Hazard identification of dangerous goods

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Summary

For long, a lot of accidents related to goods transportation proved the need of hazards identification. International regulations are in existence for air, ground (road, rail), sea and waterways transportation.

For about 25 years, a committee of experts has been dealing at United Nations level on Transportation of Dangerous Goods (TDG) and recently (beginning 2001) extended its work to Globally Harmonized System of Classification and Labelling for Chemicals.

In this lecture, will be presented first some typical accidents occurred with different types of goods : explosives, flammable substances (sinking of Ievoli Sun transporting chemicals and Erika transporting oil), toxic and corrosive, unclassified goods (Channel Tunnel in 1995, Mont-Blanc and Tauern tunnels in 1999).

Then, a brief description of international regulations and of dangerous goods will be presented. Comments will be given on classification methods and procedures.

Emphasis will be paid on issues to be dealt with such as :

- the Globally Harmonized System of Classification and Labelling for Chemicals with the objective of avoidance of discrepancies between requirements for transportation, emergency response, storage, labelling...
- the classification of energetic materials
- the unclassified (but dangerous) substances
- the OECD approach of QRA for DG road transportation in tunnels.

1 Accidents related to goods transportation

The transportation of goods is linked with a lot of accidents with possible consequences on man, environment and equipment.

All types of transportation systems are involved and data are worldwide collected with the purpose of learning from experience. In ARIA databases (France), every year, about 140 accidents (on a total of 1.100 reported) are mentioned concerning the transportation of dangerous goods.

On a total of 805 transportation accidents included in this database, 67 % are road accidents, 2 % involved inland waterways and coastal transportation and 23 % rail transportation.

Road transportation is a field in which a large number of accidents occurred, the consequences being worst with explosive, flammable and toxic materials. In many instances, the toxic products were the consequences of a fire (toxic fumes).

1.1 Road transportation of flammable liquids

Some typical examples are related to the transportation of flammable liquids (fuel and gasoline). A brakeless lorry containing soap and liquid alcohol involved in an accident at the bottom of a steep hill induced 10 fatalities (Les Eparres, France, January 7th, 1993).

1.2 Road transportation of explosives

In rare occasions, explosive substances and articles are involved : a typical example is an accident on a highway on May 13th, 1993 at Etoile-sur-Rhône, France, in which 3 tons of pyrotechnic substances were involved. A fire and an explosion were triggered by a collision and the lorry driver was killed. Fortunately, this accident occurred during the night with a very sparse traffic.

Another example is the Walden Truck accident, occurred on August 5th, 1998 in Canada, in which a transport containing about 18 tons of explosives fired after a collision on the roadside and detonated. Fortunately, an area approximately 600 meters in both directions of this four-lane highway was vacated. Nobody was hurt by flyrocks and truck fragments (maximum thrown distance : about 2.5 km). The highway has been closed for a period of 11 days.

1.3 Accidents in road tunnels

The consequences of such types of accidents are worst when they arise in a tunnel. As regards strictly dangerous goods, only very few accidents are worldwide known. But it should be emphasized that the impact of tunnel transportation is low by relationship with the other parts of road systems.

Reported accidents involved carbon disulfide (Holland, USA, 1927), gasoline (Caldecott, USA, 1964), aerosol dispensers and paints, (Tauern, A, 1999). In the Mont-Blanc tunnel, in 2000, ordinary goods were involved such as margarine. In other accidents (Mont-Blanc in France, date unknown, Fréjus in France in 1980, Gothard in Switzerland in 1980, Billwerder Moorfleet in Germany in 1963, the plastic materials were involved in three cases and cotton balls in one case (Mont-Blanc).

1.4 Rail accident in tunnel

The only opportunity where dangerous goods were involved in rail tunnel is the accident in Summit tunnel in UK in 1984, after the derailment of a white spirit wagon. The initiated fire lasted 3 days. In the Channel tunnel, in 1984, only ordinary goods were involved at the beginning of a fire in a lorry embarked in the train (fats).

1.5 Rail accidents on plant premises and marshalling yards

On plant tracks and in marshalling yards, a lot of accidents are known. Only the following examples can be briefly explained.

At Aix-les-Bains station (France, 1992), a derailment of a train with three wagons containing dangerous goods (dimethylamine and ammonia) was at the origin of a release of the liquid dimethylamine. Buildings were evacuated within 400 m from the accident. The emergency situation lasted 4 days.

At La Voulte (France 1993) 20 wagons containing gasoline derailed. 3 tanks were ruptured and exploded. The fire propagated to houses and to a sewer system. A soil pollution on 26 ha was also induced.

1.5 Wreck of ships

The wreck of chemical or oil tankers is also frequently at the origin of sea and shore pollution. In 1999, the oil tanker Erika sank close to the South Brittany shores and, in 2000, the chemical tanker Ievoli Sun 30 kms ashore of Cotentin, France, with partial release of styrene and some local pollution of shellfish.

