Marine Emergency Response Sheets (MERS) in Case of Accidents at Sea Involving Hazardous Substances: Interests and Limitations

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Abstract

Proper preparation for responding to accidents at sea involving hazardous substances involves the preparation of instructions for response teams and incident operational management. Various levels of documentation can be prepared in advance: general organization of response and information gathering, specific to the type of incident. This paper discusses the objectives and the content of the Marine Emergency Response Sheets (MERS).

The level of documentation and information needed when an accident occurs varies with the time from the onset of the incident. At the very beginning as soon as the chemicals involved are identified, the needs are very basic: exclusion zones, hazards for crew, responders and populations if any in the vicinity. It is not useful and even confusing to swamp Emergency Officers with a flow of technical information on the chemicals. The Internet can provide a lot of documentation while crisis officers need concise and accurate information, such as the volume involved, threshold limits, behaviour, toxicity and simple scenario modelling results (mass balance, extension and exclusion zones).

This paper discusses the level of accuracy of the MERS data and their legibility in terms of understanding, bearing in mind that the choice of many data depends more on the habits of the response teams than that of the experts when preparing the MERS. Certain other data are not relevant in the MERS and in fact hinder the easy access to crucial information.

On the other hand, scenarios describe situations such as atmospheric conditions and volumes involved, that do not correspond to the actual incident conditions and interpretations are needed.

This paper draws upon of a few real examples of MERS written by *Cedre* and intended for French Navy responders.

1 Introduction

In case of an incident at sea involving hazardous material and chemicals, the first hours following notification are crucial and will determine the level of success of the coming response operations.

The characteristics of the first hours following a major crisis can be described in three words: agitated, messy and uncoordinated. In other words, the organisation of the structure which runs smoothly in normal times, is completely destabilized.

The flow of information varies from too much information to too little and/or contradictory information coming from the ship or other sources.

Plans have not yet been implemented and the senior officer used to handling this kind of crisis is on leave. Everyone is running around trying to handle the many phone calls from politicians, journalists, and Central Administration, trying to find

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out more about the accident. Nobody knows where the key to the crisis room is and the Emergency phone call list is not up-to-date, making people more irritated and nervous.

As the temperature increases in the Response Centre, Operations officers phone the various experts in order to get a first risk assessment.

The Evaluation team is contacted in order to be dropped on board the disabled ship and is looking for more information on the situation. One or two hours after the first phone call, the first meeting takes place, including First Response Emergency Experts, Evaluation Team Officer, Command Centre Officers and State representative (equivalent to the Senior Duty Coast Guard Officer, in France a Navy officer but with a Public Service Task).

The goal of this first meeting is to get an early estimate of the situation on board and to assess the hazards for the Evaluation team, the crew and the population if any in the vicinity. The situation on board might be very confused and uncertain, especially if there are some fatalities. The need for clear, relevant and reliable documents is obvious around the meeting table. Here the Maritime Emergency Response Sheets (MERS) enter into force as referenced documents.

2 Requirements for MERS

The key words can be summarized in the following formulation: too much information should not be provided but just enough.

It is easy to find a lot of information on a simple chemical on the Internet. The problem is that in an emergency, responders need concise and appropriate information, especially adapted to the beginning of the crisis.

The challenge for experts in charge of the preparation of such documents is to determine the only parameters needed for the Evaluation Teams and no more. These teams are made up of Navy Firefighters, Engineers and Maritime Affairs Officers. Neither scientists nor chemical engineers are normally present on board during the Emergency phase.

The information must therefore be easy to read and to understand when on site.

The stress generated by such an operation requires procedures and a minimum thought: this is called the reflex period. Operational personnel and especially Navy Fire Brigades are trained to deal with such situations and the Response or Evaluation Team is led by a Senior Officer with a Level 2 Chemical Hazard Certificate. The MERS must be more developed that the cards designed for the chemical truck drivers (equivalent to Tremcards) but less precise than the Chemical Emergency Response Guide at Sea Guides (CERGS) that, with about 60 to 80 pages, are a bit too complex for a quick glance. 13 of this CERGS have been written by *Cedre* between 2002 and 2010, founded by the Arkema company, Total group and the Navy. Some have been translated in English and are available for free on the *Cedre*'s web site. Although the information proposed in the CERGS has an operational objective, they are not well fitted for the first site response.

