

HELCOM Manual on Co-operation in Response to Marine Pollution within the framework of the Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention), Volume 2, 1 December 2002

Response to accidents at sea involving spills of hazardous substances and loss of packaged dangerous goods

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1 Introduction

1.1 Purpose and scope

International Maritime Organization IMO estimates that more than half of packaged goods and bulk cargoes transported by sea today can be regarded as dangerous, hazardous or harmful to the environment. A great deal of these substances, materials and articles are also dangerous or hazardous from a human safety point of view.

The increasing trend in maritime transport of chemicals and dangerous goods also gives rise to an increasing number of accidents involving such products. This development makes great demands on the personnel who are responsible for actions against such accidents in order to protect man and environment from damage.

The aim of this Manual is to provide information to support proper decisions when responding to accidents in the marine environment involving chemicals and dangerous goods. However, it is not possible to provide turn-key solutions ready to retrieve from the Manual on the scene of the accident. The contents of the Manual must be thoroughly reviewed beforehand and the contents are primarily aimed for personnel who are familiar with the area.

The chapters of this Manual focus on spills and lost packages. Chapters 1 - 2 deal with spill behaviour and drift forecasting. Chapters 3 - 6 address monitoring, sampling and response. The Annexes 1 - 7 contain facts on first response, resistivity of materials, case histories, classification of spills, body protection, labelling, and measurement units. Annex 8 contains references.

1.2 General first response to chemical accidents

Definition of response: The efforts to minimize the risks created in an emergency by protecting the people, the environment, and property, and the efforts to return the scene to normal pre-emergency conditions.

Spills of chemicals at sea are rarely detected without notice in the same way as oil spills. They are most often involved in maritime accidents and can sometimes be observed, surveyed or monitored in the marine environment close to the site of the accident. Unknown lost packages of dangerous goods are sometimes detected floating at sea or washed ashore. Most often, however, such packages can be connected with known accidents.

Occurred accidents, and spills involving chemicals, as well as lost packages of dangerous goods must be reported to all relevant bodies according to national and international agreements and regulations.

When responding to accidents involving chemicals or dangerous goods some general first steps must often be taken which are the same for many accidents no matter what chemicals are involved or what the circumstances are (cf. Annex 1).

Never rush into a chemical incident, but try to use your common sense and assess the situation carefully. Plan the work on a worst possible case basis. Realize that each chemical is different and that a new incident is not going to be the same as an earlier one. There is nothing like a typical incident.

The following **list of advices** includes such **general routines** that often should be applied. In minor incidents it is not necessary to follow some of the advices, or it is quite enough to limit their extent. At major accidents it might be necessary to apply the advices to the fullest possible extent. See also “K. Example of a checklist” at the end of Annex 1.

- ♦ Get a rapid general view of the situation and judge the need for the most urgent actions to be taken, such as medical care of victims, restriction of access, evacuation, reduction of leakages, etc.
- ♦ Warn passers-by, seafarers, public, etc. Inform appropriate authorities, agencies and mass media.
- ♦ Identify all involved chemicals. Note their mode of transport (bulk, container, palleted goods, etc.) as well as type of spill or discharge (escaped chemicals, lost packaged dangerous goods).
- ♦ Judge the risk for fire, explosion, leakage as well as health risks and risks for adjacent areas (utilize e.g. the IMDG Code, Material Safety Data Sheets, Chemical Safety Cards, Chemical Information Databases).
- ♦ Establish restriction areas (risk zones) and restrict access to these areas by guarding the entrances.
- ♦ Make preparations for procedures regarding decontamination, relieving and replacement of personnel, materials and equipment.
- ♦ Make appropriate arrangements for beaches, swimming areas, fishing grounds, fresh water intakes, etc., such as restriction of access or restriction of right to use.
- ♦ Use monitoring devices continuously for fire, explosion and health risks.
- ♦ Assess emission rates, volumes, properties and reactivity for involved chemicals.
- ♦ Assess initial drift, spread and evaporation (direction, distance, volumes) and calculate these behaviours by modelling programs and make forecast maps.
- ♦ Continuously monitor drift and spread in order to assess the risk, and continuously take appropriate actions based on the judgements.
- ♦ Take appropriate steps to stop or reduce damage to environment and property.
- ♦ Contact, as soon as possible, relevant environmental bodies and plan for appropriate handling of the hazardous waste that the accident and the operation may yield.

1.3 Behaviour of chemicals

1.3.1 General physical behaviour of released chemicals in water

Certain general actions should always be taken when accidents involving chemicals and dangerous goods occur. These actions are often the same for most types of accidents, regardless of the circumstances and materials involved.

When responding to a chemical spill in the aquatic environment, it is important that the measures are adjusted for the chemical's physical behaviour in water. The patterns of spill behaviour in water of various chemical groups and packages are discussed in this Section. Figure 1 - 1 illustrates the principle ways of behaviour of chemicals when spilled into water. However, it should be stressed that this picture is simplified. A chemical spill may exhibit more than one of these properties at the same time. For example, it may float on the water surface and at the same time evaporate and/or dissolve. It may also react with water. A graphical illustration of the system is given in Figure 1 - 2. The denominations (G, GD, E, etc.) in this figure are explained in subchapter 1.4 and in Annex 4.

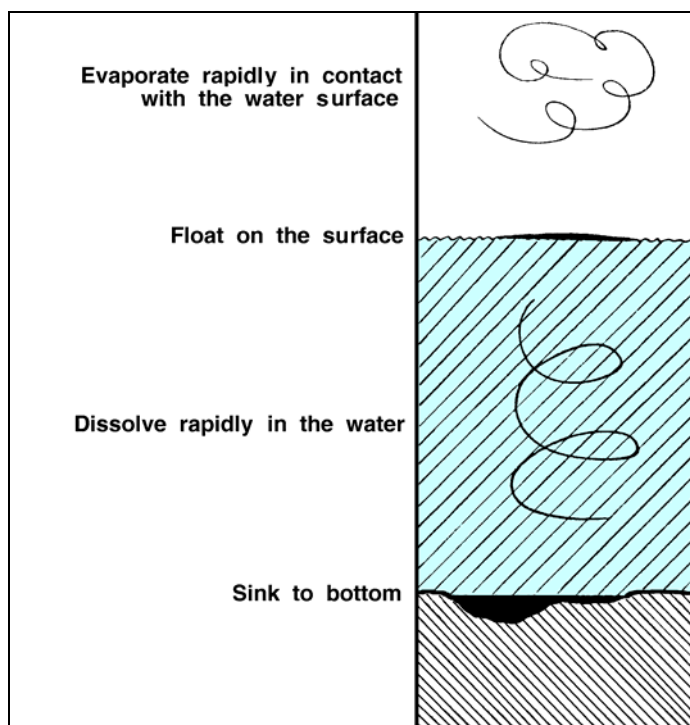


Figure 1 - 1 Principal behaviours of chemicals when spilled into water.

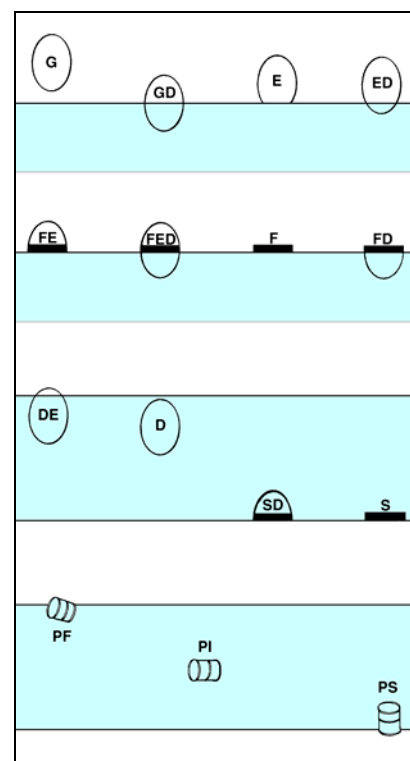


Figure 1 - 2 Graphical illustration of the behaviours of chemicals and dangerous goods in water (the designations G, GD, E, ED, etc. are further explained in Figure 1 - 12 below and in Annex 4).

1.3.2 Chemicals that react with water

General actions should be taken according to Section 1.2 above.

It is impossible to give general guidance on how to respond to chemicals that react with water. The response must be planned from case to case with extreme consideration to the reactivity of the substance.

Of commonly transported chemicals only a few react rapidly with cold water. Such chemicals, that react chemically with water, may in theory fit into any of the Property Groups of Annex 4 with regard to solubility, density and vapour pressure. But as they react with water, their pattern of behaviour does not correspond to the principles of the Property Groups. Some commonly transported chemicals, that react with water, are briefly described below.

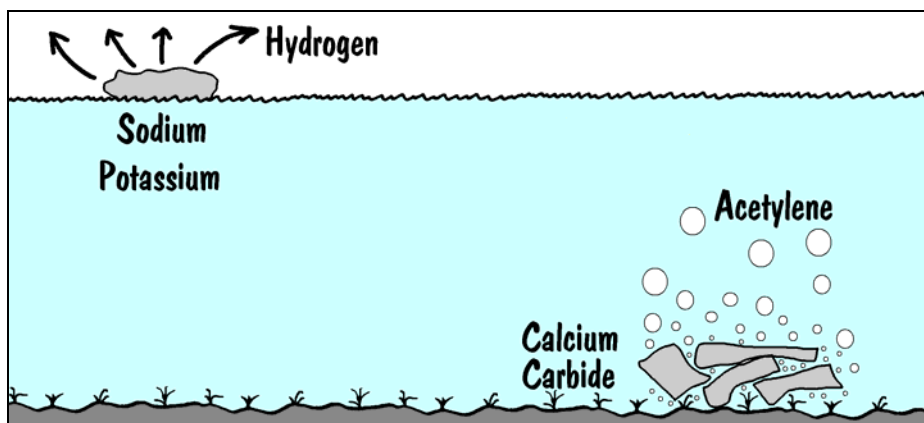


Figure 1 - 3 Examples of substances that react with water

Acetyl chloride is a fuming liquid that, upon contact with water, reacts violently and decomposes to hydrochloric acid and acetic acid.

Calcium carbide is a solid (i.e. powder or lumps) which sinks, reacting with water and forming acetylene, a highly flammable and explosive gas.

Sodium and **potassium** are very reactive metals which float and react violently with water, forming flammable hydrogen gas mixtures with air. The heat of the reaction often causes the hydrogen to ignite and explode.

Sulphonyl chloride is a fuming liquid which reacts violently with water, and decomposes to sulphuric acid and hydrochloric acid.

Toluene diisocyanate (TDI - an often used acronym) is a sinking liquid which reacts slowly with cold water to form carbon dioxide and a plastic-like product (polyisocyanate).

Concentrated **sulphuric acid** and **oleum** when mixed with water, may release large amounts of heat, resulting in extremely vigorous boiling.

1.3.3 Predicting the reactivity when mixing chemicals

Violent reactions may occur when certain chemicals are mixed because the chemicals are **incompatible**. Classes of incompatible chemicals should be segregated from each other during transportation and storage. By using Figure 1 - 4 (Ref. 62) it could be determined which chemicals can not be mixed together because of possible reactions.

EPA's Chemical Compatibility Chart

This chart gives indications of some of the hazards that can be expected on mixing chemicals. It is not possible to make such a chart complete. The chart cannot be assumed to ensure compatibility of all chemicals in the class, nor do any blanks necessarily mean that the mixture cannot result in a hazard reaction.

Example on how to use the table: Is **acetone** compatible with **nitric acid**?

Acetone is a ketone (Class 19) and nitric acid is an oxidizing mineral acid (Class 2). Find the square where column 2 meets row 19.

The codes H (heat) and F (fire) indicate that these two chemicals are incompatible (in fact they may react explosively).

[illegible]

Figure 1 - 4

The Chemical Reactivity Worksheet

The Chemical Reactivity Worksheet is a program that is used to find information about the potential reactivity of substances and mixtures of substances. The Worksheet was developed by the CAMEO Team at the Office of Response and Restoration, National Ocean Service, NOAA, and the Chemical Emergency Prevention and Preparedness Office of the Environmental Protection Agency, EPA. The program can be downloaded free from WWW (April 2002: <http://response.restoration.noaa.gov/chemaids/react.html>).

Chemical Reactivity Worksheet includes a database of reactivity information for more than 6,000 common hazardous chemicals. The database includes information about the special hazards of each chemical and about whether a chemical reacts with air, water, or other materials.

To use the Worksheet, chemicals are selected from its database, and added to a "mixture"- like the chemicals in an accident - to find out what dangers could arise from accidental mixing. The Worksheet then predicts the reactivity of this mixture.

Figure 1 - 5 and Figure 1 - 6 show how the Chemical Reactivity Worksheet is used to assess the reactivity of two substances "acetone" and "nitric acid".

Figure 1 - 5 The preliminary result is shown.

CHEMICAL NAME	1) ACETONE	2) NITRIC AC
1) ACETONE	—	B1,C1,D3
2) NITRIC ACID, [> 40%]	B1,C1,D3	—

Figure 1 - 6 Three reactivity groups are shown with indication of the hazards of the mixture.

1.3.5 BLEVE - Boiling Liquid Expanding Vapour Explosion

BLEVE is an important concept in the field of emergency response, especially in accidents involving LPG. Many disastrous accidents have occurred when LPG tanks have exploded in BLEVE's. Also other substances than LPG may be involved in BLEVE accidents.

A BLEVE may occur when a pressurized tank, containing e.g. LPG, is exposed to an external fire. If the tank cannot resist the increasing pressure it will burst and the LPG content will be thrown around, mix with air and ignite in a storm of fire.

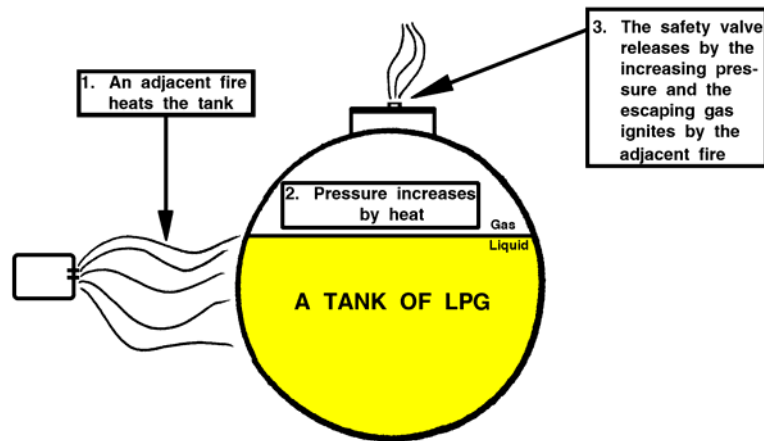


Figure 1 - 7 How a BLEVE could be initiated

The explosion is accompanied by a strong pressure wave and a fireball that for a large tank may be gigantic and has even been mistaken for a nuclear explosion.

One possible cause of the tank's bursting is when the outer fire is very violent. In such a case the capability of the safety valve may not be enough to keep the pressure down.

Another cause is when the tank wall's strength is reduced by corrosion, mechanical damage, etc.

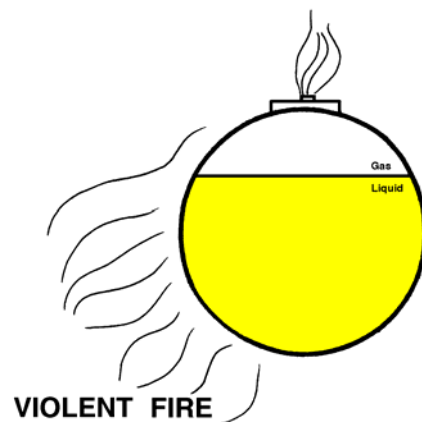


Figure 1 - 8

Figure 1 - 9 and Figure 1 - 10 show a typical development of a BLEVE when the fire softens the tank wall which then loses its strength and the tank ruptures.

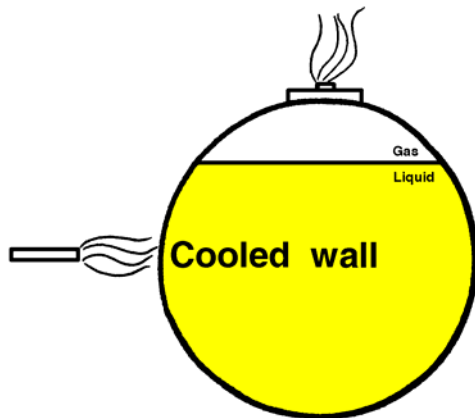


Figure 1 - 9

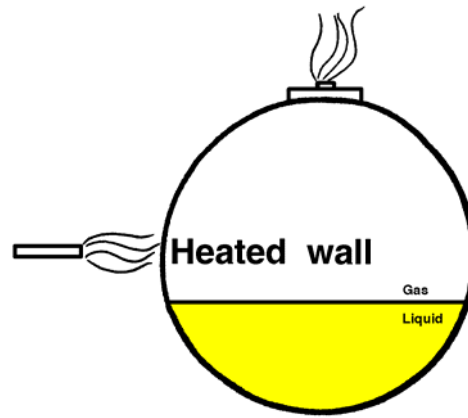


Figure 1 - 10

The tank wall is first cooled by the liquefied LPG inside. The cooling effect disappears when the evaporation causes the liquid surface to lower. The steel wall loses its strength and ruptures and a BLEVE occurs.

A BLEVE may occur in similar situations on board ships (cf. Figure 1 - 11). A response option on such an occasion is dousing with water from a safe distance. But evacuation should also be considered.

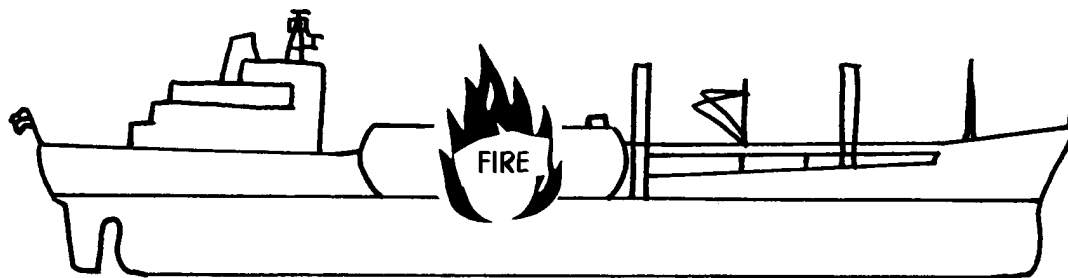


Figure 1 - 11

1.4 Selection of response measures with regard to physical properties

A joint European system for classification of chemical spills in water ("The European Classification System") is described in Annex 4.. The system is based on the physical behaviours in water (solubility, density, vapour pressure) and comprises 12 Property Groups (G, GD, E, ED, etc.) for substances and 3 Groups for packages (PF, PI and PS). Figure 1 - 12 gives an overview of the Groups for substances.

