Final report Annex 5: Guidance on how to consider additional elements (Task 5)

Development of an assessment methodology under Article 4 of Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances (070307/2013/655473/ENV.C3)

Report for the European Commission (DG Environment)

AMEC Environment & Infrastructure UK Limited

In association with INERIS and EU-VRi

December 2014

Document Revisions

No.	Details	Date
1	Preliminary version of intermediate report chapter for DG ENV comment	27 March 2014
2	Intermediate report	12 May 2014
3	Intermediate report (revised)	21 July 2014
4	Intermediate report (revised)	11Sept 2014
5	Draft final report	18 Nov 2014
6	Final report	12 Dec 2014

amec

Proposal for

European Commission, DG Environment
Directorate C – Sustainable Resources Management, Industry and Air
Unit ENV C.3 – Industrial emissions, air quality and noise
Brussels B-1049
Belgium

Main Contributors

Christophe Bolvin (INERIS)
Anabel Lahoz (INERIS)
Marion Demeestere (INERIS)

Issued by

....
Victoria Cherrier

Approved by

....
Caspar Corden

AMEC Environment & Infrastructure UK Limited

17 Angel Gate, City Road, London EC1V 2SH,
United Kingdom
Tel +44 (0) 207 843 1400
Fax +44 (0) 207 843 1410

Doc Reg No. 34075CA015i6

h:\projects\34075 pp seveso article 4 guidance\c client\reports\final report\34075ca015i6 task 5 final report 20141212.docx

European Commission (DG Environment)

Development of an assessment methodology under Article 4 of Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances

Final report – Annex 5

AMEC Environment & Infrastructure UK Limited

December 2014

This document has been produced by AMEC Environment & Infrastructure UK Limited in full compliance with the management systems, which have been certified to ISO 9001, ISO 14001 and OHSAS 18001 by LRQA.

In accordance with an environmentally responsible approach, this document is printed on recycled paper produced from 100% post-consumer waste, or on ECF (elemental chlorine free) paper

List of Abbreviations

ADAM	Accident Damage Assessment Module
ADR	European Agreement Concerning The International Carriage Of Dangerous Goods By Road
ALARP	As Low As Reasonably Practicable
ARIA	Analysis, Research and Information about Accidents
ATEX	Explosive Atmosphere
BLEVE	Boiling Liquid Expanding Vapour Explosion
BOD – COD	Biochemical Oxygen Demand – Chemical Oxygen Demand
CE	Critical Event
CFD	Computational Fluid Dynamics
CLP	Classification Labelling Packaging
COMAH	Control Of Major Accident Hazards
DA	Deterministic Approach
ECHA	European Chemicals Agency
e-MARS	Major Accident Reporting System
EU	European Union
EWGLUP	European Working Group on Land Use Planning
F&EI	Fire & Explosion Index
GHS	Globally Harmonised System
JRC	Joint Research Centre
LPG	Liquefied Petroleum Gas
LUP	Land-Use Planning
MAHB	Major Accident Hazard Bureau
MATTE	Major Accident To The Environment
M_F	Material Factor of the Dow's Fire & Explosion Index
MIMAH	Methodology for Identification of Major Accident Hazards
NFPA	National Fire Protection Agency
NOEC	No Observable Adverse Effects Concentration
PA	Probabilistic Approach
PLG	Pressurised Liquefied Gas

RID	European Agreement Concerning the International Carriage of Dangerous Goods by Rail
RMP	Risk Management Plan
STOT-SE	Specific Target Organ Toxicity (Single Exposure)
USEPA	United States Environmental Protection Agency
UVCE	Unconfined Vapour Cloud Explosion

