

The transportation of water reactive substances through road tunnels equipped with sprinkler system: A literature review

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Co-financed by the European Union
Trans-European Transport Network (TEN-T)

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Abstract

Dangerous goods transportation and consequently the amount of dangerous goods incidents are increasing. Another increasing trend is to install sprinkler systems in tunnels. This is a literature review concerning risks with water reactive substances transported through road tunnels equipped with sprinkler systems. The knowledge concerning the risks from dangerous goods and water application in tunnels is limited. Several water reactive chemicals have been identified. As they commonly are transported in liquid form, a liquid pool will be formed upon release. In most cases the pool will react exothermically with ground water, water from the substrate and in several cases water from the atmosphere. Thus, further application of water may actually improve the situation. Further and larger studies are needed to attain a better picture of the risks and benefits when transporting water-reactive DG through road tunnels, taking into consideration the risk of alternative routes.

Key words: water reactive substances; dangerous goods transportation; road tunnel fire safety; sprinkler

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SP Report 2014:37
ISBN 978-91-87461-79-8
ISSN 0284-5172
Borås 2014

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Preface

The Stockholm bypass project was granted co-funding for research, from the European Union (EU) through the Trans-European Transport Network (TEN-T). The literature review presented in this report were performed within the frame of this EU project.

In Sweden the construction of tunnels is increasing. Several are constructed to by-pass a large amount of traffic from the city centre and they have the requirement to allow dangerous goods transportation. For fire safety reasons they are equipped with sprinkler systems. Therefore the combination of dangerous goods release and sprinkler activation cannot be ignored. Consequently this pre-study was financed by the Swedish Transport Administration, who is greatly acknowledged.

The sole responsibility of this publication lies with the authors. The European Union is not responsible for any use that may be made of the information contained therein.

1 Introduction

In Sweden tunnels are increasingly being equipped with deluge sprinkler systems to limit the consequences from fire. The installation of sprinkler systems in tunnels is not new and several tunnels in Sweden and worldwide are equipped with sprinkler systems. Although this study is due to a concern that this could potentially worsen situations due to substances that react with water, a tunnel in Gothenburg, called Gnistångstunneln, was recently equipped with a deluge sprinkler system to allow for the transportation of dangerous goods through the tunnel.

Derived from a 1957 United Nations treaty that governs transnational transport of hazardous materials, the main governing regulation concerning the International Carriage of Dangerous Goods by Road is called ADR or ADR-S in Sweden. OECD and PIARC have done some work on the issue of dangerous goods transportation in tunnels, e.g. (OECD/PIARC 2001).

This is a review of dangerous goods transport through tunnels and the potential effect from reaction with a deluge sprinkler system in case of an accident. There is some literature about dangerous goods transport in general, and quite some literature on dangerous goods transport through road tunnels, however, no literature at all could be found that deals with dangerous goods transport in tunnels that treat the event of dangerous goods release and sprinkler system activation. Therefore this review aims to bring the following four areas together:

1. Dangerous goods transport in road tunnels
2. Dangerous goods accidental statistics
3. Dangerous goods that react with water
4. Dangerous goods classification

According to Åke Persson who works at Svenska Brandskyddsföreningen (SBF) as an advisor on flammable substances, there is little research and expertise in Sweden on the topic of dangerous goods. There is more expertise to be found in other countries such as Germany, Holland and France on this topic. There are around 50 000 chemicals and among these about 5000 are classified according to the new EU directive REACH. SBF offer a resource with information concerning the most common materials that are transported in Sweden. Unfortunately it has not been updated in a few years. It contains the most commonly used dangerous goods substances in Sweden and amount to almost 1000 substances.

Purdy (1993) presents a thorough presentation of risk analysis for dangerous goods on road and rail. Unfortunately tunnels are excluded as they only constitute a minor section of the road network. PIARC and OECD (2001) have developed a risk analysis model for transport of dangerous goods through road tunnels. However, the issue of sprinkler activation and potential negative reactions is not included. Although several earlier studies on dangerous goods have focused on individual risk calculations, Purdy believe societal risk is the measure of most interest as societies strive to avoid disasters.

There are at least two important risk parameters when applying water on dangerous goods (DG). First of all, extinguishing water will in many cases become highly toxic for humans, plants and animals and should be collected. Secondly, substances may react with water and cause flammable, explosive or toxic substances. This review mainly focuses on the second issue, the potential negative reaction with water. Note that many dangerous goods substances will be highly toxic also without further reactions with water, that water is available in air, substrate and ground, and that a release or fire in the open may occur during rainfall.