Property Group Designations (cf. Figure 1 - 13 below and Annex 4)	G	gas	F	floaters
	GD	gas/dissolver	FD	floaters/dissolver
	E	evaporator	DE	dissolver/evaporator
	ED	evaporator/dissolver	D	dissolver
	FE	floaters/evaporator	SD	sinker/dissolver
	FED	floaters/evaporator/dissolver	S	sinker

Figure 1 - 12

Figure 1 - 13 gives a schematic presentation of response methods against spilled substances in water. Each method has got a specific designation where F stands for Forecast, M for Monitoring and C for Combating. X-marks in the table indicate for what Property Groups of substances (cf. Figure 1 - 12) the methods are applicable. The methods are more thoroughly described in the Chapter 5.

This table shows X-marks where practical methods exist for response to accidents involving releases of chemicals into the environment									Solid Subst						Solid Subst		
									F	FD			D	SD	S		
	GAS		LIQUID														
GROUP	G	GD	E	ED	FE	FED	F	FD	DE	D	SD	S					
METHOD																	
F1 Forecasting the spread in air	X	X	X	X	X	X			X								
F2 Forecasting the spread on water surface					X	X	X	X									
F3 Forecasting the spread in water body		X		X		X		X	X	X	X						
M1 Monitoring the spread in air	X	X	X	X	X	X			X								
M2 Monitoring the spread in water body		X		X		X		X	X	X	X	1)					
C1 Combating gas clouds	X	X															
C2 Combating spills that float on water							X										
C3 Combating spills that dissolve in water		X		X		X		X	X	X	X						
C4 Combating spills that sink to the bottom											X	X					

Hazardous substance information sheet

(Fill in blanks as completely as possible)

Common Name:		Chemical Name:	
I. Physical/chemical properties (SI units)			NOTES
<input type="checkbox"/> Gas	<input type="checkbox"/> Liquid	<input type="checkbox"/> Solid	
Molecular weight	g/g-mole		
Density	g/ml		
Specific gravity			
Solubility: Water	at _____ °C		
Solubility: _____ (solvent)	at _____ °C		
Boiling point	°C		
Melting point	°C		
Vapour pressure (kPa, mm Hg, etc.)	at _____ °C		
Vapour density	at _____ °C		
Flash Point			
Open cup	°C		
Closed cup	°C		
Other:			
II. Hazardous characteristics			
A. Toxicological Hazard (IDLH, TLV, other)		Hazard?	Conc.
		NOTES	
Inhalation	Yes/No		
Ingestion	Yes/No		
Skin/eye absorption	Yes/No		
Carcinogenic	Yes/No		
Teratogenic	Yes/No		
Mutagenic	Yes/No		
Other	Yes/No		
B. Combustible Hazard			
Combustibility	Yes/No		
Toxic by-product(s)	Yes/No		
Flammability	Yes/No		
LFL/LEL	Yes/No		
UFL/UEL	Yes/No		
Explosivity	Yes/No		

*Continued.....***Figure 1 - 14**

Examples of information sheet forms for chemical data

.....continued

C. Reactivity Hazard	Yes/No	Conc.	NOTES
With			
D. Corrosivity Hazard	Yes/No	Conc.	NOTES
pH			
Neutralizing agent			
E. Radioactive Hazard	Yes/No	Exposure Rate	NOTES
Background	Yes/No		
Alpha particles	Yes/No		
Beta particles	Yes/No		
Gamma radiation	Yes/No		
F. GESAMP Hazard Classification		Values	NOTES
Bioaccumulation (A)			
Biodegradation (B)			
Oral intake (C)			
Skin contact and inhalation (D)			
Reduction of amenities (E)			
G. Miscellaneous Hazards		Values	NOTES
Acute toxicity			
Tainting			
Chronic toxicity			
MARPOL pollution category			
IMDG Code (Marine pollutant)	Yes/No		
IMDG Code (Severe marine pollutant)	Yes/No		
III. Monitoring/sampling recommended			
IV. Recommended protection			
Worker			
Public			
V. Recommended site control			
Hotline			
Decontamination Line			
Command Post Location			
VI. Other information, e.g. contacts with chemical industry, medical personnel			

1.6 Manuals and handbooks on response to maritime accidents involving chemicals and dangerous goods

Very few manuals and handbooks in English specifically address the field of response to *maritime* accidents involving chemicals and dangerous goods. The following are examples of such publications:

- ♦ CHRIS Response Methods Handbook, US Coast Guard (Ref. 49)
- ♦ Containers and packages lost at sea - Operational Guide, CEDRE (Ref. 43)
- ♦ Manual on Chemical Pollution - Section 1&2, IMO (Ref. 1a and 1b)
- ♦ Practical Guide for Marine Chemical Spills, REMPEC (Ref. 3)

The Swedish Coast Guard has elaborated an extensive handbook in Swedish (Ref. 2) containing 22 chapters with instructions for the organization's personnel. Six of the chapters in this handbook contain detailed instructions on actions against maritime accidents involving chemicals and dangerous goods. These instructions are directed at the Response Commander, the On-Scene Commander (OSC), the chiefs of the Coast Guard Environmental Response vessels, and the field personnel.

2 Predicting the drift and spread of chemical spills

2.1 Introduction

The drift and spread of a chemical spill in the aquatic environment should as early as possible after the start of the release be assessed or calculated so as to form a basis for a risk analysis. A simple, rough estimation is often better than nothing. The estimation should as far as possible be based on the spill's physical properties as well as environmental conditions like temperature, wind, water current, etc.

There exist various computer models by which an operator after some education and training can elaborate a forecast of the spill's future fate. However, it should be emphasized that the forecast's reliability depends fully on 1) the model's construction and validity, 2) how correct all input data are, and 3) how professionally the model is run.

Many computer models exhibit astounding limitations. It is usual that forecasting models for gas clouds are not able to consider the structure of the ground or water surface (e.g. flat country, forest, calm water, rough sea). Some models cannot even consider mountains as obstacles for the cloud drift.

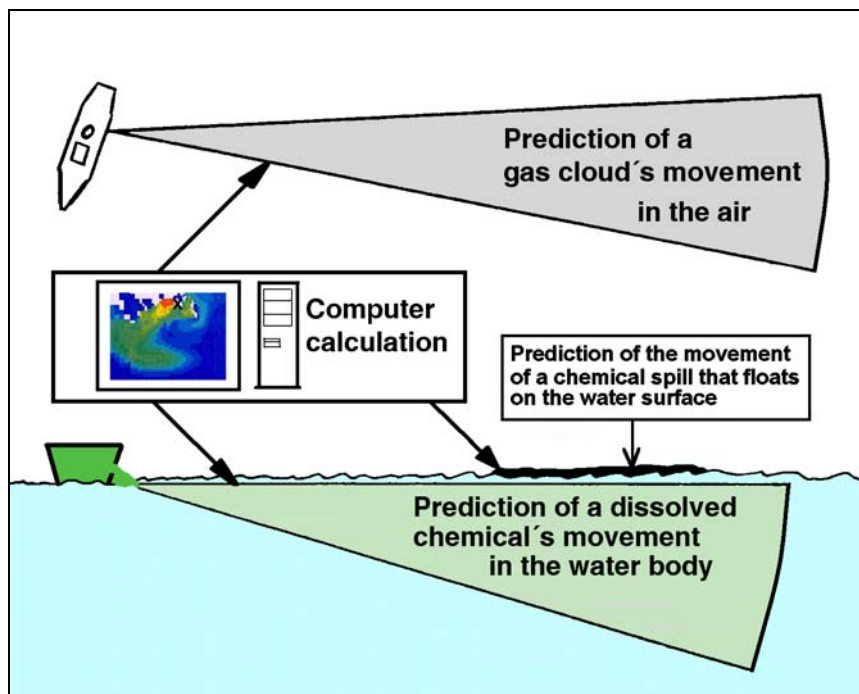


Figure 2 - 1 The drift and spread of chemical spills can be forecasted by computer models.

Some drift models are not able to account for the chemical's physical properties (e.g. water solubility) which gives a misleading or erroneous picture of their drift.

Below in Subchapter 2.6 a few examples are given on forecasting systems, just for the purpose of exemplification. The objective has neither been to try to find the "best" system, nor to evaluate or compare such systems.

2.2 Gas clouds

Forecasting the spread in air (Figure 1-13, Method F1)

Applicable for Groups G, GD, E, ED, FE, FED, DE (all Groups with G or E)

Forecasting the spread of gas clouds in air can be estimated very roughly for the Groups G and GD by means of Figure 2 - 2. Such estimates should always be regarded with reservations and never be alternatives for monitoring.

Release	Health Risk		Fire/Explosion Risk
	Ammonia, vinyl chloride, chlorine	Methane (LNG), propane (LPG), butane (LPG), ethylene, butylene-butadiene	Ammonia, vinyl chloride, methane (LNG), propane (LPG), butane (LPG), ethylene, butylene-butadiene
tonnes	metres/ /nautical miles downwind	metres/ /nautical miles downwind	metres/ /nautical miles downwind
0.1	1,000 / 0.62	200 / 0.12	200 / 0.12
1	2,000 / 1.24	400 / 0.25	400 / 0.25
10	5,000 / 3.11	1,000 / 0.62	1,000 / 0.62
100	10,000 / 6.21	2,000 / 1.24	2,000 / 1.24
1,000	20,000 / 12.43	4,000 / 2.49	4,000 / 2.49

Figure 2 - 2

N.B. The above Figure 2 - 2 can also be applied to liquid chemicals (which are flammable or especially hazardous for health) in the Groups E, ED, FE, FED and DE. The spread of evaporated gas, from spills of these chemicals, can be calculated very roughly by multiplying the values in the table by $VP/100$, where VP is the liquid's vapour pressure in kPa, which is less than 100 at ambient temperature.

It is often difficult to get time to calculate the spread of instantaneously formed gas clouds in accidents, even if handy computerized models are available.

Sometimes it is impossible to calculate and predict gas cloud distribution even with the aid of very sophisticated modelling tools. Certain atmospheric conditions and/or substance properties may result in peculiar gas behaviour that makes the forecasting difficult.

A good example of this is the following small chlorine accident (Figure 2 - 3) that occurred in very cold and calm weather. The stable, windless, atmospheric conditions caused very limited dispersion of the chlorine cloud, which moved a long way before dissipating.

The graph shows the rough appearance of a very long (10-15 km) and narrow cloud of a release of 10 kgs of chlorine gas at -30°C and calm, stable wind conditions.

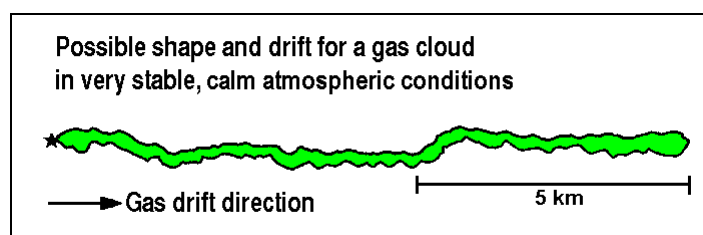


Figure 2 - 3

2.3 Floating spills

It is complicated to forecast the behaviour of a chemical spill that floats on the water surface. The spill's fate is influenced by the following processes:

- The drift on the surface
- The spread on the surface
- Evaporation
- Dissolution
- Chemical reactions and other conversion processes

Various laboratory models have been developed (e.g. Ref. 7), but very few have been validated against real spills under operational conditions at sea.

Simple forecasting models have been developed for spills of chemicals that float on the water surface. For the sake of simplicity the spills are supposed neither to evaporate nor dissolve. This principle can also be used for manual calculations and is briefly described below.

Forecasting the spread on water surface (Figure 1-13, Method F2)
Applicable for Groups FE, FED, F and FD (all Groups with F)

Figure 2 - 4 shows how a floating chemical slick's drift can be calculated by means of a vector diagram in the same way as oil spills. However, most chemical spills belonging to the above mentioned Groups, except for F, will disappear by evaporation and/or dissolution within roughly 10 hours.

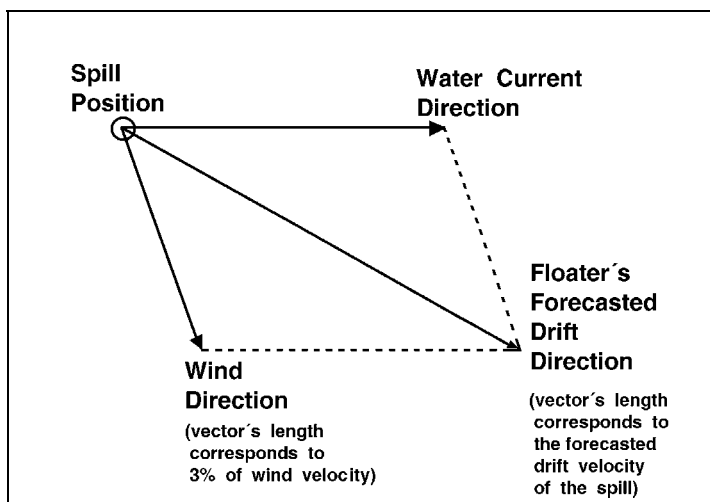


Figure 2 - 4

2.4 Dissolved spills in the water body

Forecasting the dispersion in water body

(Figure 1-13, Method P3)

The method described below is applicable to the Group D only.

If the current of the water body is slow and even the dispersion can be calculated very roughly according to Figure 2 - 5 and Figure 2 - 6. This method cannot be applied for stagnant (or almost stagnant water) or for chemicals where the density differ too much from that of the water. Nor can the method be used for very turbulent water.

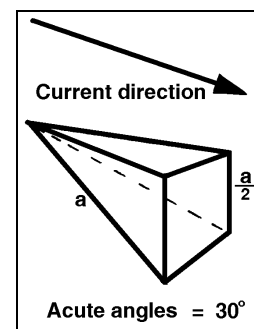


Figure 2 - 5

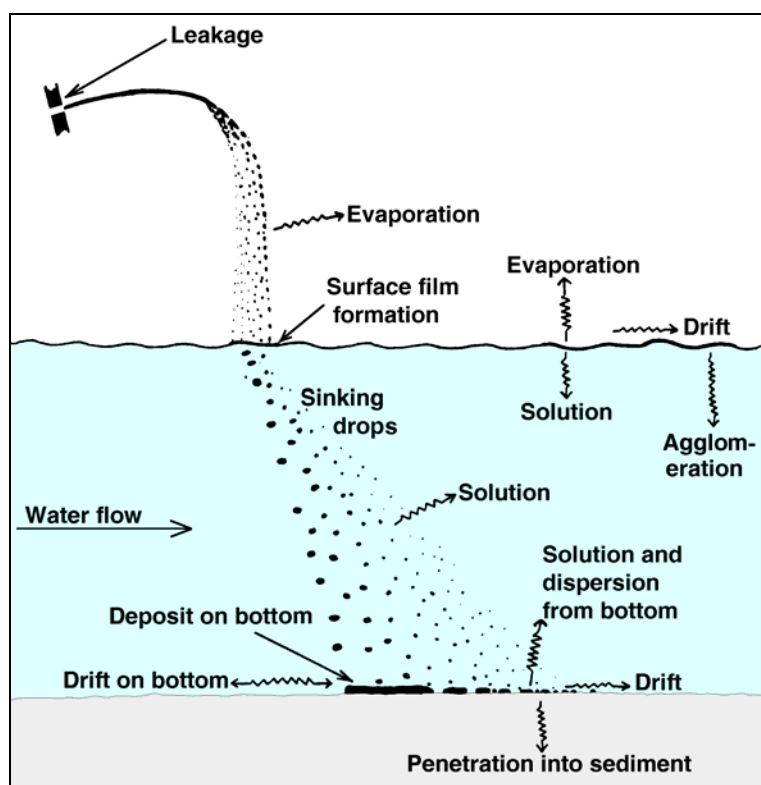
Release tonnes	Concentration 1 g/m ³		Concentration 1 mg/m ³	
	a	metres nautical miles	a	metres nautical miles
1	500	0.3	5,000	3
10	1,000	0.5	10,000	5
100	2,000	1	20,000	11
1,000	4,000	2	40,000	22

Figure 2 - 6

2.5 Sinking spills

It is very difficult to calculate the fate of a spill that sinks to the bottom. The reason for this is the number of parameters that influence the process (cf. Figure 2 - 7).

The chemical's density affects the velocity by which the chemical sinks to the bottom. Its surface tension and solubility (even if very low) influence its behaviour on the water surface as well as its dispersing and spread in the water body during its sinking towards the seabed. The water current together with the water depth and the chemical's density have a decisive importance for how long distance the chemical will move in the current's direction before it touches the bottom.



Picture source: P. Ashworth, UK

Figure 2 - 7 A sinking chemical and its behaviours (Ref. 8.)

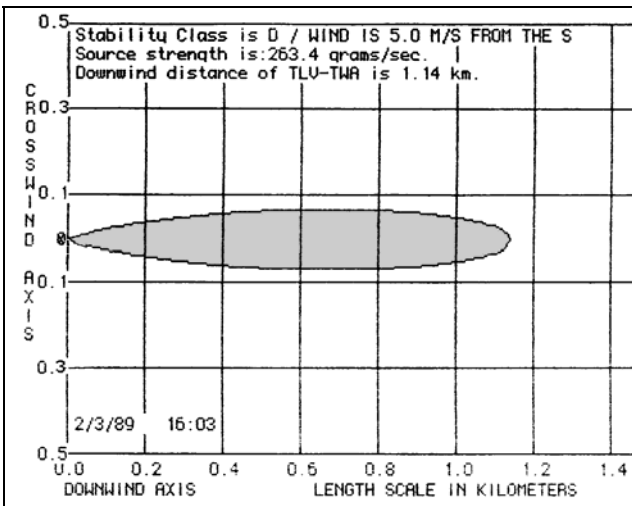
The chemical's duration on the bottom is among other factors dependant on its solubility. If the solubility is e.g. 1% or 0.001% it must obviously have a pronounced effect on its duration on the seabed. Also the existence of water currents close to the bottom influence the duration. The chemical may also penetrate into the bottom sediment. The degree of penetration depends on the sediment's properties and structure.

