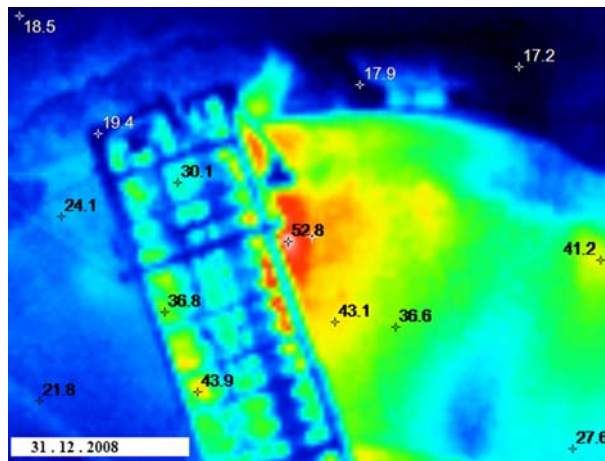


Figure 2. Thermal camera imaging of a hot spot in an underground coal storage silo (from Sipilä and Auerkari 2010).

- loosely stored heaps,
- heaps stored in semi-confined boxes,
- mechanically compressed heaps,
- compressed bales, sometimes wrapped with foil or
- totally confined fillings of underground caves.

In the latter case, the material is usually contained in big bags or steel barrels which are stored such that the intermediate space is reduced to a minimum. Besides the storage, the purpose of this technology is to stabilise the overlying rock strata.

The main hazard of such deposits results from unknown long-term chemical stability of such deposits.



Figure 3. Typical intermediate deposit of recycling products in open space heap storage with 110,000 tons capacity.

Figure 3 shows a 110,000 tons intermediate deposit of recycling materials. Despite such storage sites usually exist over years, typically no fire precaution measures are taken since they are declared to be of intermediate or provisional character.

A methodology to assess the hazard of unwanted chemical reactions has to include the following two components:

- characterisation of long-term thermal and chemical stability of the stored material,
- Prediction of the long-term thermal stability of the deposit.

The first item is basically an experimental investigation using methods of thermal analysis. The output parameters are onset temperatures for unwanted chemical reactions and kinetic data (apparent activation energy and apparent frequency factor) for the lump-reaction effect.

The second item comprises a mathematical analysis attempting to predict the temperature evolution with time within the deposit based on a balance of heat production (by the exothermal reactions) and heat transfer to the environment.

Further considerations have to comprise the effect of unwanted reactions on the public and on the environment, e.g. by large emissions of smoke and potentially harmful fire products.

Mathematical models are available at different levels of sophistication. Analytical models either predict the evolution of the average system temperature with time (zero-dimensional model) or the steady-state temperature distribution in the reactive system for the one-dimensional case.

Advanced numerical models have no such restrictions. Their application is only limited by the available computer resources.

The general features of such models are:

- They are based on physical principles like conservation of mass, momentum and energy.
- These principles are reflected by a set of partial differential equations which in most cases have to be solved numerically, e.g. by finite difference, finite volume or finite element schemes.
- The set of conservation laws is mathematically closed by so-called constitutive equations which include sub-models for chemical reactions, temperature dependence of transport coefficients and others.

In general, numerical simulations of these phenomena offer the following advantages:

- There are no limitations for geometry. Three-dimensional geometries can be treated as well as 'sandwich' materials, i.e. those consisting of different layers, each exhibiting its own material properties.
- Any kind of thermal boundary conditions (given surface temperature, given heat flux and Newtonian cooling) can be considered. In addition, the boundary conditions may vary in space and time.
- The dependence of the temperature evolution with time can be treated such that the entire process of heating, self-ignition, runaway and burnout can be followed continuously.

- Information is obtained on local distributions of the chemical species of interest and their evolution with time.
- Kinetic and transport-controlled reaction regimes may be considered, the latter including diffusion and convection of gaseous chemical species.

The challenge is now to connect the results of the experimental thermal analysis with the requirements of the application of an advanced predictive model. The input which has to be provided to the model covers

- the quantities given in Table 3,
- boundary and initial conditions and
- geometry data.

Figure 4 shows how the output of the laboratory tests and the different components of the physical and chemical model are combined to result in a general simulation model. This model allows for computing the evolutions with time of temperature and concentrations of chemical species in an either two or three-dimensional computational domain.