Physicochemical parameters

BCF	Bioconcentration Factor
EC_{50}	Median Effective Concentration
ΔH_r	Standard enthalpy of reaction
K_{st} / K_g	Maximum rate of explosion pressure rise for dust clouds/gas
LD_{50} / LC_{50}	Median Lethal Dose / Median Lethal Concentration
LFL / LEL	Lower Flammability Limit / Lower Explosion Limit
LOC	Limiting Oxygen Concentration
MIE	Minimum Ignition Energy
MTSR	Maximum Temperature of the Reaction Synthesis
NOEC	No Observed Effect Concentration
P_{max}	Maximum explosion pressure
P_{vap}	Vapour pressure
ΔT_{ad}	Adiabatic temperature rise
T_{eb}	Boiling point
TMR_{ad}	Time to maximum rate in adiabatic condition
UFL / UEL	Upper Flammability Limit / Upper Explosion Limit

Contents

1. Introduction

1.1 Purpose of this report

This report constitutes one of the outputs of a contract with the European Commission on the "development of an assessment methodology under Article 4 of Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances". The work has been undertaken by AMEC, INERIS and EU-VRi.

The present report concerns one of a number of specific tasks under the project. It should not be read in isolation, but in conjunction with the main report and in conjunction with the reports concerning the other project tasks.

1.2 Scope of Task 5

The aim of Task 5 is to provide 'guidance on how to consider additional elements which are not normally considered in consequence assessment models'.

Some additional elements mentioned in Article 4 of the Seveso III Directive are to be considered in addition of earlier steps (i.e. physical properties, identification of worst case scenarios and modelling). These elements are the containment of the dangerous substance and the generic packing.

Many different operating conditions can occur:

- The substance may be contained in different types of packaging: more or less resistant to specific conditions.
- Two establishments may use the substance under assessment in different physical forms: solid, liquid or gaseous form. The containment of the substance may therefore be different and the storage may have different temperature and pressure conditions.
- Two establishments may store the same substance in various locations and use segregation to diminish the risk of a major accident hazard.
- The substance may be contained in different packing forms: bulk versus packaged form, and the quantity stored by storage unit can be different.

These additional elements may have an impact on the accident scenarios to be considered. In other words, the additional elements may influence the worst case scenario by modifying the source term used in the modelling: quantities involved, release rate, etc. As a result, the consequences of the potential accident could be different according to whether the substance is stored in small packages or in large storage tanks because of the quantity involved for instance.

It should be noted that these factors (containment, packaging, etc.) will be relevant in the context of Article 4 only where they apply mandatorily across the EU, because exclusions from the scope of Seveso III under Article 4 are understood to be non-site-specific.

The purpose of this report is to study the influence of these additional elements in the context of Article 4.

1.3 Structure of this report

Following this introduction, Section 2 provides information regarding the types of containment. Section 3 introduces the notion of segregation of storage that is sometimes used in site-specific safety reports. Section 4 provides some extracts of transport regulations in which the question of packing is dealt with, especially when it is about limiting the quantities packed or stored. Finally, Section 5 draws together some conclusions on the use of these additional elements in the context of Article 4 of the Seveso III Directive.

2. Types of Containment

2.1 About containment

A substance can be contained in many ways, such as a vessel shell, a pipe and many others. A loss of this containment usually results in a release of the substance into the environment. If hazardous properties are associated with this substance, an accident can occur.

In order to prevent a loss of containment and a release of the substance into the environment, EU regulations and guidelines exist. As an example, the Industrial Emissions Directive sets out the main principles for the permitting and control of installations, including storage. It is based on the application of the Best Available Techniques (BAT) included in the BREF document “Emissions from storage” published by the European Commission in July 2006.

This BREF document describes the techniques to be applied in the storage, transfer and handling of liquids, liquefied gases and solids, and the BAT to apply in order to prevent a release in the environment, such as:

- Safety and risk management;
- Construction and ventilation;
- Segregation and separation policies;
- Containment of leakage and contaminated extinguishant;
- Fire protection and fire-fighting equipment.

All these techniques consist of safety measures to limit the occurrences of a loss of containment and an accidental release. They aim at making the risk as low as possible, but cannot make it impossible. In the scope of Article 4 of Seveso, a worst case scenario is to be considered and the methodology assumes that loss of containment, if possible, occurs. For this reason, the BREF documents may not be directly relevant in the context of the assessment methodology.