2.6 Forecasting modelling systems

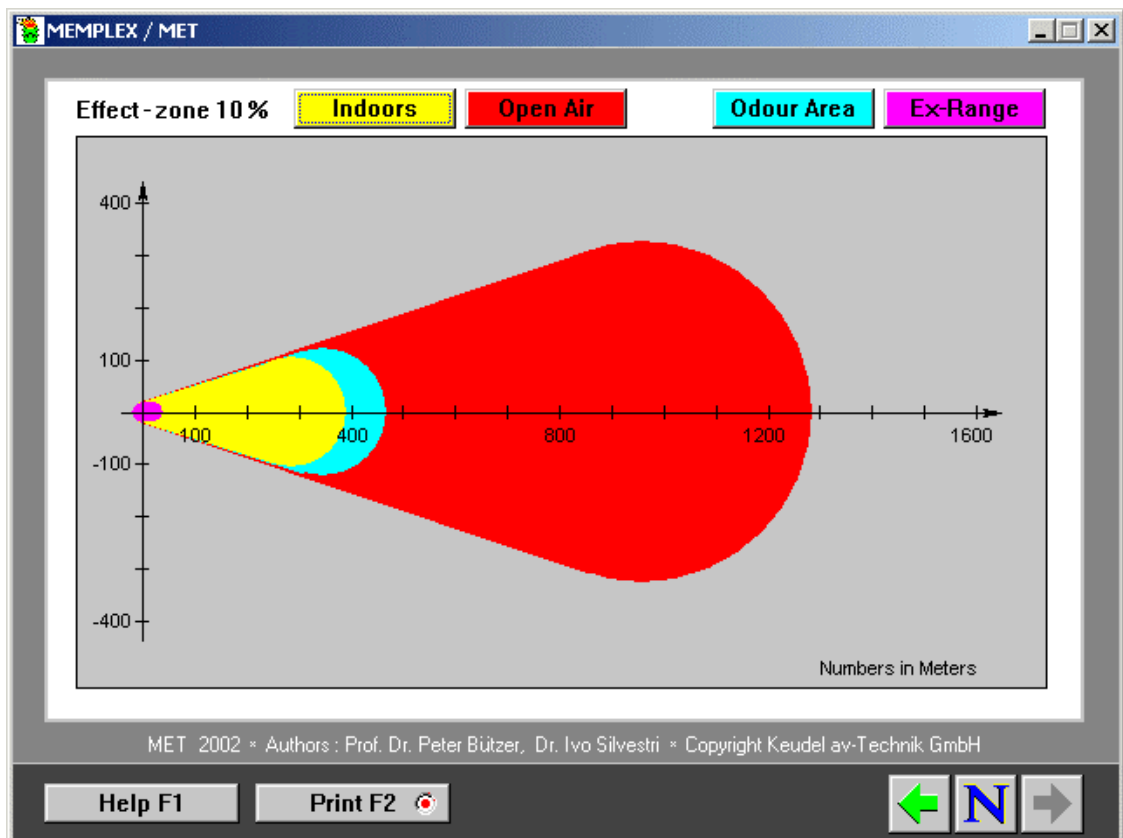
2.6.1 Introduction

There exist hundreds of highly sophisticated forecasting modelling systems for prediction of the drift and spread of chemical spills. Many of them are highly theoretical and not so easy to use. It is a difficult task to find models that might be usable in an operational organisation. A few known systems have been selected as examples below in Section 2.6.2.

2.6.2 Examples of computerized modelling systems

Forecasting computer model	
Name	ALOHA (Areal Locations of Hazardous Atmospheres)
Application	Gases
Information	<p>Emergency responders can use ALOHA to predict the behaviour of a chemical gas in the event of an accidental release.</p> <p>ALOHA is a part of the decision support system CAMEO (Computer Aided Management of Emergency Operations) developed by US National Oceanic and Atmospheric Administration (NOAA) in cooperation with US Environmental Protection Agency (EPA). (Ref. 6)</p> <p>http://response.restoration.noaa.gov/cameo/aloha.html</p>
	 <p>Figure 2 - 8 Graphical ALOHA description of a gas cloud dispersion in air.</p>
Properties	Can predict rates of chemical release from broken gas pipes, leaking tanks, and evaporating puddles, and can model the dispersion of both neutrally-buoyant and heavier-than-air gases.
Advantages	Free of charge. Technical assistance is available.
Limitations	Mainly aimed for gas releases over land under conditions where the wind speed is neither too low nor too high. Does not account for topographic effects. The earth is assumed to be flat and the mean wind speed and direction are assumed to be uniform at any given reference height.

Forecasting computer model	
Name	MET (Modells für Effekte mit Toxischen Gasen)
Application	Gases
Information	
<p>In accidents when hazardous gases are released into the air it is not satisfactory just to calculate gas concentrations in order to make rapid assessment of health risks and safety distances. The reason is that inhalation of high concentrations during short time will give the same dose as lower concentrations inhaled over a longer period. Calculation of safety distances should therefore be based on both concentrations and emission or spill rates.</p> <p>MET makes a dose-effect-coupling for effects of toxic gases and estimates risks of human injuries in the area in the wind direction of the accidental release.</p> <p>The dose as integral of concentration versus time is a good criterion in a model, since it diminishes one important but uncertain source term, the emission time. But doses also are not significant enough, since there is a further toxicological step to the main aim, to estimate the effect of toxic substances on the people in the surrounding area.</p> <p>MET consists of the following four main modules:</p> <ol style="list-style-type: none">1. The instantaneous release of toxic substances as a puff and the formation of a gas/air cloud mixture.2. The dispersion of the toxic gases and calculation of the concentrations as a function of the distance (half sphere box model).3. The transformation into doses.4. The dose/effect-coupling based on a modified pharmacological receptor theory to evaluate the health impact. <p>The input values that MET needs are: 1) escaped substance weight, 2) wind speed and 3) a threshold value for the substance. Other parameters are automatically provided by the system in order to calculate hazardous distances.</p> <p>MET has modules for simulations of 1) the washout effect of the cloud by rain, 2) the influence of a simultaneous fire and 3) the dispersion characteristics of heavy gases.</p> <p>The model is stable to the large variations of the toxic values, since it can integrate several different values. In addition the lower explosion limit is used to calculate the size of an explosive mixture of a substance and air. The effects on mixtures of substances e.g. from fires can also be calculated.</p>	



Picture copyright: MEMPLEX Keudel GmbH

Figure 2 - 9 Graphical MET description of a gas cloud dispersion in air.

Values to be entered

No fog	More than 50% clouded sky	Air pressure: 750 hPa
No fog on ground	Day	Half-year winter
Few rain	Medium fire	Country
Wind noticeably in the face, leaves rustles, vanes are moved by wind		
Instant release	Wind direction : 90 °	
Mass : 1800 kg	East	

Scenario **Default Values**

Methyl isocyanate or methyl isocyanate solutions

Calculated value for effect - zone 10 %

	Indoors	Open air	
Distance :	390 m	1290 m	Point of contact : 150 m
Cloud width:	210 m	650 m	Odour limit : 470 m
Time of entry:	2:40 min	8:30 min	Explosion limit : 40 m

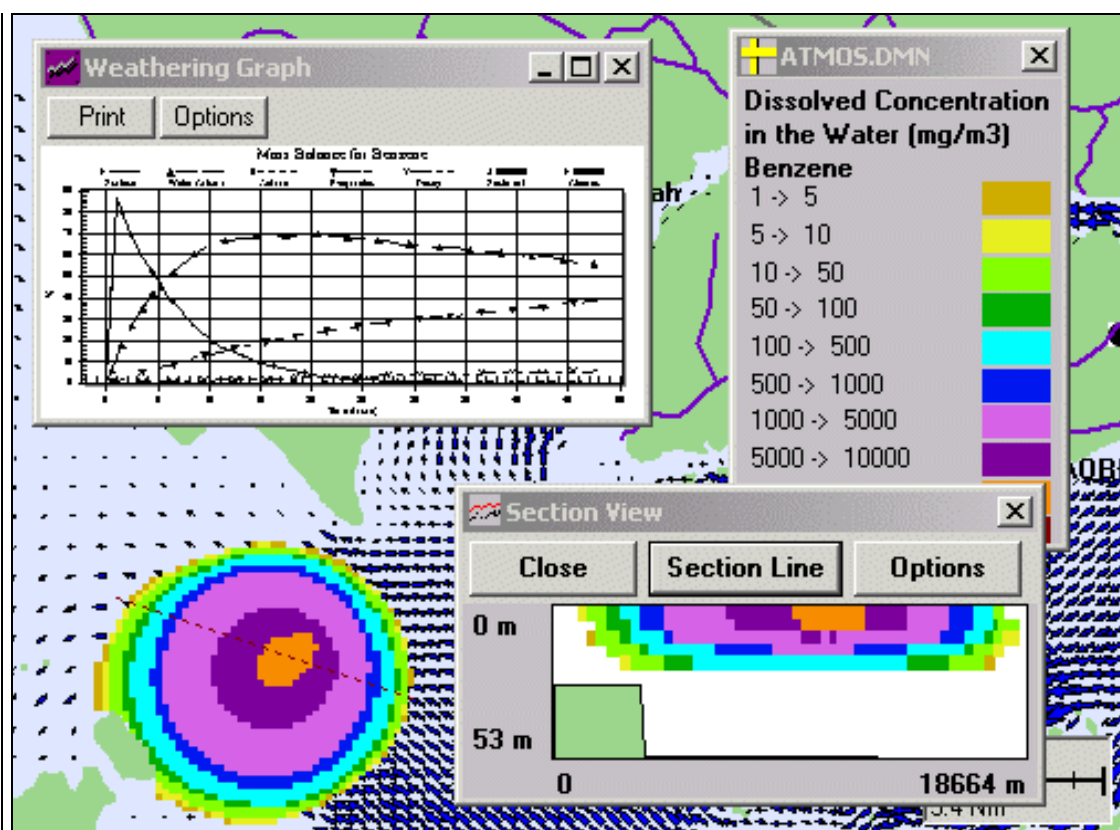
MET 2002 * Authors : Prof. Dr. Peter Bützer, Dr. Ivo Silvestri * Copyright Keudel av-Technik GmbH

Picture copyright: MEMPLEX Keudel GmbH

Figure 2 - 10 The data input menu of MET

Contact address: ISi Technologie GmbH Rorschacherstr.126 9450 Lüchingen Switzerland E-Mail: met@isitech.com Website: www.memplex.com	
Properties	Can predict hazardous distances of chemical releases.
Advantages	Technical assistance is available.
Limitations	Mainly aimed for gas releases over land under conditions where the wind speed is neither too low nor too high. Does not account for topographic effects. The earth is assumed to be flat and the mean wind speed and direction are assumed to be uniform at any given reference height.

Forecasting computer model	
Name	CHEMMAP
Application	Floaters, dissolvers, and sinkers
Properties	Predicts the dispersion and fate of marine chemical spills.
<p>Information</p> <p>CHEMMAP is developed by Applied Science Associates, Inc. (ASA), Rhode Island, USA.</p> <p>CHEMMAP predicts the likely trajectory and fate chemical spills in the marine environment. The system is particularly suited to contingency planning and emergency response for spills of chemical cargoes from ships but may be applied to any chemical discharge. The system contains GIS and a 3D spill model that predicts the movement of chemicals in the water. The model relies on environmental data such as wind and currents, physical data such as the proximity of shorelines, and chemical data that define the chemical's properties. CHEMMAP includes a biological effects model which evaluates the effects of chemical spills on fish, shellfish and wildlife.</p> <p>CHEMMAP incorporates a number of model components including:</p> <ul style="list-style-type: none"> - simulation of the initial release and plume dynamics of a product lighter or denser than water - slick spreading and transport of floating materials - transport of dissolved and particulate materials in three dimensions - evaporation and volatilization - dissolution and adsorption - sedimentation, resuspension and degradation <p>The model uses physical-chemical properties to predict the fate of a chemical spill. These include density, vapour pressure, water solubility, environmental degradation rates, adsorbed/dissolved partitioning coefficient (K_{OC}), viscosity, and surface tension.</p> <p>CHEMMAP has its own database of 900 chemicals with physical and chemical data properties. A software link is optionally available to a database of more than 40,000 pure substances and 75,000 common mixtures. The latter database also provide guidelines for how to determine the severity of the risk to health, how to handle a spill, how to store and transport chemicals, how to dispose of chemicals, what to do if a chemical catches fire and how to plan for an emergency response.</p> <p>Figure 2 - 11 shows the modelling of an instantaneous release of benzene (10,000 metric tons) at the water surface. The plume display is the Vertical Maximum Dissolved Concentration of Benzene in the water column (mg/m³) 40 hrs after the initial release. The colour-coded legend is located to the right of the plume with a cross section showing the plume in 3-dimensions below the legend. Above the plume is a graph of the mass balance that displays the percent of chemical that has surfaced, evaporated, in the water column, in or on the sediment and what has gone ashore over time.</p>	

**Figure 2 - 11***Picture source: Applied Science Associates, Inc.*

Contact address: Applied Science Associates, Inc.
 70 Dean Knauss Drive
 Narragansett, Rhode Island 02882-1143, USA
 Tel: +1 401 789 6224
 Fax: +1 401 789 1932
 Email: asa@appsci.com
 Web page: www.appsci.com

Advantages Integrated with a database of 900 chemicals. Includes a biological effects model which evaluates the effects of chemical spills on fish, shellfish and wildlife.

Limitations CHEMMAP is so far (January 2002) not validated with any field tests but the developers plan to do so in the near future.

Forecasting computer model

Name ChemSIS (Chemical Spill Information System)

Application Floaters, dissolvers, and sinkers

Properties Predicts the dispersion and fate of marine chemical spills.

Information

Provides information on the movement of spilt chemicals within the environment and their behaviour under the influence of wind, waves, current flows etc. Performs three-dimensional modelling of the chemical spill's dispersion. Involves prediction of large scale evaporation resulting in a vapour cloud as well as insoluble chemicals that can sink to the seabed. Covers chemicals that form surface slicks or disperse or dissolve within the water column.

ChemSIS has been jointly developed by BMT and AEA Technology plc. The new system is designed to form part of a tailored package of support for chemical spill and as such is supported by 24 hour cover (through the National Chemical Emergency Centre at AEA) and the availability of a wide range of chemical spill response services. ChemSIS, in common with all BMT's applications, has been developed under the Visual Marine Information Systems framework and therefore integrates directly with any existing systems such as oil spill or search and rescue (Ref. 50).

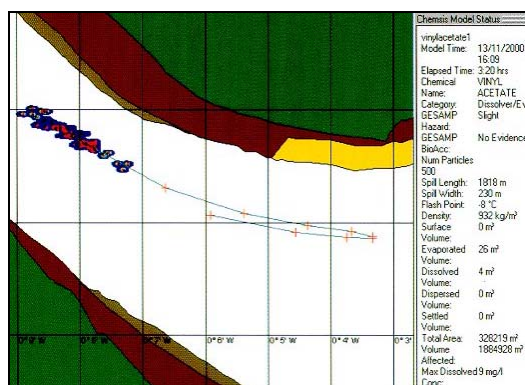


Figure 2 - 12

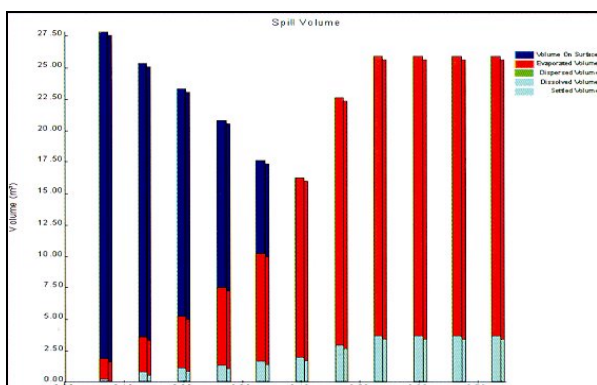
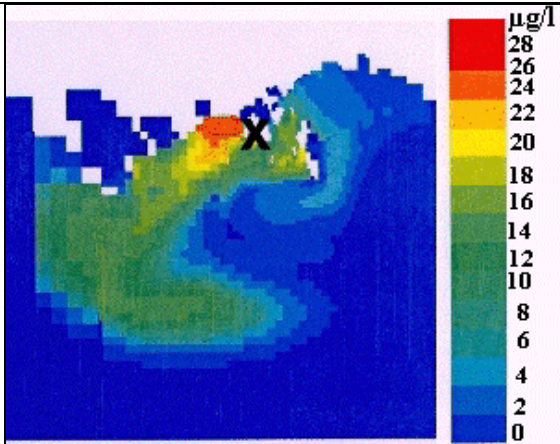


Figure 2 - 13

A modelling of a spill of 30 m³ vinyl acetate where Figure 2 - 12 shows the spill's trajectory after 3:20 hrs (spill size 230 x 1,818 m) and Figure 2 - 13 shows the degree of evaporation (26 m³) and dissolution (4 m³) after the same time and during intervals.

Contact address: See Ref. 50.

Advantages The developers of ChemSIS claim that it is the only chemical spill model available in the world that is validated under realistic field conditions.

Forecasting computer model	
Name	3D Transport and Water Quality Model
Application	Dissolvers and sinkers
Properties	<p>Calculates the drift and spread of chemical spills in the aquatic environment. The model takes the following processes into account:</p> <ul style="list-style-type: none"> • Spill volume and concentration • Water currents • Sinking, dispersion
<p>Information</p> <p>Figure 2 - 14 shows the modelled distribution four weeks after an experimental release of 100 tons of a low-toxic emulsifier <i>nonyl phenol ethoxylate</i> (water solubility appr. 10 g/l) in the sea off the Finnish coast in the Gulf of Finland.</p> <p>The spill size is 20 km across and the predicted and verified concentrations range from 26 µg/l down to 2 µg/l at the lower edges of the spill. The release site is marked with X.</p>	 <p>Figure 2 - 14</p>
<p>The "3D Transport Model" has been developed in Finland by the National Board of Waters and the Environment and the Finnish Environment Institute (Ref. 9 and Ref. 10).</p>	
<p>The "3D Transport Model" is available at:</p>	
<p>Finnish Environment Institute P.O. Box 140, FIN-00251 Helsinki Finland</p>	<p>Operational contact point Maritime Rescue Coordination Centre (MRCC) Turku, Finland</p> <p>Phone (24h): +358 204 1000 Fax: +358 2 250 0950</p>
Advantages	This model is primarily aimed for the evaluation of ecological changes in coastal waters. In this context it is used for simple three-dimensional drift calculations of water-soluble chemical spills.
Limitations	When used by itself this model cannot predict the transport and spreading of substances due to the wind, waves, turbulence and sea currents. These parameters must be estimated or calculated by a three-dimensional hydrodynamic model.