2 Dangerous goods accidents statistics during transportation

If risk is defined as the product of likelihood and consequences, as is often done (Kaplan 1992; Kaplan and Garrick 1981), the risk from dangerous goods (including fire and explosion) is smaller than the risk of regular fire or traffic accident. The expected loss of life from dangerous goods accidents was, according to a Norwegian study, less than 2% of the expected loss of life from normal traffic accidents (Lille and Andersen 1996). In Europe about 2 vehicle fires occur per 100 million vehicle km. According to Norwegian statistics, tunnels are at least as safe as or safer than similar roads in the open air. Injuries or fatalities results from traffic accidents rather than from fires (Nævestad and Meyer 2014). However, due to their catastrophic potential fires and dangerous goods deserve attention (Lille and Andersen 1996; Nævestad and Meyer 2014).

In a OECD/PIARC (2001) report on dangerous goods transport through road tunnels, only fires are identified as a consequence when previous accidents are reviewed. Four fires involved gasoline and the majority involved ordinary goods. This confirms that the likelihood of a toxic release or explosion in a tunnel is indeed very low.

A survey published in 1997 over fire accidents in process plants and transportation of hazardous materials up to the end of 1993 found that 41 % of all accidents involved fire. These fire accidents occurred in process plants (28%), during transportation (27%), in storage plants (21%) and during loading/unloading (7%). Most often, in 90%, a fluid was involved (liquid 53%, pressurized gas 17% or gas 14%). In 40% of the fires an explosion was also involved and in 41 out of 2745 cases a BLEVE occurred (Planas-Cuchi et al. 1997). From the same database the number of total accidents (5325) up to 1992 where analysed. Then 39% of all accidents occurred during transportation (Vílchez et al. 1995).

In a survey by (Oggero et al. 2006) 1932 accidents during the transport of hazardous substances by road and rail from the beginning of the 20th century were investigated. The survey indicates that the accident frequency is increasing over time. The most frequent accidents were release (78%) followed by fire (28%), explosion (14%) and gas clouds (6%). 63% of the accidents occurred on roads. Most accidents (75%) were caused by collision between vehicles. More than half of the incidents did not lead to any fatalities. 3% or 13 accidents took place in tunnels among which five were in road tunnels. Among these four were caused by road accidents.

A Chinese survey on hazardous material accidents during road transport by (Yang et al. 2010) for the period 2000-2008 included 322 accidents. The most frequent type of accident was release (85%) followed by gas clouds (13%) fires (10%) and explosions (6%). The survey suggests that, due to better safety measures, the amount of accidents and consequently fires and explosions are currently decreasing. 61 % of the accidents were caused by driver error, 31% by equipment failure and 20% by management factors.

The category of water reactive chemicals is widely used in the process industries and takes part in recent accidents, e.g. 889 incidents among which 54 were categorized as hazardous during the period 1990-2000 in the USA. The following water reactive chemicals has been identified as significant for major hazards (Kapias et al. 2001):

- Inorganic acid halides, e.g. POX_3 , SOX_2
- Organic halides, e.g. CH_3COX
- Sulphonic acids, e.g. HSO_3X
- Halides of non-metals, e.g. PX_3
- A number of silanes, e.g. HX_3Si
- Non-metal oxides, e.g. SO_3 and oleum
- Anhydrous metal halides, e.g. AlX_3
- Radioactive materials, e.g. UF_6

3 The behaviour of water reactive substances upon release

Kapias et al have developed models that account for chemical reactions and changing composition during spill of water reactive chemicals (Kapias and Griffiths 1998b, a; Kapias et al. 2001). First Kapias and Griffiths (1998b, a) studied Oleum and SO_3 which are aggressive materials widely used in the process industries. As they are usually stored and transported in liquid form, when spilled onto the ground, these chemicals create pools that can evaporate, boil or solidify depending on several conditions. The main feature of the pool behaviour is the violent exothermic reaction with water. The most important parameter that governs the behaviour of the pool is the amount of water available for reaction. Water may come from the ground, built structures, e.g. concrete, or from the atmosphere. SO_3 vapour reacts with atmospheric moisture producing H_2SO_4 which further reacts with water in the atmosphere yielding H_2SO_4 aerosol. The dispersion behaviour of such a cloud is complicated by the fact that it may be denser than air. The main water source is from free water lying on the ground. Atmospheric water is also a significant water source and it becomes dominant when the availability of water on the ground is poor.