Figure 1: last Chemical Emergency Response Guides at Sea produced in *Cedre*

Other Response Guides do exist: fire brigades in France use the Geneva Fire Brigade's Orange Guide (called GORSAP by the Fire Fighters), not well adapted to marine situations and a bit too concise although the hazard profile proposed in this Orange guide has been taken for the MERS. Five hazard parameters are described:

Health (blue)
Fire (red)
Heat Chemical stability (yellow)
Reactivity with water (white)
Explosiveness (red and yellow)

Each parameter is given a rating ranging from 0 to 4, depending of the risk level.

This hazard profile is more or less equivalent to that of the one proposed in the NFPA code (National Fire Protection Association).

Material Safety Data Sheets (MSDS), if found on the Internet, give too many details and are written in a less comprehensive manner for operational personnel. The 16 paragraphs are often written in English that is not easily understood by many responders, at least in France. Moreover some useful parametres are lost among too many details, written in too small characters, finally not easy on the eye (imagine you are on a listing ship, in heavy weather during the night).

The challenge of the elaboration of MERS lies in the level of information needed on site and the well adapted accuracy required when dealing with a chemical emergency at sea.

3 General Information Sheet

This first sheet presents the parameters that must be known in order to get a good picture of the situation. Not all response options are available for the first hours but it constitutes an aid for memorizing the questions to be asked to the ship crew or the ship owner through the Maritime Rescue Co-ordination Centres (MRCC).

<u>**Accident**</u>

Type (collision, stranding, fire…)
Time (GMT)

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Casualties
Immediate consequences: pollution, no steering, black out, fire…
Crew: still on board?
Location of the impact on the hull.
Type, name and speed of the colliding vessel (if any), dimension of the bulb of this vessel.

Ship(s)
Type
Name
Flag
Owner

Product involved
Quantity, nature, packaging
Location on board (loading plan)
Tanks impacted
Level of the impact (above or below the water line)
Presence of cargo leaks and outflow noticed.

Environment
Location
Weather, oceanic conditions and forecast

Immediate steps taken by the crew

The information collected by the MRCC is available in real time in the Marine Operational Centre through a system called “Trafic 2000”. In France three Marine Operational Centres are established, located in Cherbourg for the Channel, in Brest for the Atlantic ocean and in Toulon for the Mediterranean sea operations.

4 The Four Page MERS

The following MERS was produced for the French Navy Fire Brigades for the GALERNE project, dealing with risk assessment for Liquid gases (LNG, Butane, Propane, Vinyl Chloride monomer, Ammonia, Ethylene) and two liquids Evaporators (Benzene and Xylenes).

Seven main paragraphs are proposed;
Identification
Description, composition and behaviour
General vessel arrangement
Hazard identification and GESAMP description
First aid and Response
Scenarios
Cases history

This project has led to the preparation of 4 pages of the MERS with the following paragraphs as illustrated in figure 2 for Benzene.

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4.1 Product Identification

4.1.1 Commercial Name

Product name in English
CAS number (Chemical Abstract Service)
UN code (if any)
EINECS or CE number

Benzene

This sheet was prepared by Cedre and Ineris, to the best of their ability. Cedre and Ineris will not accept any responsibility for the consequences of its use.

<table>
<tr><td>Substance identification
Commercial name: benzene
Product name: benzene
Chemical name: benzene
Other names: none</td><td colspan="2">Quick risks identification : GORSAP classification
0 = no danger 1 = little danger 2 = danger
3 = high danger 4 = very high danger
Health = 2 Fire = 3 Chemical instability with heat = 0
Reaction with water = 0 Explosive mix with air = 3</td></tr>
<tr><td>Identification number
CAS n°: 71-43-2
EINECS n°: 620-020-008
UN code: 1114</td><td colspan="2">Risk phrases (R) / nature of risks
R11: highly flammable
R48/23/24/25: toxic, danger of serious damage to health by prolonged exposure through inhalation, in contact with skin and if swallowed
R36/38: irritating to eyes and skin
R45: may cause cancer
R46: may cause heritable genetic damage
R65: harmful, may cause lung damage if swallowed</td></tr>
<tr><td>Labour code, danger symbols
 </td><td colspan="2">Safety phrases (S)
S45: in case of accident or if you feel unwell, seek medical advice immediately (show label where possible)
S53: avoid exposure, obtain special instruction before use</td></tr>
<tr><td>Intervention sheets
GORSAP sheet n°1114
Canutec sheet n° 130
IMDG sheet code F-E ; S-D
Code Chris manual sheet BNZ
INRS sheet n° FT49</td><td>Maritime transport
No specific risks identified</td><td>Transport symbol
3 = flammable liquid
Danger code = 33