3 Monitoring and body protection

3.1 Gas monitoring by portable instruments

3.1.1 Introduction

Purpose of monitoring

In chemical accidents it is crucial to monitor the air for concentrations of hazardous substances. The aim of gas monitoring is to assess both toxic and fire/explosion hazards as well as map the area where unprotected personnel should be evacuated and judge the appropriate level of body protection for response personnel. On some occasions the read-out values can be used directly for designing risk areas (cf. Figure 3 - 1). In other circumstances the instruments can be used to check risk areas that are already assessed or defined according to some calculation method or forecasting model.

The most difficult measuring task on a site of a chemical accident is to make rapid identification of unknown airborne substances by means of portable instruments. Such work requires sophisticated instruments and trained expertise often not available when the first risk assessment is going to be made. Proper use of portable gas monitoring instruments generally require exact knowledge of the gas identity. Luckily this is often the case. Especially when a single chemical substance is involved, its identity is often known to the responders.

Monitoring instruments

In the world market there are hundreds of manufacturers offering thousands of different models of hand-held, portable, transportable or mobile gas detection and monitoring instruments that can be used during chemical accidents for risk assessment and evaluation. It is a rapidly developing market and it is difficult to give good advice on particular brands and models of instruments. Therefore this Chapter is limited to rather brief discussions on essentials in this field. Ref. 51 is an example of a broad overview of principles of hazardous gas monitors and serves as a guide to the selection of types of instruments.

Calibration

Many instruments require calibration before use! It is therefore crucial to follow the instructions carefully in this respect.

3.1.2 Trace gas monitoring

The main objectives of trace gas monitoring in case of a chemical accident are to find dangerous locations of a toxic gas contaminated area and assess the outer limits where it is reasonably safe for unprotected personnel. This type of instruments must be able to detect very low concentrations of hazardous gases (ppm-levels).

Examples of types of hand-held or mobile trace gas detection and monitoring devices:

- ♦ Gas detection tubes
- ♦ Semiconductor instruments
- ♦ Photoionization instruments
- ♦ IR trace gas detectors
- ♦ Portable gas chromatographs
- ♦ Mobile mass spectrometers

Gas detector tubes, semiconductor instruments and some photoionization instruments are relatively simple hand-held devices. Note that these instrument cannot be used for

accurate readings. The results are approximate. The monitoring should be performed according to section "Performance" below.

Portable gas chromatographs and mobile mass spectrometers are examples of more sophisticated instruments. These instruments are miniaturized and automatized laboratory equipment. They generally give rather accurate readings but require skilled personnel to handle.

Performance

Monitoring should be performed by personnel, equipped with breathing apparatus, trained in monitoring instruments and familiar with their functioning.

The measurements should be carried out from outside (gas-free area) inwards to the dangerous area. The position, where the first recording is noticed, is the fringe of the evacuation area. By doing further monitoring around the place of the accident, a map of the evacuation area can be drawn.

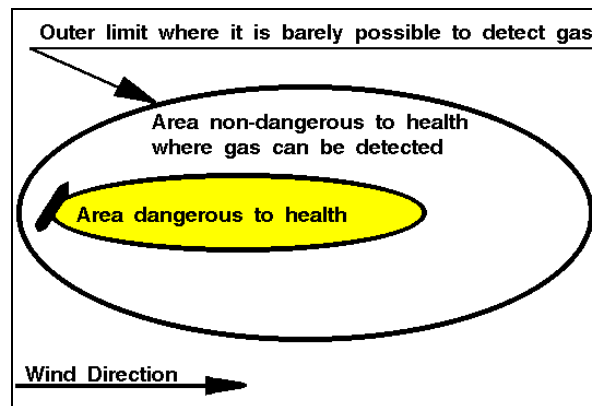


Figure 3 - 1 The outer limit of measurable concentrations and the area of gas concentrations which are dangerous to health

However, it should be emphasized that a gas cloud in the reality often doesn't give the uniform and smooth curves as shown in Figure 3 - 1. The boundary line, however, should be levelled along the outermost gas registrations.

Gas clouds often move irregularly due to the air turbulence and other environmental conditions. One extreme example of this is the chlorine gas cloud described in subchapter 2.2.

If no monitoring device is available, a safe evacuation area must be established around the scene of the accident, initially with a great margin of safety until more information can support a change of the judgement.

3.1.3 Flammability risk monitoring

Personnel who are using instruments to assess flammability/explosibility risks should fully understand the meaning of the concepts LEL/LFL and UEL/UFL. The objective of flammability (or explosive) risk monitoring is to assess the outer limits of a flammable gas contaminated area where it is reasonably safe regarding ignition. This type of monitoring should not be confused with trace gas monitoring. Toluene could be taken as an example. A safe toluene concentration regarding flammability risk is 1,000 ppm (which is 10% of the Lower Explosive Limit for toluene) while a safe health risk value for toluene regarding inhalation is only a few ppm which can only be measured with trace gas detectors.

Examples of types of flammable gas detection and monitoring devices are **explosive meters** and **combustible gas detectors**.

3.1.4 Oxygen-Deficient Air Monitoring

The oxygen level in confined spaces, such as cargo holds or tanks, can decrease because of work being done, such as welding, cutting, or brazing. It can also be decreased by oxygen-consuming reactions (metal rusting or cargo oxidation) or through microbial action (fermentation).

The oxygen concentration is also decreased if air is displaced by another gas, such as inert gas, carbon dioxide, nitrogen or hydrocarbons. If such a gas causes total displacement of oxygen, an unprotected person will rapidly become unconscious and die.

Oxygen-deficient means that there is not enough oxygen in the space to safely breathe. Normal fresh air contains 20.8 percent oxygen compared to less than 19.5 percent in an oxygen-deficient atmosphere. Air that has less than 10 percent oxygen can rapidly cause unconsciousness and levels below 8 percent can quickly cause death.

The objective of oxygen-deficient air monitoring instruments is to assess the outer limits of an oxygen deficient area where it is reasonably safe for unprotected personnel (Oxygen concentration above 19.5%). Any atmosphere with less than 19.5% oxygen should not be entered without an approved self-contained breathing apparatus (SCBA).

Examples of monitoring devices are chemical celloxygen meters.

3.2 Monitoring the water column

Monitoring the dispersion of chemical spills in the water body is often performed by taking water samples with hand-held devices at various positions and analyzing the samples for the actual chemical.

Sometimes the analyses can be made by portable equipment, but on many occasions the samples must be carried to stationary laboratories. Well-equipped portable laboratories exist which can be placed close to the site of the accident (cf. Ref. 52 and 53).

Monitoring can be achieved in some systems by probes containing parts of the analytical equipment that can perform the analyses more or less automatically. The probe is manually submerged or is towed (cf. Figure 3 - 2). Selection of measurement principle and monitoring equipment is based on the type of spilled chemical.

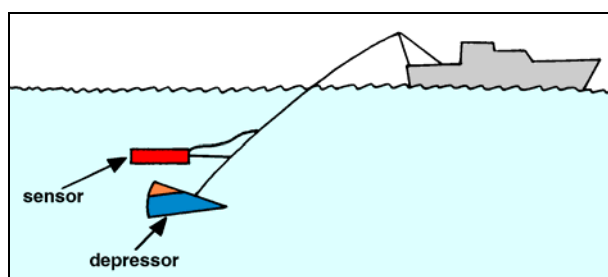


Figure 3 - 2 Monitoring the water body by a towed probe.

The physical principle of measurement may be for instance pH, light absorption, electrical conductivity or turbidity.

Low concentrations of many organic substances (e.g. hydrocarbons or halogenated hydrocarbons) may be very difficult to measure with portable equipment. However, in recent years different types of sophisticated active-service equipment have been developed capable of monitoring such substances in low concentrations. One example of equipment is based on enzymatic techniques (Ref. 54). Such monitoring must often be carried out by specially experienced personnel.

3.3 Monitoring surface spills

It is well known that oil spills on the water surface can be detected and monitored by means of various types of airborne remote sensing instruments. Oils spills are often rather viscous and form relatively thick (> 1 mm) layers that change the physical properties of the water surface and make them possible to be monitored by remote sensing techniques. But, on some occasions, even very thin oil films (< 0.1 mm) can be registered by certain instruments and thus also floating chemical spills which most often form thin films on the surface. Such thin films damp the sea surface's capillary waves, thus reducing the intensity of the backscatter caused by e.g. a Side-Looking Airborne Radar (SLAR). The smooth area of the surface slick will therefore appear as a relatively dark area in the SLAR image. The slick may also change the UV reflectivity of the surface and could be seen by an UV scanner. It can also change the surface's radiation temperature and be registered by IR instruments like an IR scanner and a Forward-Looking Infrared Imager or FLIR (an example of the latter is given in the Styrene Barge accident in Annex 3).

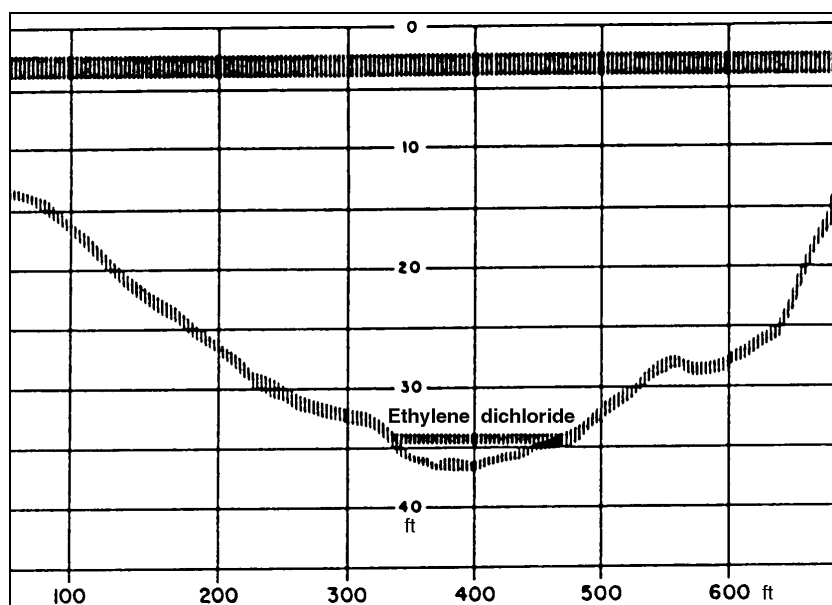
3.4 Monitoring sunken substances on the seabed

A chemical spill, that sinks to the bottom after an accident, will scatter more or less over a bottom area. Scattered spills on the seabed may be difficult to monitor. Yet it is important to map the spill in order to guide the responders.

A chemical on the bottom is always slightly soluble in water, though the solubility sometimes is very low. The solubility must be checked and the concentrations in the adjacent water must be monitored in order to evaluate the risks for environment, fishery, recreation, fresh water intakes, etc.

A liquid pool on the bottom has a phase boundary surface which can be recorded by an echo-sounder.

Figure 3 - 3 shows an echo-sounder recording of a pool of 1,300 cubic metres of sunken ethylene dichloride at the depth of 12 metres. The extension of the pool was about 40 m.



Picture source: A. Meyer et al.

Figure 3 - 3 Echo-sounder recording showing a pool of released ethylene dichloride

Other types of recordings and more detailed mapping can be done by using divers and/or submersibles (cf. subchapter 6.7).

3.5 Miscellaneous monitoring methods

Needs may arise on certain occasions to co-operate with special expertise to carry out various kinds of sampling and monitoring to assess the degree of harmful environmental interference or impact by a chemical pollutant. Examples are monitoring concentrations of chemicals in marine organisms and bottom sediments.

On rare occasions very unusual substances may have to be monitored, e.g. radioactive or infectious substances, chemical or biological warfare agents, etc. Highly specialized personnel must be engaged for such work.

Extensive trials have been made utilizing dogs to trace various chemicals (Ref. 55, 56 and 57). That this principle, "canine olfaction", is regarded as serious is shown by the fact that US Environmental Protection Agency has completed a research project in this field (Ref. 56). This project showed that dog's ability to detect airborne traces of chemicals was better than the trace gas monitoring instruments used for comparison.

3.6 Levels of body protection during chemical accidents

When response activities are conducted where atmospheric contamination is known or suspected to exist, personal protective equipment must be worn. Personal protective equipment is designed to prevent/reduce skin and eye contact as well as inhalation or ingestion of the chemical substance.

Protective equipment to protect the body against contact with known or anticipated chemical hazards are divided into four categories Level A – D. These levels are briefly indicated in Figure 3 - 4 below and are specified in some detail in Annex 5.

Level	Remark
A	Highest level of respiratory, skin, and eye protection
B	Highest level of respiratory, skin, and eye protection; The breathing apparatus is worn outside the suit
C	The types of airborne substance is known and the criteria for using air purifying respirators are met
D	A work uniform affording minimal protection, used for irritating contamination only

Figure 3 - 4

Level A protection should always be used if the airborne substances are unidentified. The type of environment and the overall level of protection should be reevaluated periodically during the operation when more information is gained about the hazards.

4 Sampling

4.1 General

4.1.1 Purposes of sampling

General

Sampling and subsequent analysis shall answer questions regarding spills' origin as well as their properties and effects. To accomplish this, samples should be taken for several different purposes, which are dealt with in this Chapter.

Some spills may involve contacts and co-ordination with other countries regarding sampling and analysis. Occasionally, foreign agencies should be contacted to exchange samples, analysis results, examination reports, etc.

The following list describes eight purposes of sampling after incidents or accidents involving hazardous substances or packaged dangerous goods. Most often only a few of them are appropriate in a specific case.

1. **Occupational safety**
When necessary, the spill should be examined (analysed) to establish whether there are any health risks for the response personnel. The substance may be flammable and cause fire and/or explosion, or may be toxic and cause danger to health if inhaled or exposed to skin.
2. **Penal liability**
The responsible polluter should, if possible, be identified and be charged for the spill. This can be done by comparing chemical analyses of samples from the spill with samples from suspected sources. If identity is established between the spill and a suspected source, this can help to identify the polluter.
3. **Polluter's economical liability**
The results of sampling have often been used as a basis for compensation claims against the polluter. These claims may concern costs associated with response and cleanup measures, or damage to property, fishery, recreational areas, etc. Above all, it is important to tie the suspected polluter to the damage in order to confirm the claims.
4. **Spill response planning**
On some occasions, special analyses can give important information that can support planning of response and cleanup work. It is important to study chemical and physical property data of the substance when selecting equipment and methods as well as safety routines for the response operation.
5. **Short term environmental protection**
The substance's acute deleterious effects on the environment can vary considerably depending on its properties. Many chemicals show acute toxic effects to the marine life and some substances have a tendency to smear beaches, plants and animals. Besides identifying the substance it may be necessary to sample and analyse the water column, sediment, organisms, etc.

6. Long term environmental protection

Certain substances may cause long term deleterious effects on the environment, and some species may be knocked out, or the environment be polluted for a long time. Assessment should be made to judge how the environment can be restored. It may be necessary to sample and analyse the substance itself, as well as water, sediment, organisms, etc.

7. Information service

Many and sometimes tricky questions are asked about the substance's properties and effects, especially when facing a large or hazardous spillage. In such cases it is important to give rapid and correct information in order to reduce anxiousness and circulating of rumours. Sampling and analysis can thereby provide the basis for information to be given and for the choice of information channels. When informing the public, and those who are directly affected by the spill, it is important to account for certain data, for example:

- ♦ the spill's origin and extension
- ♦ the substance's properties and spread in the environment
- ♦ effects on human and environment
- ♦ consequences for various parties and bodies
- ♦ ongoing work regarding response, cleanup and disposal

8. Disposal

The selection of techniques for the subsequent disposal is based on the type of substance and its properties, and the spill's volume. Many disposal plants are specialized for certain hazardous materials and cannot process other types.

4.1.2. Responsibilities during sampling

Spills occur every day in the marine as well as inland aquatic environment. Although most of the spills are very small, they still often require sampling to get a chance of linking them to the responsible polluters and assess the damage to environment. It is therefore important to trace all conceivable polluters as soon as possible. There is a great need for co-ordination as the sampling activities for spills and suspected sources may go on simultaneously at different places. This work may very well be performed by a **permanent Sampling Co-ordinator** within the environmental response organisation. This Co-ordinator should be subordinated to the District Chief of the Environmental Response Organisation. During the Organisation's everyday work the Sampling Co-ordinator keeps record of spill samples from various sites and initiates sampling on board suspected sources when overlooked by the field officers.

The sampling activities may increase considerably during more significant accidents involving spills of hazardous materials. Many different samples may be taken for several different purposes. Many authorities and institutions may be involved in the sampling activities and a confusing situation may arise where different bodies work, perhaps without being aware of each other. On such occasions, it is crucial to co-ordinate the activities to avoid duplication of work, as well as to avoid missing chances of important sampling. Such co-ordination could also promote prevention of anxiousness and circulating of rumours which often happen during major and hazardous spill accidents. In this situation, the Environmental Response Commander should appoint an **ad hoc Sampling Co-ordinator** to be responsible for the overall co-ordination of all sampling work during the run of the response operation.

If co-operation starts, during a major spill accident, between two or more different national response services, an agreement should be settled on a joint ad hoc Sampling Co-ordinator. The Sampling Co-ordinator should be responsible for the overall co-ordination of all sampling on land and at sea during the run of the response operation. When the accident response phase is finished, and the long-term cleanup work has started, the responsibility for sampling is normally handed over to the local Municipality. However, it is convenient that the original ad hoc Sampling Co-ordinator maintains the duty for sampling concerning the polluter's penal and economic liabilities.