Later a generic model for the pool behaviour of water reactive chemicals was developed. Similarly to the previously mentioned model, most substances are transported in liquid form and consequently spillage will create a liquid pool. The pool will react with any water in the ground, extract water from the substrate, or absorb atmospheric moisture. It may also react with compounds in the substrate. The reaction with water is usually highly exothermic, providing the pool with energy, raising the temperature and thus increasing the vapour evolution rate. Depending on the pool temperature and the boiling and freezing points of the liquid it may boil, evaporate or solidify. Products formed in reactions may be released as a gas or be soluble or insoluble in the pool. In all cases water reactive chemicals will encounter free ground water and will extract substrate water. Most will also absorb atmospheric moisture. If water is in excess the mass of water that reacts will be equal to the amount required to consume all the available water reactive chemical. In Kapias et al. (2001) and subsequent publications more details on the modelling of water reactive chemicals can be found. Model results indicate that the pool behaviour is principally affected by the way that the reaction of the chemical with water occurs, and by the amount of water available for reaction. Surface roughness and wind speed also have significant effects (Kapias et al. 2001).

4 Dangerous goods classification

According to Kapias et al (2001), all chemicals that react violently with water or release toxic gas in contact with water are included in international legislation on major hazards. All DG is classified in ADR (2013) in classes as follows:

Table 1 Classification of dangerous goods

Class	Description
1	Explosives
2	Gases
3	Flammable liquids
4.1	Flammable solids and self-reactive substances
4.2	Substances liable to spontaneous combustion
4.3	Substances that emit flammable gases in contact with water
5.1	Oxidising substances
5.2	Organic peroxides
6.1	Toxic substances
6.2	Infectious substances
7	Radioactive material
8	Corrosive substances
9	Miscellaneous dangerous substances

Of these, class 4.3 is of particular interest for this report as it concerns substances for which the application of water can cause flammable gases and explosions. Note however, that several other substances react with water and cause toxic or corrosive substances which are not flammable. Class 4.3 is further classified as follows:

Table 2 Further classification of class 4.3, substances that emit flammable gases in contact with water

Class	Type of substances that emit flammable gases from contact with water
W	Flammable gases without secondary danger
WF1	Flammable liquids
WF2	Flammable solids
WS	Solids that may self-ignite
WO	Oxidising solids
WT	Toxic
WC	Corrosive
WFC	Flammable and corrosive

All substances are further classified according to unique UN and CAS numbers. The UN number can be found on the dangerous goods sign on bulk carriers.

SBF have listed the most common dangerous substances that are used in Sweden and give advice in the event of release or fire for each listed substance¹. In particular 14 water reactive substances are identified. Among these only three belong to class 4.3. Four belong to class 4.2. Seven other classes are represented. Note that for some of these substances, e.g. UN1942, unmanned application of water is the recommended extinguishing method, which makes extinguishment with a deluge sprinkler system ideal. For others, e.g. UN 1402, water must not be applied.

¹ An online database is provided by Svenska Brandskyddsföreningen (SBF), see <http://www.brandskyddsforeningen.se/>

Another classification useful to distinguish dangerous material that react with water is Annex III and IV in (EEC 1967) were risk phrases (R) and safety advice (S) were specified to account for various aspects of dangerous substances. In particular the following are of interest (Cozzani et al. 1998; Kapias et al. 2001; EEC 1967):

Table 3 Risk phrases and safety advice for dangerous materials that react with water.

R 14	Reacts violently with water
R 15	Contact with water liberates extremely flammable gases
R 29	Contact with water liberates toxic gas
S 24	Never add water to this product
S 103	In case of fire, use appropriate equipment. Never use water.

ADR defines five tunnel categories concerning the transportation of dangerous goods through tunnels, see table below.

Table 4 Tunnel classification for the transportation of dangerous goods (ADR-S 2013).

Class	Restrictions
A	None
B	DG that can lead to large explosions
C	DG that can lead to large explosion or toxic release
D	DG that can lead to explosion, large fire or toxic release
E	All DG above 8 tonnage, except a few exceptions

For each tunnel class, ADR defines which classes of substances are allowed. As can be seen the current tunnel classification is not precise enough to exclude substances that react with water. Probably a set of UN numbers would have to be produced covering the substances that must not be transported through tunnels, if there are such substances.

5 Discussion

Based on Table 2, it seems that class 4.3-W would not lead to increased risk from the application of water as this already is a flammable gas. Several other classes may also benefit from the application of water despite that they react, e.g. solids that self-ignite which may cause a devastating fire without the application of water. Looking at the sheets from SBF more specific guidance can be found on how to deal with certain substances that react with water. Among these substances the application of water should be avoided for UN 1717, UN 1397 and UN 1402. For other substances that react with water, it is difficult to judge whether water will worsen the situation or not, there may already be an explosive or toxic environment and the application of water may cause less dangerous conditions. In particular, although reactive with water, UN 2249, UN 1045 and UN 2203 may lead to an improved situation with the application of water if there already is a fire.