(highly flammable liquid)</td></tr>
<tr><td colspan="3"></td></tr>
</table>

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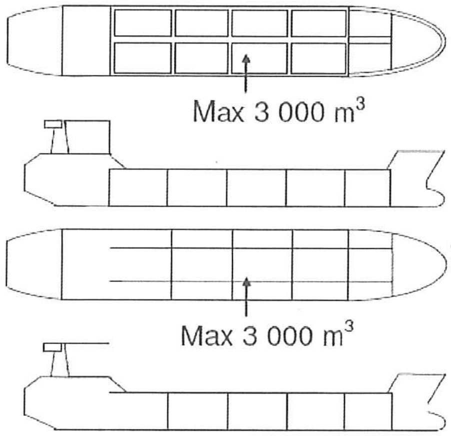
Typical ship plans



Ship with lateral tanks only central one | Ship with lateral tanks on sides of

Technical ship information

Benzene can be transported in chemical tankers (up to 5000 t) or chemical/oil tankers (up to 40 000 t).

Products constants and weathering

Formula: C6H6
Relative vapour density compared to air: 2.7
Molar mass: 78 g/mol
Physical state at 20°C: colourless liquid with
Characteristic diesel smell
Physical state for transport: liquid
Boiling point: 80 °C
Flash point: -11°C
Auto-ignition temperature: 561°C
Explosive limits in air: 1.3 % - 8 %
Vapour tension (20°C): 10kPa
Relative liquid density (20°C): 0.88
SEBC classification: E (evaporator)

Decomposition by fire generates

* Complete combustion: CO2, water vapour, NOx.
* Partial combustion: as above plus carbon monoxide,
soot and cracking products (aldehydes, ketones, carbon, PAH)

Risks for human health

Highly flammable and excessively volatile.
Vapours form explosive mixtures with air at all temperatures.

Reaction in case of :

shock: no reaction
contact with air: no reaction
contact with water: no reaction

Solubility and toxicity in water

Solubility in freshwater at 20°C: 1 780 mg/l
Solubility in freshwater at 25°C: 1 830 mg/l
Solubility in seawater at 20%C: 350 +- 100 mg/l
Acute toxicity in freshwater:
- Weed Selenastrum cornutum CE50b 72h = 28 mg/l
- Weed Selenastrum cornutum CE50c 72h = 100 mg/l
- Crustacean Daphni magna CL50 48h = 10 mg/l
Acute toxicity in seawater:
- Crustacean Palaemonetes pugio CL50 96h = 27 mg/l
- Fish Onchorhynchus mykiss CL50 96h = 5.3 mg/l
- Fish Morone saxatilis CL50 96h = 9.6 mg/l

Dangerous chemical reactions :

Reacts violently with oxydants, nitric and sulphuric acids and halogens, with risks of fire and explosion.
Attacks plastics and rubber

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Toxic by repeated inhalation (blood poisoning, narcosis with respiratory paralysis). Irritant for respiratory tracts, eyes and skin. ***Effects related to types of exposure*** Inhalation: dizziness. drowsiness, headache, nausea, breathlessness, convulsions, loss of consciousness Skin: drynees, redness, pain (warning: benzene can be absorbed by skin) Ingestion: stomach pain, sore throat, vomiting ***Conversion factor in air (20°C)*** 1 ppm = 3,25 mg/m^3 1mg/m^3 = 0,31ppm	***Toxicity limits*** By inhalation (at 25 °C and 101 kPa, 1 ppm = 3.2 mg.m-3), values based on INERIS studies in emergency situations: Lethal effects SEL (1%) 1000 ppm - ERPG3 Irreversible effects (SEI) 150 ppm - ERPG2 Reversible effects (SER) 50 ppm - ERPG1 ***Other limits*** Odour threshold: 5 ppm IDLH: 500 ppm Maximum Mean exposure value (8h): 1 ppm / 3,2 mg.m-3 (France) ***Risks for environment*** MARPOL classification: Y

SIMULATION - Model scenarios (PHAST model) concerning a spill of 2200 tons (2500 m^3) of Benzene