The contact network for the Sampling Co-ordinator and various bodies is shown in Figure 4 - 1

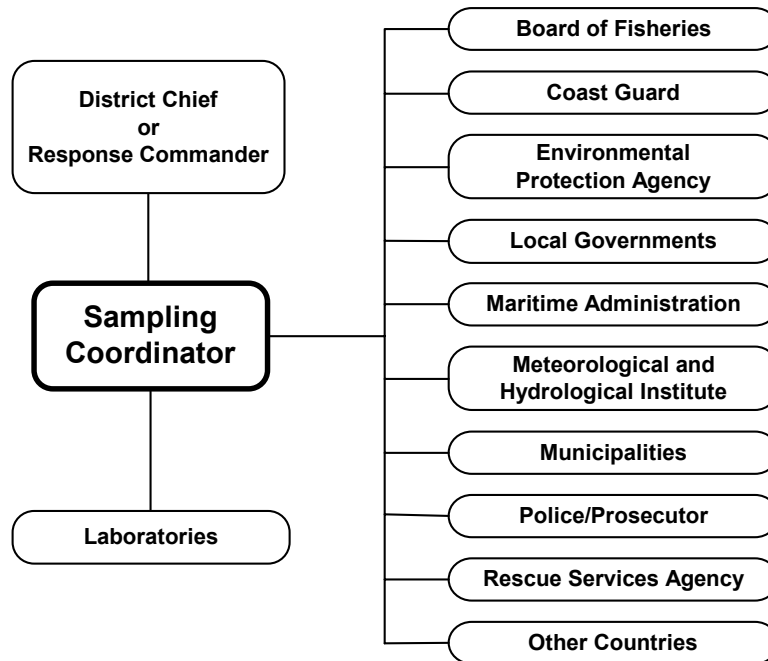


Figure 4 - 1

4.1.3 The duties of the Sampling Co-ordinator

1. Establish a plan for documentation of the sampling work.
2. Make arrangements for appropriate sampling if health risks are liable to occur.
3. Make sure that necessary samples are taken concerning extent and accuracy of both spill and contaminated items as well as suspected sources.
4. Judge if special examinations of the spill are needed to facilitate spill response measures.
5. Judge if short term and/or long term environmental impact may be expected. In such a case, contact appropriate agencies.
6. Judge if special examinations and analyses are needed when providing for general and specific needs for information.
7. Contact responsible bodies for transport and disposal. Check what special information is needed in this context and make arrangements for relevant analyses.

4.1.4 General checklist for sampling

1. Sampling actions on unknown materials should be taken on a “worst possible case basis”, i.e. if nothing is known whatsoever about the substance it should be considered as extremely hazardous and due safety precautions should be taken.
2. **All** spills encountered and **all** potential sources of spills should be sampled. It is important to take samples from both spill and source even on such occasions where it seems quite clear from where the spill originates. Use at first hand the type of sampling equipment and routines described in this Chapter.
3. Sampling procedures, which are connected to liability investigations, must be performed with great care and accuracy concerning spills as well as suspected sources. Every action should be taken to prevent a decrease in the samples' value as evidence.
4. If a spill has scattered on the water surface and only thin sheens remain, yet every possible effort should be made to take at least a small sample. No sample volume is too small to be shipped to the laboratory. The laboratory can often analyse very small samples, for example water samples that seemingly consist of pure water or sample pads that do not show any trace of substance.
5. Assistance should be received from appropriate expertise on occasions of hesitation. All sampling of chemicals on board vessels or in other sources should, if possible, be left to the crew or staff, or should be carried out in close co-operation with the crew/staff. Special safety precautions must be taken during sampling activities in atmospheres that might be explosive.
6. Samples and sampling equipment should be handled and stored so that the samples cannot be manipulated, mixed up, or else be contaminated by strange substances. Samples should be handled as legal evidence and should be kept in a “chain of custody” until identification and possible legal procedure has been completed. Therefore, always use a type of sealable and individually numbered safety bags described later in this Chapter.
7. A bottle containing a sample should not be placed in the sampling kit together with the clean equipment. Reusable sampling equipment should always be very carefully cleaned, and put into clean plastic bags, before restoring in the sampling kit case. Used sample bottles must not be used again - not even after careful washing.
8. Make notes of all relevant information about samples and sample sites. Use a miniature camera or a video camera to record observations which are considered important for the investigation.
9. The samples should be immediately sent to the Sample Co-ordinator. Quick handling of samples is important. If the transmittal is delayed the samples should be kept under a temperature of less than +4°C

10. Consumed equipment should be replaced as soon as possible so that the sampling kit case always is fit for use and so that new samples can always be quickly taken, packed and sent away.

4.1.5 Handling of spill information

A whole chain of activities leads to the information to be presented about the spill. This chain consists of:

- ♦ Sampling
- ♦ Sample keeping and transmittal
- ♦ Identification, labelling, documentation
- ♦ Chemical, physical and biological analyses
- ♦ Judgement of the analysis results
- ♦ Presentation of the analysis results

Each step must be taken with care and accuracy. This is a prerequisite for a compilation of an information report which is as capable as the circumstances allow. Points to be observed during sampling and subsequent handling of samples, are for example:

- ♦ Several samples must be taken from spills covering large areas or divided in several locations.
- ♦ Sampling in a suspected source must be performed in such a careful way that the suspected polluter with certainty can be tied to, or cleared of, the spill.
- ♦ All samples must be labelled so that they can be unmistakably referred to the sampling points.
- ♦ Sample containers must be labelled, closed and kept in such a way that any supposition on confusion or manipulation can be excluded.
- ♦ All sampling documentation, as well as other evidence, must be available during the investigation, but also be protected from loss, confusion and manipulation.
- ♦ Continuing record-keeping must be made regarding all transmissions of samples, other evidence and documentation between officials.

The Sampling Co-ordinator is responsible for transmission of samples to the appointed laboratories.

4.2 Sampling chemical spills on the water surface

4.2.1 Thick waterborne layers, small globules and balls

If possible, focus the sampling on thick parts of the spill. If the spill is large it is important to take samples in several positions of the spill to get a representative sample selection.

Globules, balls and thick parts can often be sampled directly by a sample bottle. Fill the bottle with as many balls as possible or skim substance from the surface by repeated sweeps with the bottle. Remove the water which has entered the bottle (see Section 4.8.2 item 2). Then continue to skim substance and try to get as much as possible of dewatered chemical (a few millilitres are better than nothing).

Floating films (thickness greater than appr. 1 mm) or balls on the water surface can with advantage be sampled by a polyethylene cornet (cf. Figure 4 - 2). The cornet should have a wide hem into which a metal ring could be threaded. First cut off the tip of the cornet as shown in the picture.

A holder is fitted onto the ring and by means of this holder the device can be fastened to a boathook or the like.

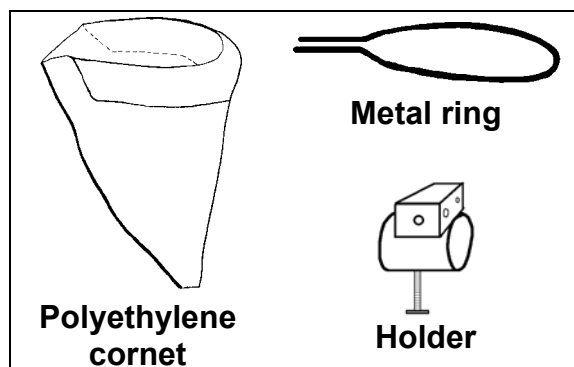


Figure 4 - 2

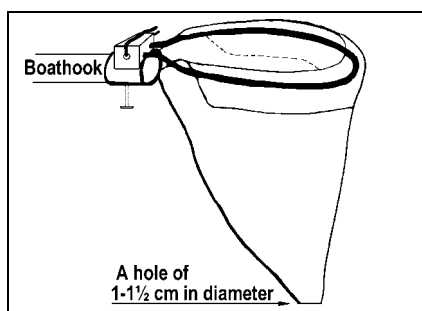


Figure 4 - 3

The assembled device is swept through the spill so as to skim as much substance as possible.

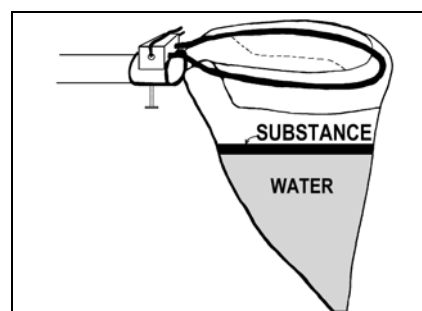


Figure 4 - 4

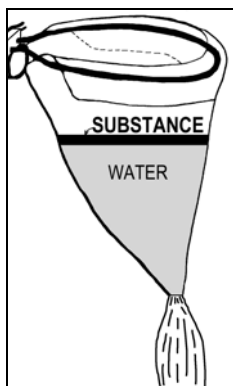


Figure 4 - 5

The water in the cornet is slowly let out and the drainage is stopped when the last drop of water has escaped. Then the substance in the cornet is filled into a 100 ml wide-neck sample bottle. The same procedure is then repeated once or several times until the bottle is approximately three-quarters full of dewatered substance. *N.B. Do not fill the bottle to a higher level than up to 2 cm below the lower edge of the lid.*

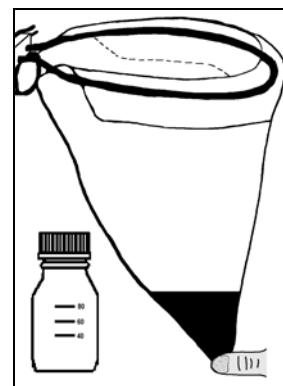


Figure 4 - 6

4.2.2 Thin waterborne films (sheens)

A special teflon pad may be used if the substance film on the water surface is very thin (thickness less than appr. 1 mm). The pad material should be teflon because other materials may interfere with the succeeding analytical process in the chemical laboratory.

A practical arrangement for handling a pad is shown in Figure 4 - 7. Great care must be taken during sampling to avoid contamination of the sheen by traces of substances from the sampling vessel or from other sources. The pad should be swept in the spill many times until reasonable assurance is gained that the pad has absorbed at least an amount of substance enough for the analysis.

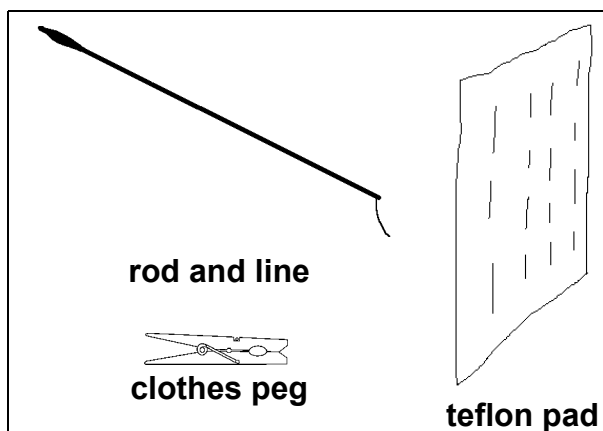


Figure 4 - 7

After a sufficient number of sweeps the teflon pad is carefully put into a sample bottle. The peg can be used to push the pad into the bottle. Another clean wooden peg of any kind can, if necessary, be used to assist in the procedure. It is important to avoid contact with any item that could possibly contain traces of strange substances.

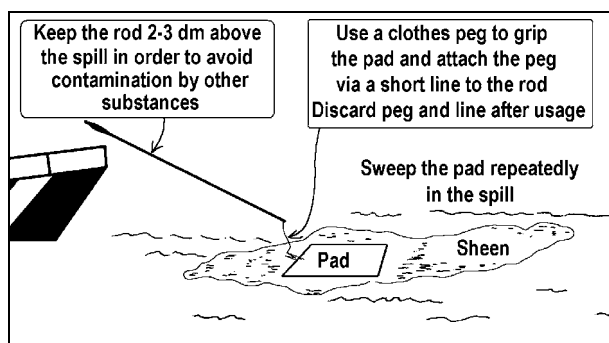


Figure 4 - 8

4.3 Sampling chemical spills in the water column

Chemical spills that disperse or dissolve in the water column can be sampled by ordinary water sampling equipment. There exist a great variety of such equipment. Bottles mounted in holders (Figure 4 - 9) may be used for sampling the upper 0-30 m water layers. Other sophisticated, more or less automatic devices (Figure 4 - 10) may be more suitable for taking samples at greater depths.



Figure 4 - 9



Figure 4 - 10

Picture source: HYDRO-BIOS GmbH

4.4 Taking samples from sunken chemicals

Sunken chemicals lying on the seabed are most often sparingly soluble or at least of rather low solubility. Sampling can be performed in various ways. In shallow water a SCUBA diver might be able to do the job with a sample bottle. However, due consideration must be given to the level of hazard of the substance and the diver's safety. See item 1 under Section 4.1.4 above.

An alternative sampling method on the seabed is to use a sediment sampler (Figure 4 - 11) of which there are many various types also for deep waters.

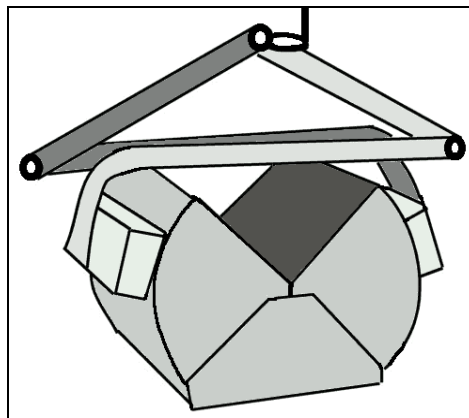


Figure 4 - 11 A Ponar sampler
(its width is appr. 20 cm)

4.5 Taking samples on beaches and from smeared animals

Take samples in every continuous slick. In a spill which is scattered over a long coastline as many samples should be taken to enable a mapping of the substance distribution on the shores.

The substance should be scraped off smeared items and transferred into sample bottles. Avoid, if possible, contamination in the bottles by sand, grass and other debris. In exceptional cases when it is difficult to obtain clean substance samples, it is acceptable to place small contaminated items (pebbles, small pieces of wood, etc.) in the bottles.

Never take whole animal samples, body tissues, etc. which may become rotten during shipment. Try to cut off small parts of smeared feathers, fur, etc. Put the material directly into a sample bottle.

4.6 Taking samples from packages

Different scenarios may arise that justify different approaches. Taking samples from damaged leaking containers with unknown contents require much higher safety levels than if the containers do not leak.

To draw hazardous samples from various types of containers require specialized skill and training. Emergency response personnel should not try to perform such sampling but call for assistance from chemical institutes or plants with special expertise.

4.7 Taking samples on board vessels

4.7.1 General

Samples must be taken on board ships observing appropriate caution in accordance with current safety regulations. During sampling on board ships the recommendations under Section 4.7.2 below should be followed carefully.

It is often difficult to obtain relevant samples on board suspected sources. Yet, it must be emphasised that it is of the utmost importance for a spill investigation that suspected sources of the spill are traced as far as possible and that reference samples are taken. Sometimes during sampling on board a vessel it is necessary to get assistance by the crew under control. However, it is quite wrong to accept unknown samples straight off which are handed over by representatives from the ship or the shipping company.

Use a miniature camera or a video camera to record observations which are judged to be valuable for the investigation.

It may be difficult to obtain samples from tanks on board ships without opening manhole covers or drawing off pipes or pumps. However, it is often possible to use sounding pipes with a sample collector and glass tubes according to Figure 4 - 12. It is used with a steel measuring tape equipped with a carbine hook and a ground wire.

A clean, unused glass tube is put into the sample collector which is hooked onto a steel measuring tape which must be grounded before starting the sampling. The sample is collected through a sounding pipe and transferred to a 100 ml sample bottle. The glass tube is discarded and the sample collector must be thoroughly cleaned!

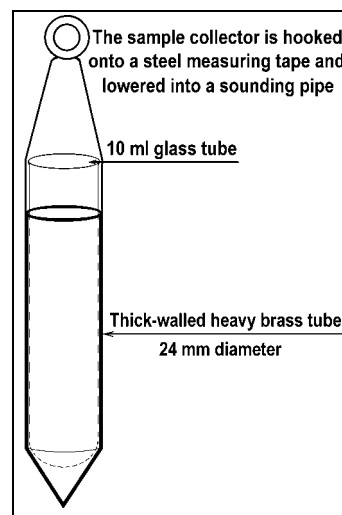


Figure 4 - 12

4.7.2 Advice and directions for safety routines

Directions must be acquired from the ship's officers regarding how sampling should be performed considering the current safety regulations on board the ship. Sampling in tanks and spaces within the ship's Hazardous Areas should in the first place be carried out by the ship's own crew. If the ship has sampling equipment of its own, this should be used on first hand. The sampling should be performed under supervision of the personnel which is responsible for the sampling. If this is not possible, sampling should be performed by means of external equipment only after approval by the ship's officers or by a ship-surveyor.

When samples are taken in tanks containing volatile noxious the following advice shall be observed:

- ♦ Level A protection shall be used (cf. Annex 5).
- ♦ Only one hatch at a time should be opened.
- ♦ One person should perform the sampling and another should supervise the sampler (safety guard). The latter shall observe the sampler's condition and

see to that he or she is taken away to a safe place if influenced by noxious gases (intoxication symptoms).

- ♦ Explosion proof equipment (EEx-marked) only, should be used.
- ♦ The sampler must not have loose items in the pockets. They might fall down into the tank.

During loading	Equipment made of metal for sampling and ullage-sounding must not be brought into the tank, or be left in the tank, during loading and within 30 minutes after loading has stopped. Examples of such equipment are steel measuring tapes and steel measuring sticks. Non-conducting equipment without metal parts may generally be used at any time. Cords, however, used for lowering equipment into tanks must be made of natural fibres (not synthetic materials).
----------------	---

After loading	Equipment made of metal for sampling and ullage-sounding can be used 30 minutes after loading has stopped. However, it is important that the equipment is firmly grounded to the ship's hull before it is brought into the tank. The equipment must remain grounded until it has been removed from the tank.
---------------	--

Miscellaneous	Sounding and sampling by means of pipes, designed for this purpose, is allowed at any time.
---------------	---

4.8 Handling of samples

4.8.1 Sample custody and documentation

Samples and sampling equipment should be handled and stored so that the samples cannot be manipulated, mixed up, or else be contaminated by strange substances. Samples should be handled as legal evidence and should be kept in a "Chain of Custody" until identification and possible legal procedure has been completed. Such a Chain of Custody can be maintained by means of durable (approved) sealable and individually numbered safety bags with e.g. three detachable adhesive number labels (see upper part of Figure 4 - 13) with identical number and the same as on the bag.

Each safety bag number is unique for one specific sample. The number is the identification of the sample. One of the detachable number labels shall be affixed onto the glass sample bottle label (Figure 4 - 14). The next number label shall be placed on the outer plastic jar (Figure 4 - 16) and the third label on the Letter of Request (cf. Subchapter 4.9).



Figure 4 - 13

A sample label (cf. Figure 4 - 14) shall be affixed to each sample bottle.