However, if the containment may not prevent an accident from occurring, it can be an important parameter to consider in the definition of the worst case scenario, as described in Task 4.

2.2 Containment and substance properties

As introduced in the Task 1 report, it is very important to check:

- How the substance is used,
- Where the substance is used, and

- Under what conditions the substance is used.

Most of the physicochemical properties of a substance depend on the conditions of pressure and temperature under which the substance is contained/ used. As a result, the nature of the containment can have an influence on the substance's behaviour.

The same substance can be contained in different conditions of temperature and pressure. As an example, liquid ammonia can be stored in three different ways, as illustrated in the table below (Table 2.1).

Table 2.1 Different types of containment for ammonia

Storage of liquid ammonia	Temperature (°C)	Pressure (bar)	Capacity of the storage
Cryogenic storage	- 33	1	> 5000 tonnes
Refrigerated storage	0	4	Between 200 and 3000 tonnes
Atmospheric storage	20	9	< 800 tonnes

Hydrogen can also be contained in different ways (Table 2.2).

Table 2.2 Storage conditions for hydrogen

Physical form	Conditions of storage
Liquid form	Hydrogen is stored at -250°C (below its boiling temperature).
Gas form	Hydrogen can be stored in a vessel, at a pressure from 10 to 900 bar.
Solid form	Metal hydrides include magnesium hydride, lithium hydride, and several others. They can be used to reversibly bind hydrogen gas for storage at ambient temperature and pressure. Hydrogen stored by these mechanisms has a good energy density by volume but still has a lower energy density by weight than leading hydrocarbon fuels.

These two examples show that the nature of the containment may have a strong influence on the accident scenario: if a release occurs, the behaviour of ammonia in cryogenic tank will differ from an atmospheric pressure tank. Hydrogen stored in solid form will only be released if it makes contact with water.

Therefore, in the context of Article 4, it may be relevant to associate a substance with a type of containment, as the definition of the worst case scenario described in Task 4 depends on its parameters, in particular temperature and pressure conditions. But once again, the type of containment will not directly eliminate the possibility that a major accident may occur.

3. Location and Segregation of Storage

Regarding storage of hazardous substances, it is known that the location and segregation of the stored quantities may be used to minimise the foreseeable risks of a major accident hazard. Segregation or minimisation is one of the fundamentals of "inherently safer design" (see Kletz, 2010).

In its Annex I, the Seveso III directive introduces the 2% rule that allows quantities equal or less than 2% of relevant qualifying quantity to be ignored, if their location within an establishment is such that it cannot generate another major accident elsewhere on the site. It is therefore considered by the directive that segregation of a substance stored in small enough quantities and in an isolated enough area may eliminate the risk of a major accident hazard.

What would these small enough quantities and long enough isolation distances be? In the UK, for some substances, general principles of segregation of hazardous materials have been decided and are available in guidelines. As an example, the LPGA Code of Practice for Bulk Storage at Fixed Installations[1] provides guidance on separation distances from other hazardous materials such as flammable liquids or toxic substances. The document entitled "The storage of flammable liquids in tanks", published by the HSE in 1998, also provides recommended separation distances between tanks, depending on their diameter. In safety reports, respecting these safety distances may be a way to minimise the strength of a potential accident, as it could justify an argument that a tank should not be able to be impacted by another one.

However, these distances are very site-specific, and may be very difficult to assess in the context of Article 4, where the demonstration needs to be made in an EU-wide context. As we are here, as described in Task 4, dealing with a worst case scenario, it will be impossible to demonstrate that an accident involving all the tanks or vessels could not occur in every European plant using the substance under investigation.

Furthermore, potential candidates for the Article 4 methodology may not be well known substances such as LPG or flammable liquids, for which many experiments and studies have already been conducted: it may be impossible to reach to a European agreement regarding such parameters.

In the context of Article 4, segregation does not seem to be a relevant issue to explore further.

[1] Document available at: http://www.uklpg.org/

4. Size of Storage Unit and Quantities

4.1 A question raised by transport regulation

The transport of hazardous materials may present risks to the transporter, the crew, the public and the environment. As with fixed installations, the most serious hazards arise from loss of containment.