SCENARIO A	Breach in full lateral tank, above water line					
Effects	Spill generating evaporating slick, toxic cloud, risk of flash fire					
Meteorology	Wind Beaufort 2 (6-11 km/h)			Wind Beaufort 10 (89-102 km/h)		
Hole size	20 cm²	5 dm²	2 m²	20 cm²	5 dm²	2 m²
Maximum slick radius	100 m	450 m	450 m	60 m	400 m	380 m
LEL distance	450 m	2400 m	750 m	200 m	600 m	500 m
1/2 LEL distance	600 m	2600 m	1600 m	250 m	700 m	600 m
Flammable cloud height	< 5 m	< 5 m	< 5 m	< 5 m	< 5 m	< 5 m
Distance RET 60' (ERPG1)	5000 m	> 10 km	> 10 km	300 m	8200 m	10 km
Cloud height at ERPG1 60'	15 m	25 m	30 m	25 m	100 m	100 m
SCENARIO B	Hole in full lateral tank below water line					
	Effects, meteorology, hole sizes identical to scenario A A small amount of the product will dissolve in water during upward phase to surface. That will not change significantly the scenarios results.					

RET = reversible effects threshold LEL = lower explosive limit o

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Case Histories

Panam Serena
On 1 January 2004 at Porto Torres (Sardinia) an explosion occurred onboard the chemical tanker Panam Serena while unloading her cargo of benzene. A fire engulfed the ship and raged for 2 days in spite of swift response by fire fighters. Two of the 15 crew members were lost. Most of the benzene burnt and no water pollution was reported.
Samho Brother
On 10 October 2005, the chemical tanker Samho Brother, carrying 3 000 t of methyl benzene, 85 t of bunker fuel and 16 t of diesel, capsized after a collision with a cargo vessel off the north Taiwan coast. There were no casualty, but sea conditions prevented any salvage attempt. Authorities attempted to sink the wreck with bombs and missiles. She sank overnight, 9 miles from the coast. Surveys the following day showed silver grey slicks on the sea surface. Investigations on site by an oceanographic vessel on 2 November showed no air pollution but a 3 miles long slick on the sea surface. The monitoring showed no evidence of benzene pollution

Figure 2: MERS concerning Benzene

4.1.2 Hazards Pictograms
4.1.3 Response Guides References
4.1.4 Quick Hazard Identification,
4.1.5 Risk phrase (Phrase R)
4.1.6 Special Cares (phrase S)
4.1.7 Sea Transport Identification
4.2 Vessel General Tank Arrangements
4.3 Chemical Properties

Raw formulation
Molar mass
Physical state (20°C)
Physical state when transported
Colour
Odour thresholds
Boiling point
Flash point
Self ignition point
Flammability thresholds
Vapour pressure (20°C)
Liquid density
Vapour density compared to air
SEBC (Standard European Behaviour Classification)
Conversion factor (mg/m3 in ppm)

4.4 Hazards

For human health
Effects depending on form of exposure
Combustion decomposition products
Reactions; shocks, with air, with water
Hazardous chemical reactions

Toxicity threshold (the source is indicated)
ERPG1, 2, 3
IDLH
Mean exposure level (8 hours)

Environment
MARPOL classification

4.5 Response

First aid
Fire and explosion response
Response equipment
Detection
PPE
Equipment; pumps, hoses…
Spill response (on board and at sea)

4.6 Accident Scenarios

Two scenarios are defined
Hole above the water line
Hole below the water line

Two atmospheres were chosen, stable and unstable, and in an area equivalent to the Channel (water temperature around 10°C and tidal zones.

Three holes size: 20 cm², 5 dm², 2 m²

The following data are provided:
LIL or LEL
50% LIL
Height of flammable cloud
ERPG1 distance
Gas Cloud height at ERPG1
Distance to odour threshold

The results of modelling for each scenario are given in a diagram or a table, depending on the habits of the responding teams.

4.7 Case History and a Reference for More Information

This paragraph gives a few examples of similar passed accident, their main consequences and the main steps taken to face the pollution.

5 Conclusions

It is important to remember that the MERS must be adapted to a specific use for specific users in the very first hours of the crisis. These MERS are not well suited to fire brigades on land even if the data are comprehensive for them. They are intended to constitute a reference on board the disabled vessel but of course as soon as the crisis is well advanced, more expertise is required and therefore more detailed information sources. This is when CERGS should be referred to. After the first hours delay, the experts advices come into force and simulations based on real accident data are run.

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