<i>(Space for a number label from an individually numbered safety bag)</i>		Sampling date:
		Judged date for spill:
		Sampling site:
<input type="checkbox"/> Spill <input type="checkbox"/> Ref. sample (e.g. from a ship)		Suspected source:
TEMP. Water °C:	Air °C:	Spill information (volume, extension, judged substance type etc.)
SAMP- Name: _____	Field unit: _____	
LER Phone: _____	Alt. phone: _____	

Figure 4 - 14

The following documentation is important when samples are taken and shipped:

- ♦ **A Letter of Request** with a specification of the request and information on enclosed samples (cf. Subchapter 4.9) . Necessary information in the Letter of Request and/or in the sample bottle label is the following:
 - District, sampler, unit
 - Date and position (or sampling site on board vessel) of sampling
 - Spill's volume/appearance, substance type
 - Suspected source
- ♦ **Sample labels** (cf. Figure 4 - 14) shall be affixed onto all sample bottles.
- ♦ **Number labels** from individually numbered safety bags (cf. Figure 4 - 13) shall be affixed onto all sample bottles.

4.8.2 Filling and labelling of sample bottles

1. As sample containers use 100 ml thick-walled wide-neck high quality glass bottles (Figure 4 - 15). A suitable inner neck diameter is 30 mm. The lid tightening should be of high quality. Use a new (unused) 100 ml sample bottle for each sampling site.
2. If possible, avoid getting water into the bottle. One method to remove water from the bottle is to screw on the lid and hold bottle upside down for a minute. Then let the substance float upwards to the bottom of the bottle so that the water can be drained by opening the lid carefully.
3. Do not fill the bottle to a higher level than to 2 cm below the lower edge of the lid. If the bottle is completely filled of cold substance it may later leak when the substance volume increases at room temperature.
4. Check that the bottle lid gasket is undamaged and that the lid fits tight. Carefully wipe excess substance and water from the outside of the bottle.
5. Affix a filled-in sample label (cf. Figure 4 - 14) onto each bottle.

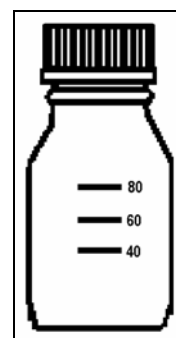


Figure 4 - 15

4.8.3 Packing of samples

1. A sample must be packed appropriately before it could be shipped to a laboratory for analysis. The sample is usually in either of the following forms:
 - ♦ Free substance
 - ♦ Sample pad containing substance from spill
 - ♦ Smear item (feather, piece of wood, stone, etc)
2. Allow excess water to drain off from the sample. Check that the sample does not contain animal tissue which might rotten during transport. Insert the sample into a sample bottle. The insertion of a sample pad can be facilitated by pushing the pad with the used clothes peg or a clean peg of any kind. Perform this without touching with fingers or contact with items that might contain disturbing contaminants.
3. Affix a sample label (Figure 4 - 14) onto the sample bottle (Figure 4 - 15) and a number label from an individually numbered safety bag (Figure 4 - 13).
4. Insert the bottle into the safety bag and seal the bag according to the bag's instruction.
5. Put the bottle package into a 600 ml plastic jar (Figure 4 - 16) which is used as an outer container. Affix the second number label onto the outside of this jar. Keep the third number label for the Letter of Request (cf. Subchapter 4.9).



Figure 4 - 16

Plastic jar used as an outer container for the sample bottle which is enclosed in a safety bag.

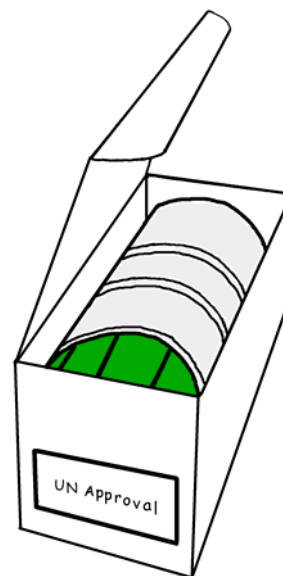


Figure 4 - 17

Cardboard box (with approval inscription) for shipment of the sample.

6. The samples should be sent immediately to the Sample Co-ordinator. A quick handling of samples is important. If the transmittal is delayed the samples should be kept under a temperature of less than +4°C. The Sample Co-ordinator watches the continued shipping of the samples.

7. The plastic jar with its content of a sample bottle inserted in a sealed safety bag (Figure 4 - 13) should be placed in a cardboard box, before shipment, as shown in Figure 4 - 17.

The whole packaging must be type approved for transport of dangerous goods and the cardboard box must wear an inscription which shows this approval (c.f. Figure 4 - 18) (cf. also Sections 6.1.2 and 6.2.2.1).

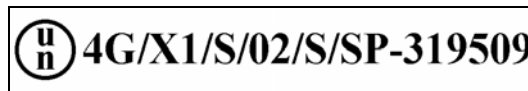


Figure 4 - 18

The following table shows the meaning of the codes in Figure 4 - 18:

	The United Nations packaging symbol.
4	Type of packaging (4 = box).
G	Type of packaging material (G = corrugated fibreboard).
X	Tested for packing groups I, II and III.
1	The maximum gross in kilograms for packagings intended to contain solids or inner packagings.
S	Intended for the transport of solids or inner packagings or, for packagings (other than combination packagings) intended to contain liquids, the hydraulic test pressure which the packaging was shown to withstand in kPa, rounded down to the nearest 10 kPa.
02	The last two digits of the year during which the packaging was manufactured.
S	The State authorising the allocation of the mark (S = Sweden).
SP	The name of the manufacturer or other identification of the packaging specified by the competent authority.
319509	Approval Certificate No.

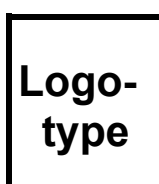
4.8.4 Shipping of samples

The Sample Co-ordinator collects all samples and fills in a Letter of Request which is sent to the laboratory together with the samples.

The Sample Co-ordinator should also call in special expertise if required from external institutes or laboratories to assist in the sampling activities.

Samples of many chemicals are to be considered as dangerous goods when they are shipped. However, if contained and packaged as described above, they can often be shipped as "limited quantities" which means simpler shipping requirements than for normal dangerous goods. IMDG Code rules as well as local regulations should always be followed.

4.9 Example of a form for Request for Analysis



Sending Unit

Date

Commanding Officer

To: Laboratory name and address

Request for analysis

Request analysis of the samples listed below

Sampling date: No. of samples: No. of pages:

<u>General information</u> (Occurred incident, weather, spill size, suspected source, judged substance type, etc.)	Number label from safety bag	Information which is not given on the sample bottle *

*Information: Sampler: Name/field unit
Spill : Latitude & longitude, and sampling site's geographical name
Ship: Ship name and sample site on board the ship

Signature

Name in block letters

Rank

5 Techniques for corrective response to accidents involving spills of hazardous substances in the marine environment

5.1 Gases and evaporators

5.1.1 Gases

Examples: Ammonia, vinyl chloride, chlorine, methane, propane, butane, LPG

General actions should be taken according to Subchapter 1.2. In order to perform these and other actions it is necessary to have knowledge about how various gases are stored and how they behave, as well as how they escape from the container and how they spread out over large areas.

Water sprays may be used on some occasions to:

- ♦ Wash down (knock down) water soluble gas clouds (cf. Figure 1-13, Method C1)
- ♦ Reduce the risk of fire and explosion in flammable clouds of gases, by cooling down hot surfaces or putting out sparks and suppressing flame formation
- ♦ Stop, steer or disperse gas clouds which are sparingly soluble or insoluble in water

At discharges of liquefied ammonia into water, part of the ammonia boils away very rapidly and moves in the wind direction as a dense, hazardous, white cloud. Approximately 60 % dissolves in the water when released above the surface and more than 90 % when released below. The dissolved ammonia forms alkaline ammonium hydroxide solution which is dangerous for the environment. Neutralizing agents should therefore be utilised to reduce environmental damage from ammonia discharges in confined, vulnerable water areas with low water turnover (cf. Section 5.3).

Dissolved ammonia forms a chemical equilibrium with water where most of the ammonia exists as ammonium ions NH_4^+ and hydroxide ions OH^- (Figure 5 - 1).

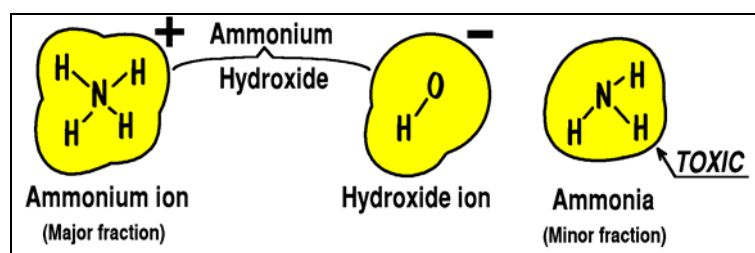


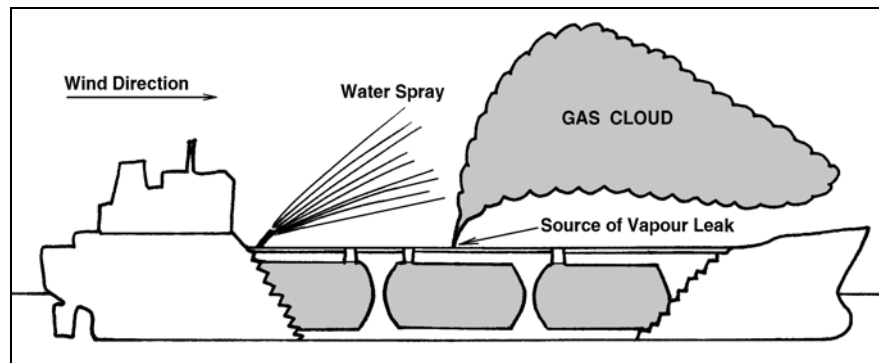
Figure 5 - 1 Dissolved ammonia in water

However, a minor fraction of ammonia is un-ionized (neutral) NH_3 and it is mainly this part that is responsible for the toxic effects on the aquatic organisms.

The fraction of un-ionized NH_3 increases with higher water temperature and higher pH, from e.g. 0.2 % at 10°C and pH 7.0 to 15% at 25°C and pH 8.5. Some fish die after short exposure, at the latter temperature and pH, in a solution of 1g ammonia in 1 tonne of water.

Combating water soluble gas clouds

(Figure 1-13, Method C1)

Method Water spray ("water mist")**Application** Water soluble gases like ammonia and sulphur dioxide (Group GD).**Description** Small confined gas clouds of water soluble gases can be "knocked down" (washed down), at low wind speed, by fine, scattered water sprays (water mist) cf. Figure 5 - 2**Figure 5 - 2** Small water-soluble gas clouds can be "knocked" or washed down by water spray**Limitations** Applicable to small/limited gas clouds only.
Difficult to manoeuvre response vessels in narrow waterways.**Combating non-water-soluble gas clouds**

(Figure 1-13, Method C1)

Method Water spray ("water mist")**Application** Non-water-soluble gases like methane, propane, butane, butadiene, ethylene, propylene, LPG mixtures, vinyl chloride (Group G).**Description** Small confined gas clouds of non-water-soluble gases can be stopped, steered, pushed and dispersed at low wind speed, by fine, scattered water sprays (water mist).

The risk of fire and explosion can be reduced by cooling down hot surfaces or putting out sparks and suppressing flame formation.

Limitations Applicable to small/limited gas clouds only.
Difficult to manoeuvre response vessels in narrow waterways.

Fighting gas clouds by recondensing into the liquid state

(Figure 1-13, Method C1)

Method

Recondensing leaking gases by covering the container with a flat tarpaulin or collecting the jet stream with a tarpaulin made as a funnel or a cone.

Application

Mainly ammonia, sulphur dioxide and chlorine.

Description

(Picture source:
Swedish Rescue
Services Agency)

Releases of ammonia, sulphur dioxide and chlorine form aerosol clouds which are extremely dangerous for both health and environment. The method of recondensing is based on the fact that the aerosol droplets in the clouds, under certain conditions, can be merged into the liquid state. Released gases from tank containers and similar reservoirs can be recondensed by covering with a tarpaulin according to Figure 5 - 3.

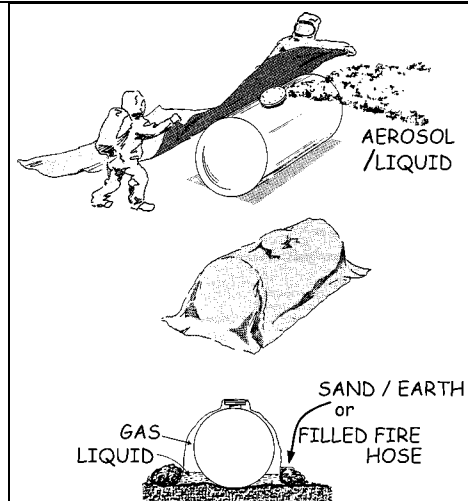


Figure 5 - 3 Recondensing by means of a tarpaulin

A release giving rise to a jet stream within easy reach, can be recondensed by a funnel or a cone (cf. Figure 5 - 4) with appropriate anchoring close to the point of release.

The jet stream is lead into the cone after which the recondensed liquid is collected in a pool (Figure 5 - 4, Figure 5 - 5 and Figure 5 - 6).

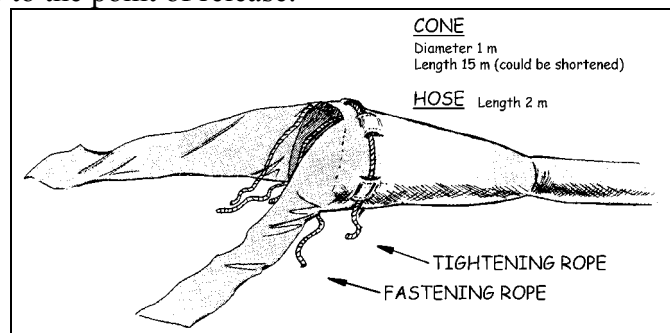


Figure 5 - 4 A cone for recondensing a gas release

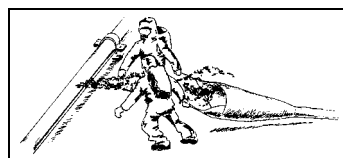


Figure 5 - 5

The cone is anchored at the point of release

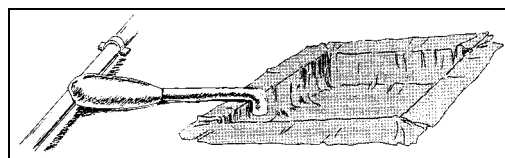


Figure 5 - 6

The recondensed liquid is collected in a pool

Limitations

Applicable to small/limited gas releases only.

Supervising a momentary release of a hazardous gas cloud

(Figure 1-13, Method M1)

Method Supervising a released gas cloud by ships, helicopters and aircraft and seeding the cloud by ammonia to make it better visible.

Application Large gas clouds at a safe distance from populated areas.

Description

Figure 5 - 7 shows an example of using explosives after an accident off the coast of the Netherlands. (Annex 3, accident Sindbad) (Ref. 44).

Sunken steel cylinders containing chlorine were broken by explosives and the gas escaped through the water column into the air.

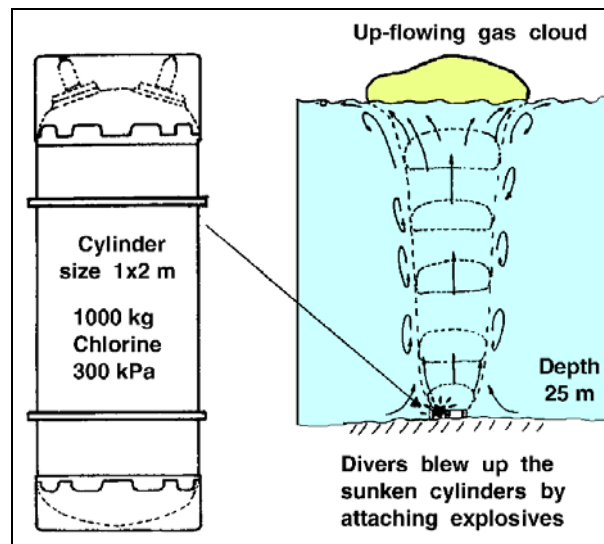


Figure 5 - 7

The rising chlorine gas cloud was strictly supervised by fully protected personnel. An exclusion zone was established (Figure 5 - 8) and patrolled by ships, helicopters and aircraft.

Ammonia gas was released upwind as an indicator gas that seeded the chlorine gas cloud and made it clearly visible as a white smoke over a large area.

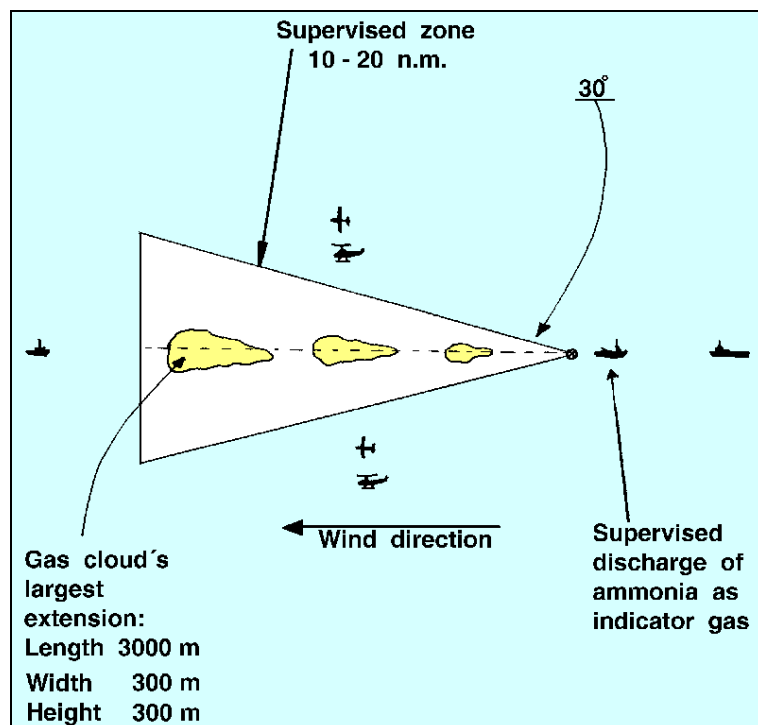


Figure 5 - 8

Limitations Very careful planning is necessary with safe distance to populated areas and strict warnings to seafarers and population.