Modes of transport such as road, rail, waterways and pipelines can give rise to release of flammable gas or vapour, which may result in a flash fire or a vapour cloud explosion. Transport accidents are particularly liable to cause pollution, since the dangerous substance is dispersed into the environment. As with fixed installations, in the context of transport of dangerous goods, the question as to whether it is safer to handle a given quantity of hazardous substance in a few large units or in many smaller ones arose.

The transport of dangerous goods is regulated to prevent or mitigate, as far as possible, incidents that could endanger public safety or harm the environment. As described in the document "Guiding principles for the development of the UN model regulations", the aim of regulation of transport of dangerous goods is "*to make transport feasible and safe by reducing risks to a minimum*". The focus in this task 5 report is on the regulation of the transport of dangerous goods by road. The regulation is based on the United Nations Agreement[2] (the European Agreement Concerning the International Carriage of Dangerous Goods by Road (ADR)).

4.2 Reminder of guiding principles used for the development of regulations for transport

Substances, including mixtures and solutions, are assigned to one of nine classes according to the hazard or the most predominant of the hazards they pose in transport. The Guiding Principles indicates that: "the system of classes was established keeping in mind the type of containment to be used, the chemical and physical characteristics of the substances and response procedures that would be most appropriate in the event of an accidental release". Consequently, in the UN Model Regulations each substance has a name (called a Proper Shipping Name) and a four digit UN number and, according to its chemical and physical characteristics, is assigned to a class and a packing group.

The nine classes covered by the ADR are:

- Class 1 Explosives;
- Class 2 Gases;

2 More precisely, it is based on a UNECE (United Nations Economic Commission for Europe) Convention.

- Class 3 Flammable Liquids;
- Class 4 Flammable solids; substances liable to spontaneous combustion; substances which, on contact with water, emit flammable gases;
- Class 5 Oxidising substances and organic peroxides;
- Class 6 Toxic and Infectious substances;
- Class 7 Radioactive material;
- Class 8 Corrosive substances;

Class 9 Miscellaneous dangerous substances and articles.

For the purposes of selecting the appropriate packaging for dangerous goods, substances are further divided into groups in accordance with the degree of danger they present:

- Packing Group I: high danger;
- Packing Group II: medium danger;
- Packing Group III: low danger.

Criteria for classification and assignment to a Packing Group are consistent with those set out in the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

In certain cases, where the hazard posed by dangerous goods is considered low, exemptions from labelling may be provided.

4.3 Examples of exemptions

4.3.1 Introduction

Many sorts of exemptions exist in the European Agreement, for which not all of the provisions laid down in ADR apply.

First, exemptions related to the nature of the transport operation (chapter 1.1.3.1 of ADR) exist. For example, the provisions laid down in ADR do not apply to the carriage of dangerous goods by private individuals, the carriage undertaken by the competent authorities for the emergency response, or the carriage of uncleaned empty storage vessels. Another exemption is related to the carriage of liquid fuels (chapter 1.1.3.3 of ADR) contained in the tank of the vehicle and destined for its propulsion.

Three other exemptions seem to be relevant in the context of the assessment methodology:

- Exemptions related to special provisions or to dangerous goods placed in limited or excepted quantities (chapter 1.1.3.4 of ADR).
- Exemptions related to quantities carried per transport unit (chapter 1.1.3.6 of ADR).
- Exemptions related to special provisions (chapter 3.3 of ADR).

4.3.2 Exemptions due to "limited quantities or excepted quantities" (chapter 1.1.3.4 of ADR)

Limited Quantities

There is evidence that limited quantities present significantly reduced risks in comparison to dangerous goods loads in higher quantities. More precisely, dangerous goods packed in small quantities and in good, robust packaging pose a lower risk in transport than do the same goods packed in larger volumes.

For these limited quantities, some relief from the requirements may be accepted. For example:

- The labelling and display on trucks requirements; and
- Segregation requirements.