It is noted that the deluge sprinkler situation is similar to heavy rainfall. To our knowledge all DG is allowed in heavy rainfall. This is an argument for allowing DG and sprinklers. A risk analysis can evaluate whether alternative routes are better than routes containing tunnels with deluge sprinkler systems, taking into consideration the likelihood of rainfall. It may be that the risk of release and rainfall is larger than the risk of release and fire inside the tunnel. One exception could be substances that result in an exothermic reaction with water. If enough water is found in the air and surrounding structure to cause enough heat to activate the sprinkler the reaction would further intensify. Although the amount of water is important, the excess water will not react and will instead cool the exothermic reaction.

From a tactical point-of-view there are a few key parameters that determine the optimal path of action for given substances, e.g.:

- What substance is it?
- Is there a release?
- Is there a fire?
- What can happen if water is applied?
- What can happen if the fire is not extinguished or suppressed?

The answer to these questions would hopefully give the best course of action, e.g. to apply water for cooling in case of a fire but no release.

It seems that no suitable tunnel classification exist that would exclude water reactive chemicals. In the ADR classification system the risk phrase and safety advice seems to be the best classifier for identifying water reactive chemicals and the best course of action. A sixth tunnel class could be created containing all dangerous goods for which water, under no circumstances should be applied. Then these could be prohibited for tunnels with sprinkler systems. Although it must be proven that the alternative route is safer for these chemicals, taking into consideration the potential release during rainfall.

6 Conclusions

The knowledge concerning the risks from dangerous goods and water application in tunnels is limited. Further and larger studies are needed to attain a better picture of the risks and benefits when transporting water-reactive DG through road tunnels, taking into consideration the risk of alternative routes.

Several water reactive chemicals have been identified. As they commonly are transported in liquid form liquid pool will be formed upon release. In most cases the pool will react exothermically with ground water, water from the substrate and in several cases water from the atmosphere. It is difficult to judge whether further application of water would improve or worsen the situation. One could expect though that water-reactive chemicals will find plenty of water in tunnel environments so that further application of water from a sprinkler system will mainly cool any exothermic reactions including fire. This is unlikely a worse situation than a release on roads above ground, why this may be an issue of minor relevance, given that these substances are allowed for road transportation.

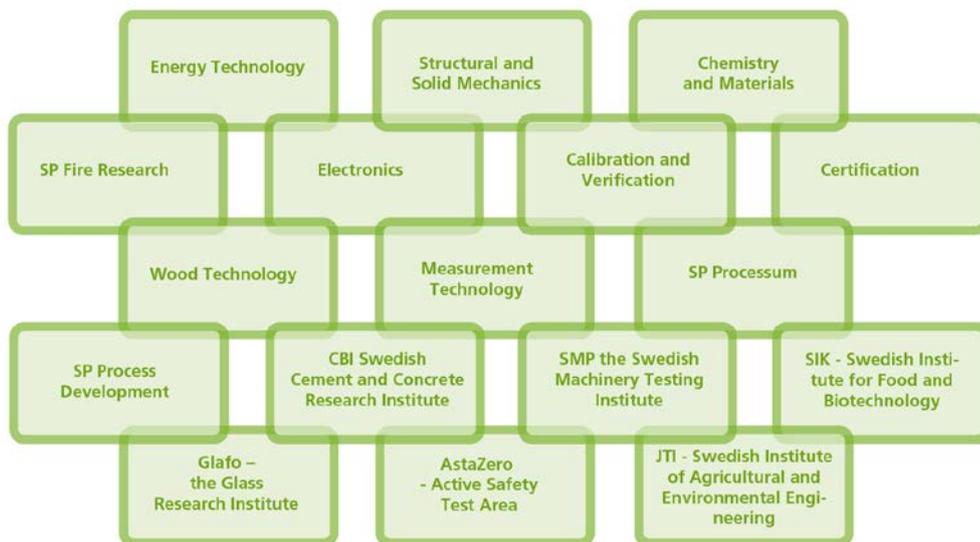
The most suitable classification for identifying water reactive chemicals is the risk phrases R 14, R 15, and R 29 and, more specifically, for identifying the cases when water must not be applied, safety advice S 24 and S 103.

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Fire Research

SP Report 2014:37

ISBN 978-91-87461-79-8

ISSN 0284-5172

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