5.2 Chemicals that float on the water surface

Combating chemical spills that float on the water surface (Figure 1-13, Method C2)

Examples: Amyl acetate, butyl acetate, butanol, butyl acrylate, cyclohexanone, dibutyl phthalate, dioctyl phthalate, dipentene, fish oil, heptane, hexanol, isodecanol, olive oil, rape seed oil, tall oil, toluene, turpentine, xylenes

General actions should be taken according to Subchapter 1.2.

A spilled chemical that floats on the water surface will spread and form a large contact surface to the air. Depending on its vapour pressure, it may evaporate rapidly and give high gas concentration in the air. When responding to floating chemical spills on the water surface (Ref. 11 and Ref. 12) it is therefore especially important to monitor air concentrations in order to assess fire and explosion risks as well as danger to health.

Corrective response actions can be carried out mainly for spills of liquid and solid chemicals, in Group F, that float on the water surface and neither evaporate nor dissolve. These processes occur very slowly in Group F. Actually, quite a few tanker transported substances belong to Group F but many of these are less hazardous fatty oils. However, even these substances in Group F may sometimes be difficult to combat (pick up). Because of low viscosity some of them may very rapidly distribute over the water surface and form extremely thin layers.

These chemicals (Group F) float on water, evaporate very slowly and are sparingly soluble in water. They can be:

- ♦ treated with foam to reduce vaporizing and reduce the risk of fire and explosion
- ♦ treated with sorbents and some other types of treating agents
- ♦ contained by booms (for a short time only, due to chemicals' generally low viscosity)
- ♦ picked up by recovery equipment (oil skimmers)
- ♦ combated by combinations of the above.

During all such response work, special attention must be given to risks of health, fire and explosion. On some occasions, these risks can be reduced by covering the spill with foam as pointed out above.

Use of treating agents on a chemical spill on the water surface can restrict its spread and facilitate containment and recovery. There are special sorbents which are capable for chemical spills (Ref. 14 and Ref. 15) but conventional oil spill sorbents can sometimes also be used. Other types of treating agents are so called gelling agents. An example of a gelling agent is the substance which is mixed with gasoline as a "thickener" when making napalm. However, special gelling agents are needed against floating chemical spills on the water surface. Some gelling agents have been tested, but yet (year 2002) there are no gelling agents available on the market specially designed for chemical spills on the water surface.

Some sorbents, shaped like small cubes or pellets made of foam plastic, are used by special systems with broadcaster, harvester as well as regenerator that removes the sorbed substance and makes the sorbent ready for redistribution by the harvester (Ref. 17 and 18).

Suppressing vapours from floating spills

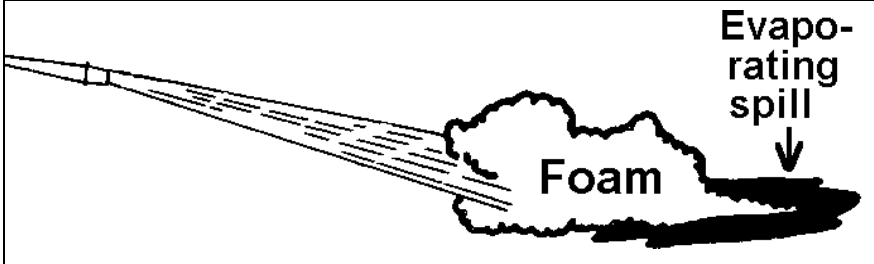
Method	Applying foam by means of fire fighting equipment.
Application	Spills of substances that float on the water surface and give off toxic or flammable vapours.
Description	<p>Confined chemical spills which do not form too large slicks on the water surface can be covered with various types of foams which are normally aimed for fire-fighting (cf. Figure 5 - 9).</p> <p>The foam cover can temporarily suppress vapour formation from the spill and thus reduce the risk of formation of noxious or flammable gas concentrations.</p> 
Limitations	Applicable to relatively small/limited surface chemical slicks only. Different types of foams are applicable to certain groups of chemicals only. Foams reduce the surface tension of the floating spill which will make it more difficult to be recovered by certain skimmers.

Figure 5 - 9

The following summary tables (Figure 5 - 10 and Figure 5 - 11) have been prepared by Environment Canada as general guides to the types of foams available and their potential uses. Brief guidelines are presented in the tables as well as references to foam types applicable against spills of specific chemicals.

Foam Type		Formulation	Application	Comments
Protein-based:				
1)	Protein	hydrolyzed protein with additives to retard biodegradation	flammable liquid hydrocarbons	low expansion; provide short-term control; good heat resistance, cohesiveness and stability
2)	Fluoro-protein	protein plus fluorinated surfactants	flammable liquid hydrocarbons	low expansion; short-term control; resist hydrocarbon saturation and burnback
3)	Alcohol	alcohol-based protein foam	flammable polar solvents	low expansion; short-term control; stable with some alcohols, ketones esters, etc.

Figure 5 - 10

Generally, protein-based foams are low expansion and add water at a relatively fast rate particularly to reactive liquefied gases and liquids. Higher water drainage does not favour the mitigation of vapours although alcohol foams are stable against polar, low molecular weight liquids such as acetone. These foams have been developed primarily for fire control.

Foam Type		Formulation	Application	Comments
Surfactant-based:				
1)	Low expansion	synthetic detergents	flammable liquid hydrocarbons	short-term control; more suited to vapour control in higher winds
2)	High expansion	synthetic detergents	flammable liquid hydrocarbons	longer-term control; low water drainage; best for reactive liquefied gases and liquids; use in low winds (<4.5 m/s)
3)	Aqueous film-forming foam (AFFF)	fluoro-surfactants	flammable liquid hydrocarbons	designed for quickly extinguishing fires; vapour control is satisfactory with some substances
4)	AFFF/Alcohol	fluoro-surfactant plus alcohol concentrate	flammable polar solvents and hydrocarbons	low expansion; designed for quick fire control; avoid water-reactive liquids although low water drainage indicated by manufacturer; vapour control should be satisfactory with a range of substances
5)	Alkaline-resistant	surfactant plus additives	alkaline materials <u>not on fire</u>	medium expansion; slow drainage rate claimed; foam stable with specified materials for vapour control
6)	Acid-resistant	surfactant plus additives	acidic materials <u>not on fire</u>	medium expansion; slow drainage rate claimed; designed for vapour control of spilled acidic liquids

Figure 5 - 11

For the most part, surfactants have been developed for fire control and are suitable for both low (10:1) and high (100:1) expansion applications except as indicated. High expansion foams require less water, exhibit lower vapour concentrations above the foam blanket but are more influenced by wind (above 4.5 m/s), rain and temperature (above 21.1°C).

Using bubble barriers to contain spills that float on the surface or disperse in the water body

(Figure 1-13, Method C2-C3)

Method Applying bubble screens (also called bubble barriers, air curtains or pneumatic booms) around floating or dispersing spills by pumping compressed air into a perforated hose which is placed on the bottom around the incident site.

Application In shallow water (bays, harbours) for spills floating on the surface or disperse into the water column.

Description

Figure 5 - 12 shows how an air bubble screen could be created by means of compressed air and a perforated hose (seen in cross section). The following three figures show how a floating substance, escaping from a vessel, can be contained inside the air bubble barrier which acts as a pneumatic boom.

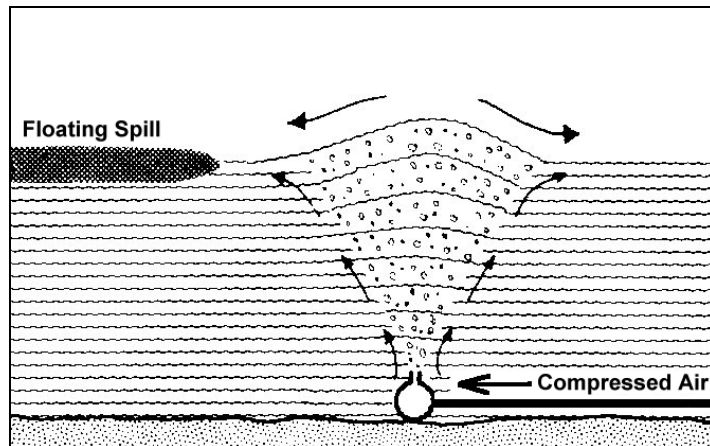


Figure 5 - 12

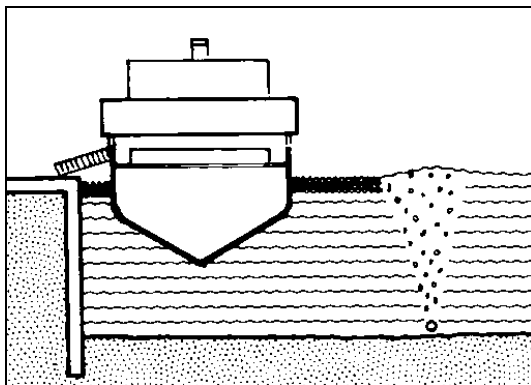


Figure 5 - 13

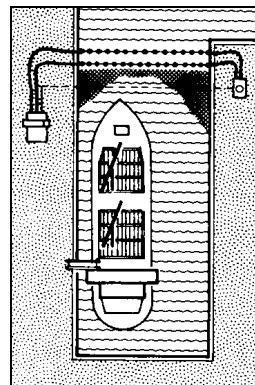


Figure 5 - 14

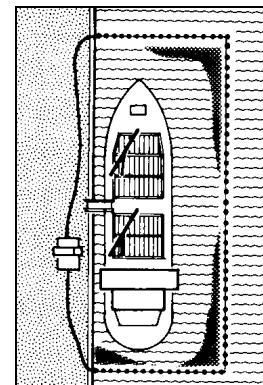


Figure 5 - 15

A close-fitted and well-operated bubble screen system can also be used for temporary containment of spills that disperse (dissolve) in the water.

The use of a bubble air curtain has been demonstrated (see Figure 5 - 16) in a dredging operation against a sunken spill of polychlorinated biphenyl (PCB) at depth of 15 m (cf. Annex 3, accident PCB, and Ref. 24).

The perimeter of a contaminated river area was physically cordoned off by a bubble air curtain established by pumping air through a perforated fire hose lying on the bottom around the area. The purpose of the bubble screen was twofold - protect migrating fish and prevent PCB from spreading.

The bottom area was dredged by a pipeline dredge handled by divers. During the dredging operation, the river level depth was checked by means of fathometer readings over a cross section of the spill area. The depth checks were made aboard a Coast Guard cutter that was in attendance throughout the operation.

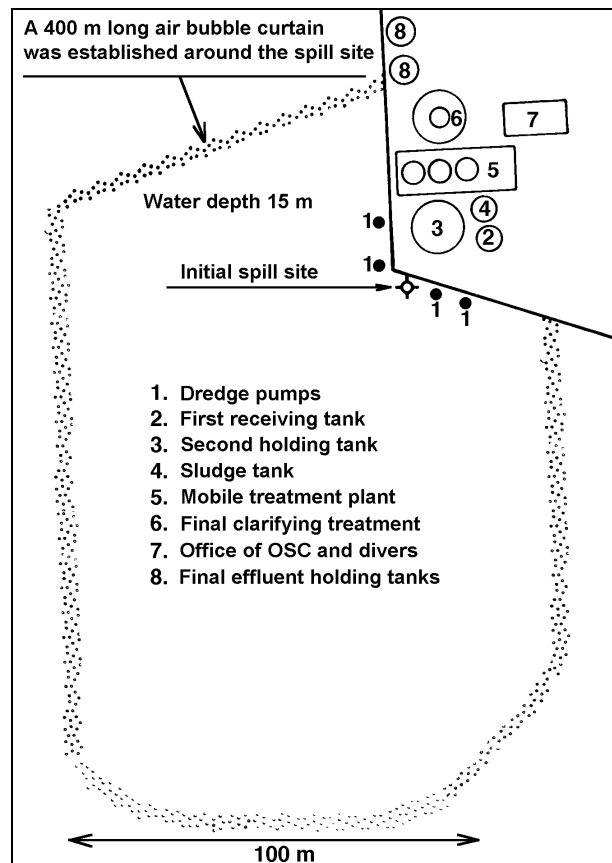


Figure 5 - 16 Use of a bubble curtain barrier

Limitations

Applicable in shallow and almost stagnant water, especially harbours with pre-installed equipment that can quickly produce air barriers.

Recovery of floating spills using polypropylene sorbent plates (Figure 1-13, Method C2)

Method Distributing sorbents over the floating spill on the water surface and recovery of the sorbent-spill mixture.

Application Spills of substances that float on the water surface and do not evaporate or dissolve significantly, e.g. alfa-methyl styrene, dipentene, ethyl hexanol, fatty oils, isodecanol, nonyl alcohol, octanol, phthalates, 1,2,3-trimethyl benzene and vinyl toluene (Group F).

Description Sorbents can sometimes be used for chemical spills on inland or coastal water surfaces. Normally they are useless in the high sea. There are a lot of different sorbents, designed for chemical spills, available on the market. These agents have various appearances and compositions. Most of them are aimed and tested for spills on land and only a few are suitable for absorbing spills from the water surface

(Picture source:
Environment Canada)

In a Norwegian overview of 43 different sorbents it appeared that 10 could absorb floating chemicals on the water surface (Ref. 13, written in Norwegian). Four of these were contained in small booms ("sausages") and five were in the form of small mats or plates. One agent consisted of a granulated material (processed volcano ash).

The most efficient products, in this overview, were made of polypropylene. This polymer is available as foam plastic plates or felt-like pieces that can be easily distributed over the spill (Figure 5 - 17).

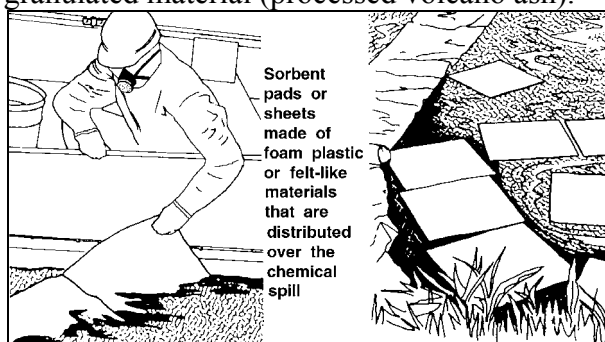


Figure 5 - 17 Treating a chemical spill on the water surface with sorbent plates or pads

Limitations Possible risks of health, fire and explosion.

Recovered substance may have deleterious effects on response equipment.

As with all sorbents the risks of bleeding and sinking must be evaluated as well as the agent's efficiency (sorbent/chemical ratio).

Generally not applicable in heavy sea (open sea) and adverse weather.

Very careful planning is needed regarding both recovery and disposal.

Recovery of floating spills using blankets or pillows packed with powdered sorbents

(Figure 1-13, Method C2)

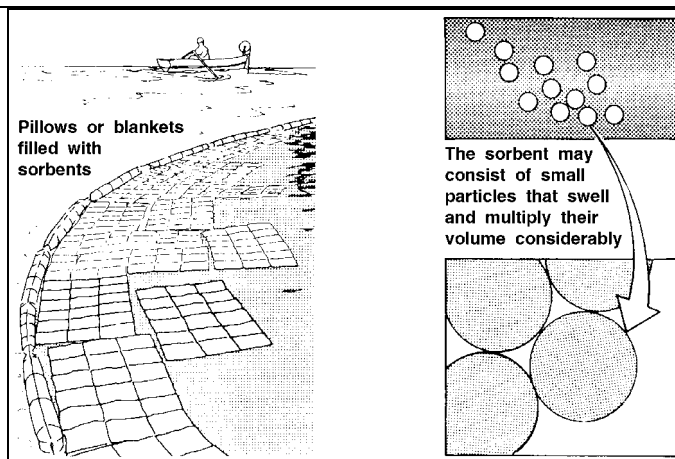
Method Distributing blankets/pillows over the floating spill on the water surface and recovery of the blanket/pillow-spill mixture.

Application

Spills of substances that float on the water surface and do not evaporate or dissolve significantly, e.g. alfa-methyl styrene, dipentene, ethyl hexanol, fatty oils, isodecanol, nonyl alcohol, octanol, phthalates, 1,2,3-trimethyl benzene and vinyl toluene (Group F).

Description

Some synthetic sorbents for chemical spills are made of rather small particles (around 1 mm in diameter) or even powders. For convenient application of such sorbents at sea, they are sometimes packed as pillows or in cloth-cases as "blankets" (Ref. 16), see Figure 5 - 18.



Picture source: Environment Canada

Figure 5 - 18

Powdered or granulated sorbents can also be distributed by means of an ejector pipe (cf. Figure 5 - 28). Such a device can facilitate an even spread of the sorbent onto the spill. However, there is a risk that the pipe stops up if the sorbent is fluffy like soft foam plastic. Sometimes the sorbent can be spread onto the spill in a rather unconventional way directly from manually held bags, especially if its weight by unit of volume is not too low and the wind speed not too high.

Low viscous chemical spills on the water surface spread out rapidly as very thin films. When treating such spills it is therefore necessary to apply high sorbent/chemical ratios in order to obtain efficient absorption.

Limitations

Possible risks of health, fire and explosion.

Recovered substance may have deleterious effects on response equipment.

As with all sorbents the risks of bleeding and sinking must be evaluated as well as the agent's efficiency (sorbent/chemical ratio).

Generally not applicable in heavy sea (open sea) and adverse weather.

Very careful planning is needed regarding both recovery and disposal.

Recovery of floating chemical spills, lumps and small packages using oil trawl systems

(Figure 1-13, Method C2)

Method Applying certain types of trawls or net bags on floating high viscosity chemical spills or lumps (or small packages).

Application Spills of substances that float on the water surface and form high viscosity layers or lumps that neither evaporate into the air nor disperse into the water (Group F). Also applicable to floating small packages as well as to substances moving in the water body just under the surface.

Description

An oil trawl system consists of the guide booms, the entrance net, and detachable trawl bags. It can be very rapidly deployed by means of small work boats. No hydraulic power or heavy mechanical equipment is required - only a simple air blower for inflation of the guide booms, or even less if foam filled booms are used.

**Figure 5 - 19***Picture source: RO-CLEAN DESMI*

The trawl bags are attached to the middle of the sweep. The forward movement of the sweep will force the substances or items into the trawl and they will be stopped and collected by the trawl's masks. The bags can be disconnected and recovered during the operation at sea.

**Figure 5 - 20**

Two of the more well-known systems are the ScanTrawl (Figure 5 - 19 and Figure 5 - 20) and the Jackson Trawl.