2. General background of regulations

In order to avoid or minimize the consequences of these accidents, regulations were developed (and are still under further development), respectively on :

- road transportation ADR, last version, restructured applicable as from July 1st, 2001 :
- rail transportation RID, last version restructured applicable as from July 1st, 2001
- sea transportation IMDG, Code, edition 2000, IMO, London, 2001
- air transportation IATA, 42nd edition, 2001
- inland waterways ADNR, edition 1999.

In these regulations, requirements are given for the training of persons involved in the carriage and safety obligations of the participants. As regards safety obligations, appropriate measures shall be taken according to the nature and the extent of foreseeable hazards, so as to avoid damage or injury and, if necessary, to minimize their effects. When there is an immediate risk that public safety may be jeopardized, the participants shall immediately notify the emergency services and shall make available to them the information they require to take action.

2.1. Classes of dangerous goods

Class 1 : explosive substances and articles
Class 2 : gases
Class 3 : flammable liquids
Class 4.1 : flammable solids, self reactive substances and solid desensitized explosives
Class 4.2 : substances liable to spontaneous combustion
Class 4.3 : substances which, in contact with water, emit flammable gases
Class 5.1 : oxidizing substances
Class 5.2 : organic peroxides
Class 6.1 : toxic substances
Class 6.2 : infectious substances
Class 7 : radioactive materials
Class 8 : corrosive substances
Class 9 : miscellaneous dangerous substances and articles.

2.2. Principles of classification

For the majority of classes, the assignment is made in accordance with defined tests, procedures and criteria (see "UN Manual of tests and criteria").

Limitative classes :

- classes 1, 7 and partially 4.1 (self reactive substances) and 5.2 (organic peroxides)

Non limitative classes include remaining classes, and generally include tests, procedures and criteria.

More explanations about the criteria for classification can be found in table 1.

Table 1 : classes of dangerous goods

Class	Substance	Limitative class	Main criteria for classification
1	explosive substances and articles	yes	explosive properties
2	gases	no	critical temperature < 50°C or vapor pressure at 50°C < 3 bar
3	flammable liquids	no	boiling point flash point
4.1	flammable solids, self reactive substances and solid desensitized explosives	partially	exothermal reaction, bulk combustion
4.2	substances liable to spontaneous combustion	no	self ignition
4.3	substances which, in contact with water, emit flammable gases	no	water action
5.1	oxidizing substances	no	burning velocity
5.2	organic peroxides	partially	decomposition temperature
6.1	toxic substances	no	inhalation, ingestion, action on skin or mucous membranes
6.2	infectious substances	no	no
7	radioactive materials	yes	
8	corrosive substances	no	action on skin or mucous membrane
9	miscellaneous dangerous substances and articles	no	see below

The heading of Class 9 covers substances and articles which, during carriage, present a danger not covered by the heading of other classes.

The substances and articles of Class 9 are subdivided as follows :

M1 : substances which, on inhalation as fine dust, may endanger health
M2 : substances and apparatus which, in the event of fire, may form dioxins
M3 : substances evolving flammable vapor
M4 : lithium batteries
M5 : life-saving appliances
M6-M8 : environmentally hazardous substances :

- M6 : pollutant to the aquatic environment, liquid
- M7 : pollutant to the aquatic environment, solid
- M8 : genetically modified micro-organisms and organisms

M9-M1 : elevated temperature substances :

- M9 : liquid
- M10 : solid

M11 : other substances presenting a danger during carriage, but not meeting the definitions of another class.

2.3. Packing groups

The requirements are different according to the various classes.

The packing is a maximum volume of 450 l or can contain a maximum amount of 400 kg.

There is a testing and approval procedure dealing with drop test, tightness, internal pressure, storage and specific tests.

As regards the packaging, the compatibility between material and goods shall be examined.

3. Issues to be dealt with

For about ten years, strong efforts were devoted to harmonization of classification and labelling of chemicals. Considerations were also paid to more relevant methods for characterization of energetic materials and still unclassified substances. Another important international work (OECD, UE DG Environment) concerned the DG transportation in road tunnel considering a QRA approach.

3.1. The Globally Harmonized System of Classification and Labelling for Chemicals

Since 1992, the work on the Globally Harmonized System of Classification and Labelling for Chemicals (GHS) has been carried out by the International Labour Office, the Organisation for Economic Co-operation and Development and the UN Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling for Chemicals. Two sub-committees are involved :

- the sub-committee of experts on TDF
- the sub-committee of GHS.

The sub-committee of GHS had been created to keep the GHS up-to-date and to promote its effective implementation.

A first GHS guiding document should be finalized by July 2002 : the draft document will be ready for discussion in December 2001.