Example: Hydrochloric acid, UN 1789 (Strong PG II)

The maximum receptacle (inner packaging) size is 1 litre. This means that as long as the individual "bottles" are not larger than 1 litre, and the box containing these bottles does not weigh more than 30kg, then, some ADR requirements do not apply.

Excepted quantities

This exemption system is more severe than the limited quantities exemption, in the sense that even smaller quantities are required. It allows the substances that fall under this system to be transported by plane. The Guiding Principles recall that "*the substances permitted and the provisions applied are based on some 20 years' experience in air transport, with no reported incidents*". Regarding transport by road, there is no requirement for such dangerous goods to be labelled or for transport document provisions to be met. However, a suitable mark, based on the established air transport mark, is used to aid identification of packages.

4.3.3 Exemptions due to quantities carried per transport unit (chapter 1.1.3.6 of ADR)

The small load exemption allows carrying up to a specified amount of dangerous goods with minimal requirements being imposed.

Small load exemptions relate to the total quantity of dangerous goods carried in packages by the "transport unit" (usually the van or lorry, but also any trailer). It is the transport category that determines the load limits.

Requirements that still apply when taking advantage of a small load exemption (for full details refer to ADR 1.1.3.6.2) are:

- Transport document must be carried in the vehicle (indicating the total quantity for each transport category);
- Vehicle must be equipped with a suitable 2kg fire extinguisher;
- Driver and crew must have received appropriate general training;
- Driver and crew must not open dangerous goods packages;
- There must be no smoking during handling in or around the vehicle;
- Any torch carried must be non-sparking.

Illustration: Methanol is in transport category 2. The "small load threshold" is 333 litres. This means that as long as no more than 333 litres of methanol are transported in e.g. a lorry, then, subject to some conditions, some ADR requirements do not apply.

4.3.4 Special provisions applicable to certain substances

Special provisions (more than 660) are applicable to certain substances. These provisions are described in chapter 3.3 of ADR.

These provisions may concern a wide array of subjects:

- Carriage prohibitions,
- Exemptions from requirements,
- Explanations concerning the classification of certain forms of the dangerous goods concerned, and
- Additional labelling or marking provisions.

Some special provisions give explicit exemptions and dangerous goods are not subjected to any requirements of transport regulation. These provisions, for which exemptions exist, can be classified into three groups:

- Special provisions regarding “specific material”, for example:
    - 590: Ferric chloride hexahydrate is not subjected to the requirements of ADR.

In the context of article 4, what should be addressed are the inherent hazardous properties of the substance and how these hazardous substances may generate an accident.

- Special provisions regarding “the concentration of the substance”:
    - 65: Hydrogen peroxide aqueous solutions with less than 8% hydrogen peroxide are not subjected to the requirements of ADR.
    - 533: UN No. 1198 formaldehyde solutions, flammable are substances in Class 3. Formaldehyde solutions, non-flammable, with less than 25% formaldehyde are not subjected to the requirements of ADR.
    - 597: Acetic acid solutions with not more than 10% pure acid by mass are not subjected to the requirements of ADR.

In the context of article 4, the concentration will influence the hazard generated by the substance.

- Special provisions regarding “the form of the substance”, and for example:
    - 32: This substance (Silicon powder amorph) is not subjected to the requirements of ADR when in any other form.
    - 37: This substance (Aluminium Silicon powder uncoated) is not subjected to the requirements of ADR when coated.
    - 242: Sulphur is not subjected to the requirements of RID (European Agreement Concerning the International Carriage of Dangerous Goods by Rail) when it has been formed into a specific shape (e.g. prills, granules, pellets, pastilles or flakes).

The form of the substance is to be considered in the identification of a worst case scenario. The substance, that can be coated or in a solid form, could be exposed to a fire and generate a major accident.

In conclusion, many special provisions in the context of the transport regulation exist. Certain hazardous goods can be transported with no specific requirements. In the context of article 4, those substances could be studied regarding their physical properties and a review of accident scenarios should be made, in order to demonstrate that any major accident is impossible in practice (Task 4). It might be possible to draw parallels between substances exempted under ADR and the same or similar substances in the context of Seveso.