Based on such a model, fire scenarios can be predicted which allow a precise assessment of the hazard of thermal runaway and subsequent fire propagation.

A typical result of such a predictive scenario is given in Figure 5. A deposit of recycling material of 19,000 m³ was stored at an average ambient temperature of 10 °C which is about the yearly average of Berlin. Note that due to the high thermal inertia of such a deposit, neither the daily nor the yearly alterations of the ambient temperature affect the internal temperature significantly.

3. Attempting a generic approach for risk assessment of storage processes

Despite existing differences in material behaviour and in the conditions of storage between the different energy carriers discussed in this study, a generic approach for risk assessment – without neglecting the peculiarities – seems possible. The con-

Table 3. Experimental quantities to characterise the self-ignition behaviour of bulk materials.

Material properties	Reaction stoichiometry	Reaction kinetics	Heat and mass transfer
Particle density	Elemental composition	Apparent activation energy	Diffusion coefficient
Bulk density	Ash content	Apparent frequency factor	Heat transfer coefficient
Porosity	Humidity		Mass transfer coefficient
Permeability	Composition of flue gases		
Thermal conductivity			
Specific heat			
Calorific value			
Viscosity			

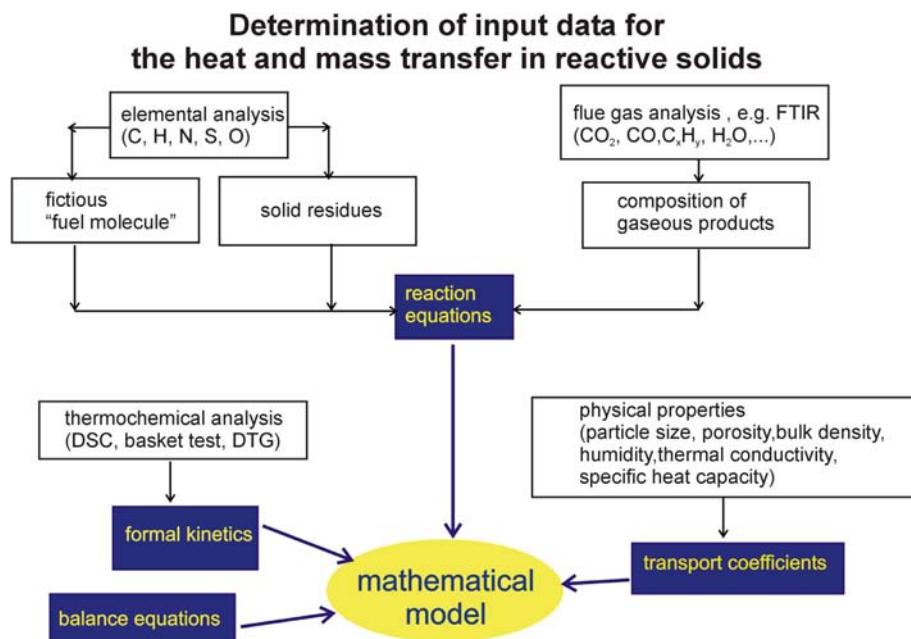


Figure 4. Components of a mathematical model for thermal phenomena in a solid-phase reactive system.