The GHS will be taking into account the classification criteria for :

- physical hazards : about the physical hazards, the work is completed except for criteria for the flammability of aerosols. The criteria proposed are :
  - definition of gases, liquids and solids
  - test conditions
  - flammability (solids, liquids and gases)
  - reactivity (pyrophoric substances, self-heating substances, substances which, in contact with water, emit flammable gases, oxidizing substances, organic peroxides, self reactive substances, explosives and substances that are corrosive to metals)
  - compressed gases

- health hazards

- hazards to the environment : the Globally Harmonized System of Classification and Labelling for Chemicals covers the nine hazard endpoints considered in existing classification systems : hazards to the aquatic environment, acute toxicity, skin irritation/corrosion, sensitisation, germ cell mutagenicity, carcinogenicity, reproductive toxicity and target organ toxicity. In addition, this system will also include the following hazards not yet covered by existing systems : neurotoxic effects, immunotoxic and effects hazardous to the terrestrial environment.

3.2. Classification of energetic materials

Energetic materials are those materials with a high or medium energy content typically greater than 800 J/g. They comprise explosives in Class 1, desensitized explosives in Classes 3 and 4.1, selfreactives in Class 4.1, organic peroxides in Class 5.2 and a lot of substances allocated to different Classes for various reasons, e.g. :

- nitromethane as a flammable liquid – Class 3
- ammonium nitrate as an oxidizer – Class 5.1
- nitrocompounds as toxic substances – Class 6.1.

So there is no unified scheme for classifying energetic materials even for transport. Moreover the GHS exercise for physical hazards demonstrated recently how important are the difficulties for merging systems dedicated to different purposes : UN for transport, EC for labelling chemicals, OSHA in US, etc.

Finally the best approach is to concentrate on properties, like detonability, deflagrability, behaviour in heating under confinement, thermal stability, sensitiveness to mechanical stimuli, for identifying properly the hazards and to adapt as far as possible the conditions of transport, storage, handling accordingly.

As an example, the transport of nitromethane authorized in tanks in the past has been forbidden after a severe rail accident in USA resulting in a mass explosion due to a cavitation process after impact.

Because of the actual situation which is not really satisfactory, the trend is to push to refound the UN classification system for energetic materials, creating a new Class for these materials beside the Class 1 for explosives. It will provide the opportunity to have unified classification procedures and methods and will allow industry to reduce the explosion hazard by dilution or by other means. Nevertheless attention is to be paid to such a process as addition of diluants may emphasize thermal effects in a case of extended fire.

3.3. Unclassified (but dangerous) substances in tunnel

Further to a recommendation following the enquiry on the Mont-Blanc tunnel accident, some liquid substances or substances to be easily liquefied, solid substances with heat of combustion similar to hydrocarbons should be studied for a possible classification in the road transportation legislation.

About one hundred products (oil, fats, polymers, animal or natural fats) having a high heat of combustion can be taken into consideration for such transportation and can burn. When a fire is induced in the vicinity, these material melt and can flow with a possibility of developing a pool fire.

It means that the following characteristics shall be determined :

- heat of combustion and burning rate
- formation of thick and opaque fumes with soot and toxic substances production
- interaction with the packing.

For these substances, possible regulations (in France and abroad) are still under discussion, considering either classification in class 9 or prohibition of transportation in tunnel or possible transportation without classification when tunnels are adequately designed as regards the development of such fires, or grouping as proposed by OECD/AICPR.

3.4. QRA and decision making for DG road transportation

OECD developed a research program for defining a quantitative risk assessment for the transportation of dangerous goods in road tunnel. This program gave input data for a decision making system and helped for defining practical measures for minimizing the risks. All this work was funded both by OECD and European Union (DG VII). INERIS (France), W.S.Atkins (UK) and University of Waterloo (Canada) were involved in the QRA research.

The final objective of this QRA model is the production of quantitative data on DG transportation risk levels on various routes, some of which being tunnels.

The risk is characterized by the probability of occurrence and the severity (as a number of fatalities or injuries, damages to buildings and structures or environment). F/N curves qualifying the societal risk (annual frequency F to get an accident in which more than N people are killed) were defined ; individual risks are also determined considering the frequency for permanent populations. Damages to structures are semi-quantitatively defined and damage to environment are only qualitative.

A lot of simplifications were introduced in the model in which a limited number of relevant scenarios (ten) are included.

Two lorry fires scenarios (not considering DG) are also included because of the very severe risk (Mont-Blanc and Tauern accidents in 1999) in tunnel. Such scenarios are really more frequent than those implying dangerous goods.

Some ventilation configurations and the safety measures adopted (traffic control, flammable liquid drainage, monitoring system) have been studied to examine their influence on the F/N curves.

At the end of the work programme, the QRA model was produced as a software tool, available in a CD-ROM and includes a user guide and specialized guidance documents.