4.4 Link between exemptions and major accidents

In the ADR regulation, it is therefore considered that dangerous goods placed in limited or exempted quantities will reduce risks enough to consider that the full regulation may not apply to these goods.

However, this conclusion is very specific to transport where the danger is not permanently present in the vulnerable location. In the context of the Seveso directive, which applies to industrial plants, it may be difficult to justify an argument that all the risks that could reasonably be foreseen are eliminated.

A 2002 report by INERIS mentioned in its conclusion:

"*Whatever the risks studied, whether to the environment, from corrosion or from fire, packing hazardous substances in limited quantities does not do away with the risk, although splitting them up into smaller amounts can limit the consequences of an accident.*

However, there is no simple relationship (for example of proportionality) between the extent to which a load of hazardous substances is split up and the seriousness of the consequences of an accident which may happen to this load.

The consequences – as measured from the tests studied – are substantial: hazardous goods transported under the « limited quantities » system cannot be regarded as harmless in safety terms".

This reinforces the conclusion that the exemptions provided by the ADR do not seem to be relevant in the context of the assessment methodology and exclusions from the scope of Seveso under Article 4.

5. Conclusion

The purpose of this report was to study how the containment and the packaging of a dangerous substance could influence the risk of a major accident hazard, and see if it could make a major accident impossible in practice. While much guidance is provided in European and national guidelines about storage, in order to limit the possibility of uncontrolled emissions in the environment, none of these could totally prevent a loss of containment and make a major accident hazard impossible in practice.

This does not mean that the containment will not have an influence on the assessment methodology, as well as all criteria enlisted in Article 4. The accident scenarios are directly linked to the physicochemical properties of the substance, which are influenced by the type of containment. As a result, dangerous phenomena and worst case scenarios may vary from one containment type to another, as a substance could be stored in many conditions of pressure and temperature. However, it is difficult to assess if one type of containment will be better than another to minimise such a risk, in the context of Article 4, at least in any generalised way.

Some European regulations regarding hazardous materials allow total or partial exemptions, in cases where the hazard is considered as low: the European Agreement concerning the International Carriage of Dangerous Goods introduces criteria of limited quantities in a single containment, under which it can be considered that the major accident hazard is no longer relevant. However, in the context of Article 4 of the Seveso directive (and related exclusions from scope under Article 4), it cannot be concluded that that all risks are eliminated. If a loss of containment is identified, it is not possible to consider that a dangerous substance exempted from European Agreement concerning the International Carriage of Dangerous Goods cannot generate a major accident.

In conclusion, containment and packing should be considered in the light of Task 4. Even if there is no way to exclude a dangerous substance from the scope of Seveso III in the way that the ADR does, considerations about packaging and containment may enable the definition of dangerous phenomena and modelling of the worst case scenario to be refined, in cases where such packaging and containment is required in all cases across the EU.

Furthermore, the consideration of containment within the scope of Article 4 assessment methodology could be relevant in that it is (presumably) foreseeable that a substance could be excluded not in general terms (i.e. under all conditions) but rather in specific situations, such as when stored in specific packaging or under certain conditions. This is understood only to be applicable where such packaging or storage conditions are mandated at European level.

6. References

United Nations, European Agreement concerning the International Carriage of Dangerous Goods by Road, volume 1 & 2, January 2013.

European Best Practice Guidelines on Cargo Securing for Road Transport, European Commission, DG for Energy and Transport.

Guiding principles for the development of the UN model regulations, UNECE, 2010.

HSE (1998): The storage of flammable liquids in tanks, Health and Safety Executive,HSG176.

Industry Guidelines for the security of the transport of dangerous goods by road, January 2013.

Kletz T.A. and Amyotte P, Process plants: a handbook for inherently safer design, 2nd edition, 2010

Lees' Loss Prevention in the Process Industries, 2012.

Study on the relevance of the system of exemption for the transport of hazardous goods packed in limited quantities, INERIS, 2002.