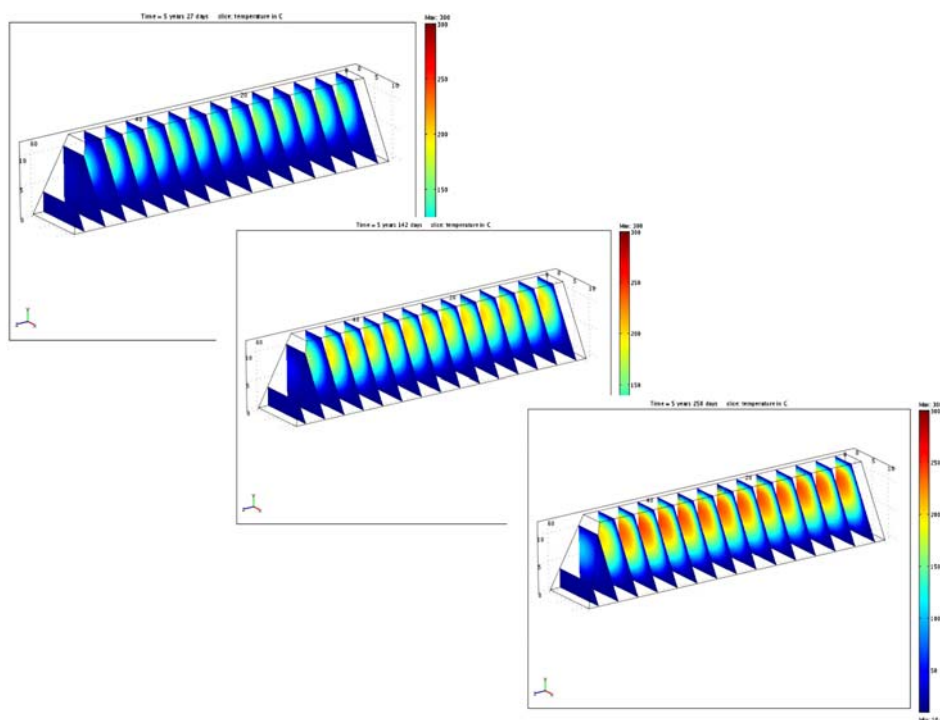


Figure 5. Temperature evolution with time in a 19,000 m³ deposit of recycling material (60% combustibles and 40% inert material), $T_{\text{ambient}} = 10^{\circ}\text{C}$. Left – after 5 years and 27 days; middle – after 5 years and 142 days; right – after 5 years and 248 days.

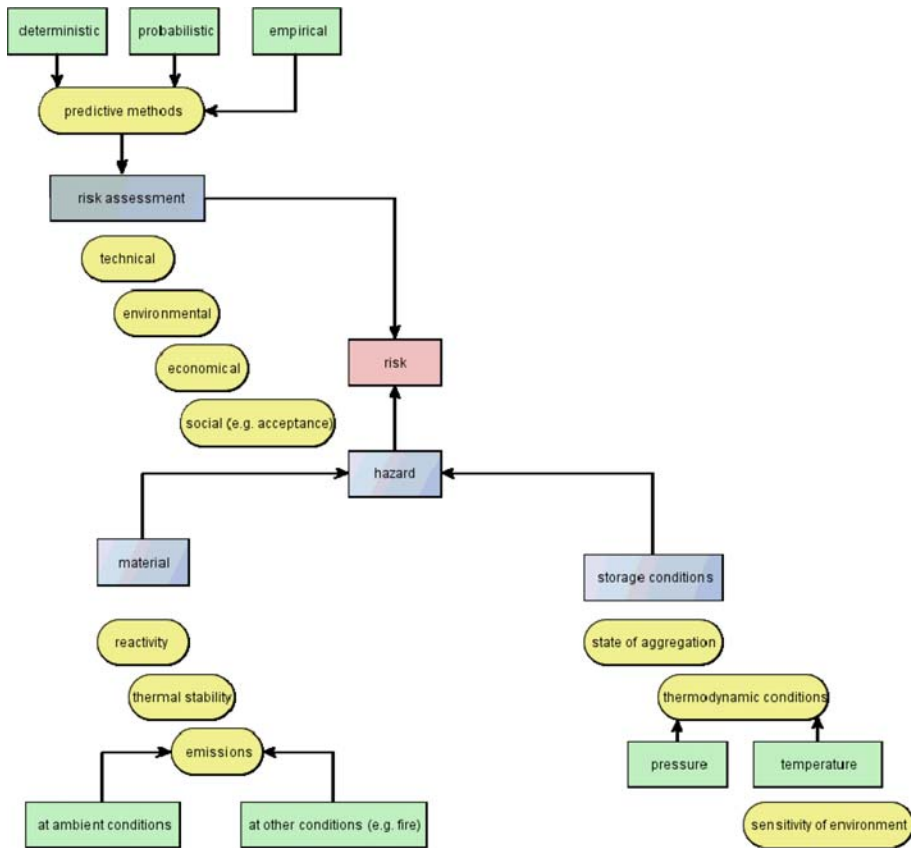


Figure 6. Structure of hazard evaluation and risk assessment for storage processes.

tents of such an approach are still under development and reported here as ‘work in progress’ without claiming completeness.

The essential components of such an approach are depicted in Figure 6. The hazards connected with storage processes may be dependent on the material and on the conditions of storage. Entities exposed to the hazard may be the operating companies themselves, the neighbouring community, the environment and e.g. in case of breakdown of infrastructure, even parts of the society.

Identification of the hazards together with calculating the effects leads to risk assessment. Calculations may be based either on deterministic, probabilistic and empirical methods as follows:

- Deterministic: prediction of possible effects of incidents (e.g. parameters of fire, explosion and dispersion scenarios).
- Probabilistic: prediction of the probability of occurrence of incidents or events leading to incidents.
- Empirical: estimation of the response of the society to hazards scenarios, estimation of what the accepted risk is.

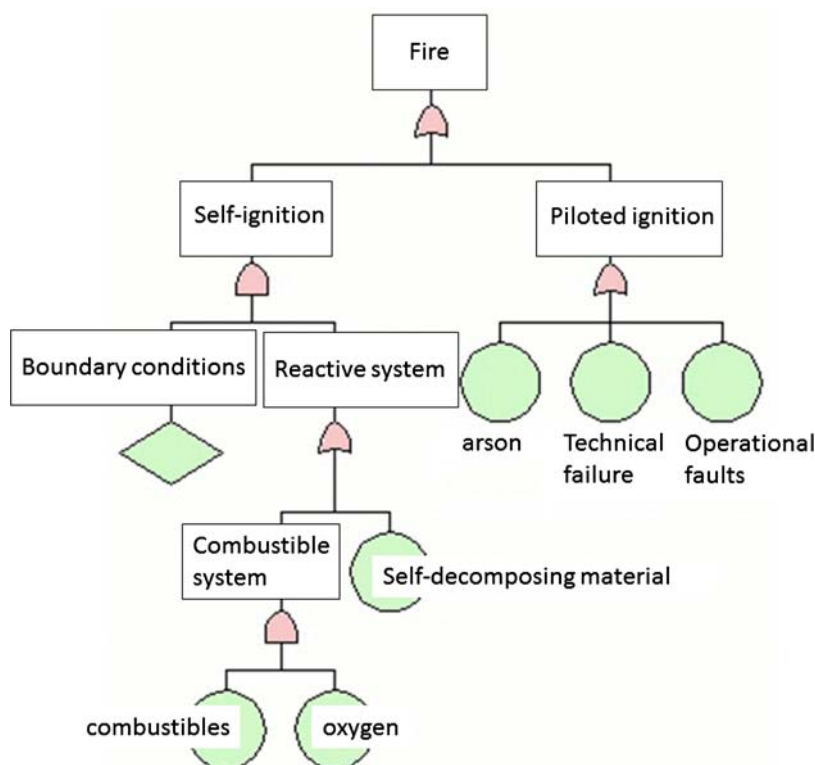


Figure 7. Qualitative fault tree for the analysis of the fire hazard in stored solid material.

Based on the hazard evaluation scheme in Figure 6, a fault tree is given as an example for the fire hazard of stored solid material. This fault tree could be applied to examples described in Section 2.

The outbreak of a fire is defined as the top event. Pre-conditions leading to this event are either self-ignition or piloted ignition. The basic events to trigger piloted ignition are connected to the presence of ignition sources. Such ignition sources may originate from technical failure or malfunction, e.g. of electric appliances or from operational faults, e.g. accessing the storage site with unprotected vehicles, improper execution of 'hot work', etc.

In order to trigger self-ignition besides the presence of a reactive system, favourable boundary conditions are necessary Figure 7. These conditions were described in detail in Section 2 and are not worked out further in the fault tree.

4. Conclusions

The main hazards in storage processes arise from the high energy density. If accidentally released, this may lead to excessive fires, explosions or accidental releases. In the case of fires, this is usually connected with excessive emissions of smoke which contain toxic or otherwise harmful components and this imposes a threat to people affected.

The effects of an accidental release depend first of all on the state of aggregation of the material stored. Accidental release of gases stored at high pressure leads to a pressure wave which at circumstances could even be amplified, if the release evolves into an explosion.

In the present article, a methodology has been described which allows to identify the technical hazards originating from the storage of large amounts of hazardous materials and the evolution of a fault tree for a specific hazard has been demonstrated.

However, in the present state, the analysis is still qualitative and safety measures to be taken would focus on eliminating the factors leading to the undesired event.

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