Limitations Possible high risks of health, fire and explosion.

Recovered substance may have deleterious effects on response equipment.

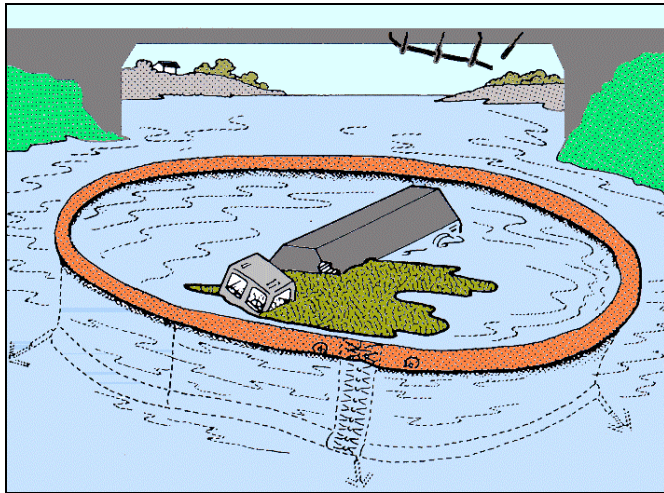
Applicable to such members of Property Group F only, that form very high viscosity layers or lumps. However, also applicable to floating small packages.

**Containment of floating chemical spills
by using special barriers in shallow water**

(Figure 1-13, Method C2)

Method Sea Curtain Barrier**Application** Leaking substances in shallow water**Description**

A large leaking container in shallow water can be boomed to limit the discharge of the chemical. With a conventional boom there is a risk that the leaking substance may flow under the boom. On such occasions a Sea Curtain Barrier can be used according to Figure 5 - 21. It is made of a robust buoyant cushion which holds a barrier stretching down to the bottom where it is held down by an anchored weight collar (Ref. 36).

*Picture source: Environment Canada***Figure 5 - 21**

Sea Curtain Barrier which stretches down to the bottom where it anchored.

Limitations Mainly applicable in shallow and almost stagnant water.

Recovery of floating chemical spills using oil spill booms and skimmers

(Figure 1-13, Method C2)

Method Applying certain types of oil containment booms and oil skimmers on the floating chemical spill.

Application

Spills of substances that float on the water surface and do not evaporate or dissolve significantly, e.g. alfa-methyl styrene, dipentene, ethyl hexanol, fatty oils, isodecanol, nonyl alcohol, octanol, phthalates, 1,2,3-trimethyl benzene and vinyl toluene (Group F).

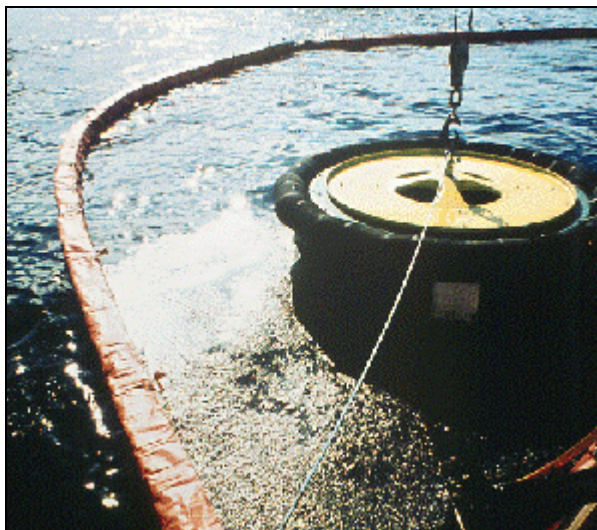


Figure 5 - 22

Booms

The spread of spilled chemicals on the water surface can sometimes be confined by booms. The containment may sometimes be facilitated by pre-treatment with sorbents and similar agents.

Skimmers

Spills of *mineral oils* on the water surface can be routinely picked up by various types of oil skimmers during the response operation. *Floating chemicals*, however, may be more difficult to recover from the water surface as their viscosities are often too low and they spread out rapidly and form very thin films on the surface. But it has appeared that some chemicals spilled on the water surface actually can be collected, under certain circumstances, by means of oil skimmers (Ref. 18). Sometimes the process could be more easily performed if the spill is pre-treated with certain agents. However, some types of skimmers should not be used on spills mixed with response agents. A few skimmers, suitable for chemical spills, are discussed in the connection with Figure 5 - 23, Figure 5 - 24 and Figure 5 - 25.

Limitations Possible high risks of health, fire and explosion.

Recovered substance may have deleterious effects on response equipment.

Recovery problems may occur in wave height > 1.5 m and water current > 0.8 kn.

Applicable for Property Group F chemicals only (with low solubility and evaporation).

Recovery of floating spills using various types of skimmers

(Figure 1-13, Method C2)

Method

Applying certain types of oil skimmers on the floating spill.

Application

Spills of substances that float on the water surface and do not evaporate or dissolve significantly, e.g. alfa-methyl styrene, dipentene, ethyl hexanol, fatty oils, isodecanol, nonyl alcohol, octanol, phthalates, 1,2,3-trimethyl benzene and vinyl toluene (Group F).

Description

(Figure 5 - 23 and Figure 5 - 24:
Picture source:
Environment Canada)

Belt skimmers (Figure 5 - 23) has turned out to be usable for recovery of certain chemicals, e.g. octanol and dioctyl phthalate (Ref. 18). The process may sometimes be facilitated by pre-treatment with e.g. sorbents.

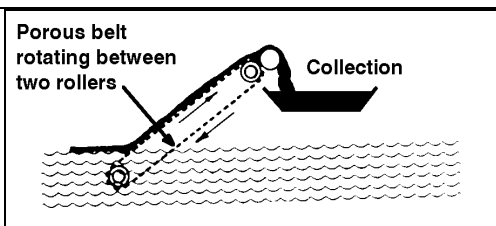


Figure 5 - 23 Recovery of floating chemicals on the water surface by belt skimmer

Sorbent rope systems (Figure 5 - 24) can sometimes be used to pick up chemical spills from the water surface. When using these systems, the chemical should not be pre-treated with any response agents. Very good results have been gained on octanol and dioctyl phthalate (Ref. 18).

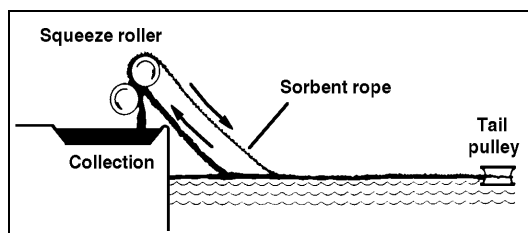


Figure 5 - 24 Recovery of floating chemicals on the water surface by sorbent rope

Vortex systems can be used for recovery of chemicals on the water surface in the same way as light petroleum products (Figure 5 - 25). The chemicals should not be pre-treated with response agents when applying vortex recovery systems.

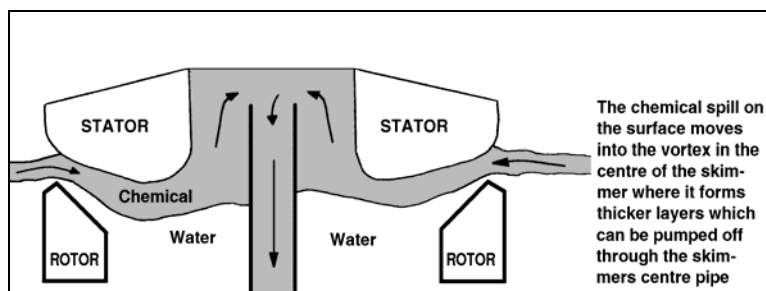


Figure 5 - 25 Recovery of floating chemicals on the water surface by a vortex system

Limitations

Possible high risks of health, fire and explosion.

Recovered substance may have deleterious effects on response equipment.

Recovery problems may occur in wave height > 1.5 m and water current > 0.8 kn.

Applicable for Property Group F chemicals only (with low solubility and evaporation).

5.3 Chemicals that dissolve in water

Combating chemical spills that dissolve in water (Figure 1-13, Method C3)

Examples: Acetone, ethanol, phosphoric acid, glycols, isopropanol, methanol, methyl ethyl ketone, monoethyl amine, sodium hydroxide solution, propionic acid, propylene oxide, sulphuric acid, acetic acid, ammonium hydroxide (from dissolved ammonia)

General actions should be taken according to Subchapter 1.2.

A spilled chemical, that dissolves in water, will form a growing "cloud" in the water body. It is important to monitor the concentration gradients in the cloud to track the chemicals' spread and drift in order to judge the hazards for the environment, fishery, recreational areas, fresh water intakes, etc.

Chemical spills that dissolve in shallow water may sometimes be mixed in with various treating agents (useless in open) in order to reduce deleterious effects on humans and the environment (Ref. 19, Ref. 20 and Ref. 21). Examples of such treating agents are:

- | | | |
|-----------------------|--------------------|---------------------|
| ♦ Neutralizing agents | ♦ Oxidizing agents | ♦ Complexing agents |
| ♦ Activated carbon | ♦ Reduction agents | ♦ Ion exchangers |

The use of neutralising agents is described as a standard method on next page.

A reduction agent, ferrosulphate, has once been used in an accident to treat leaking chromium compounds from a sunken ship north of the Island of Öland in the Baltic Sea. The treatment was performed simply by emptying bags of altogether 11 tonnes of ferrosulphate from a surface vessel so that the agent descended and spread over the sunken ship on the bottom at 17 m depth (c.f. Annex 3 "Viggo Hinrichsen").

Examples of other treating agents are *flocculation agents* (for fine particle dispersions) and *gelling agents* (for floating slicks before they dissolve).

Agents which just absorb the spilled substance and settle on the seabed (e.g. activated carbon and flocculation agents) should be used with care and *only in consultation with environmental expertise*.

Flocculation agents, gelling agents, activated carbon, complexing agents and ion exchangers can also be used for treatment of mixtures of chemicals and water that have been recovered from a spill site and pumped into barges or other intermediate storing containers (examples in Ref. 23, Ref. 24 and Ref. 25). Activated carbon is often used in this way and is a well-known, efficient agent for absorption of many different organic chemicals. Activated carbon can also, according to some investigations, be used successfully for chemical spills in flowing waters (Ref. 26, Ref. 27, Ref. 28 and Ref. 29) while other sources (Ref. 30) maintain that activated carbon is not suitable for direct treatment of chemical spills in the environment.

The method of adding treating agents to dispersed chemical spills in the water body can be used especially against substances belonging to Group D, but sometimes also against other chemicals (the Groups GD, ED, FED, FD and SD).

Containment of dissolving chemical spills in shallow water by using barriers

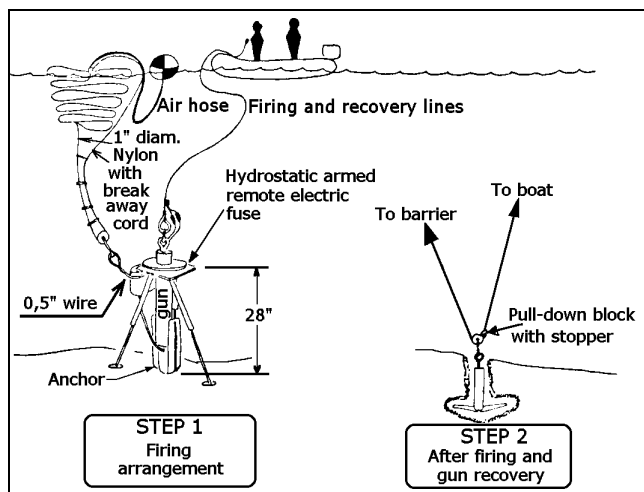
(Figure 1-13, Method C3)

Method Sea Curtain Barrier

Application Substances that dissolve in shallow water bodies

Description

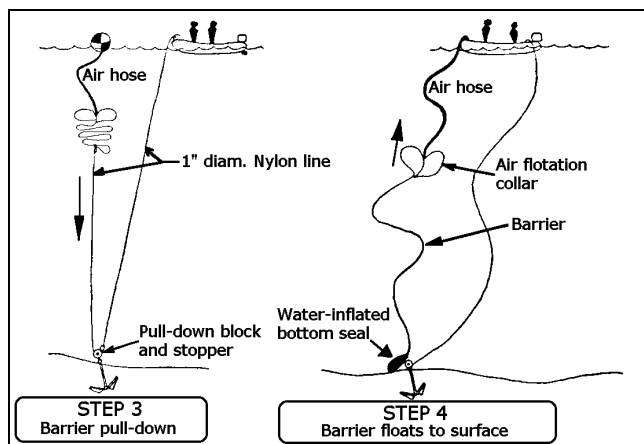
Field trials with a Sea Curtain Barrier have been performed by US Environmental Protection Agency at about 8 m depth. A prototype device was tested that effectively contained a spill of rodamine (Ref. 36).



Picture source: US Coast Guard

Figure 5 - 26 Anchoring of a curtain barrier

The anchoring of the curtain barrier requires a special technique as the barrier may be subjected to very strong stress from water currents. Anchors are shot down into the bottom by special guns. The procedure is shown by Figure 5 - 26 and Figure 5 - 27.



Picture source: US Coast Guard

Figure 5 - 27 Anchoring of a curtain barrier

Limitations Mainly applicable in shallow and almost stagnant water.

Treating dissolving spills in the water body with neutralizing agents

(Figure 1-13, Method C3)

Method Adding neutralizing agents to a spill site in the water body.

Application Spills of acids and bases that dissolve when spilled into the water and change its pH significantly. Examples are ammonium hydroxide, fluo-silicic acid, phosphoric acid, sodium hydroxide solution, propionic acid, nitric acid, sulphuric acid and acetic acid (Group D)

Description

Releases of acids and bases in streams, creeks and rivers have, on some occasions, turned out to give devastating ecological effects even if the volumes are relatively small. The explanation to the serious impacts is that such a spill, if it is momentary or occurs in a short time, forms a relatively concentrated "cloud" that moves downstream and damages or destroys the life in the water all along its course. Spills of acids and bases in confined water areas should therefore be quickly located, mapped, and then treated with neutralizing agents. The following neutralizing agents have turned out to be suitable choices (Ref. 22):

For spills of **acids**:

Sodium acid carbonate

(sodium bicarbonate, NaHCO_3)

For spills of **bases**:

Sodium dihydrogen phosphate

(monosodium phosphate, NaH_2PO_4)

Treating agents should be used in consultation with an appropriate environmental protection authority, that should also advise on dosage. The agent can be spread out by means of ejector pipes (Figure 5 - 28) or directly from bags. If there is any uncertainty about dosage, the following is recommended: Find out the weight of spilled chemicals. The theoretically correct dosage is approximately the double amount of neutralizing agent. Apply an overdose of 50 per cent and distribute in a suitable way over the whole spill site. The pH should be monitored continuously.

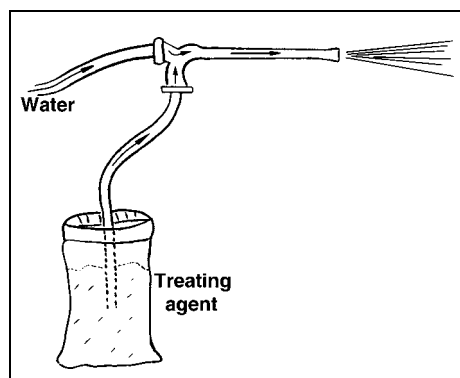


Figure 5 - 28 Use of an ejector pipe for distribution of a treating agent

At discharges of **liquefied ammonia** into water, part of the ammonia boils away very rapidly. The rest of the discharge dissolves in the water body and forms alkaline ammonium hydroxide solution which is dangerous for the environment. Neutralizing agents should therefore be utilised to reduce environmental damage from ammonia discharges in confined, vulnerable water areas with low water turnover.

Limitations Not feasible in open sea, deep waters, strong currents, high wind speed, high sea state or adverse weather.

When treating very large spills there might be problems to acquire, transport and handle large volumes of the treating agents.

Using a mobile treatment unit to remove dissolved spills in confined water bodies

(Figure 1-13, Method C3)

Method Using the US Environmental Protection Agency's Mobile Hazardous Material Spills Treatment Trailer.

Application Dissolved or dispersed substances in dams, ponds, water supplies and small lakes.

Description

The US Environmental Protection Agency (EPA) has used a trailer-borne self-contained water treatment system (cf. Figure 5 - 29) to remove several classes of hazardous materials from water. The trailer can be rapidly carried by road to distant sites and can treat 0.8 m³ contaminated water per minute. It has the following data:

Length	15 m	Capacity:	1100 m ³ /24 hr
Width	2.5 m	Gasoline-powered Generator:	100 kW
Weight	43 tons	Cost:	\$ 250,000

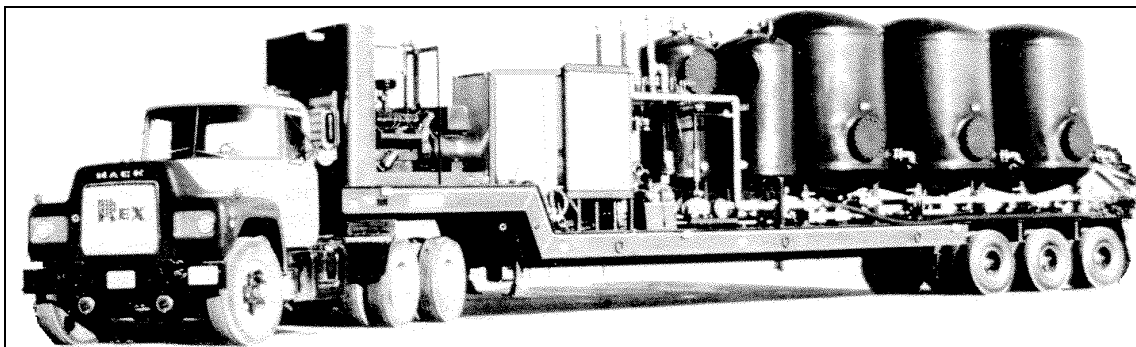
The main features of the trailer are:

- three mixed-media filters for removal of suspended or precipitated material
- three activated carbon columns for the removal of many soluble organic chemicals

The system also includes:

- A 60 m³ deployable portable tank for flocculation, precipitation or neutralization
- Several 11 m³ pillow tanks for effluent or sludge storage
- Hoses and pumps to allow positioning the unit up to 100 m from the site

After an accident the unit was used to purify 2,300 m³ of watery sludge. Two hundred drums of PCB-contaminated mud was collected and later carried to a disposal site (cf. Annex 3, accident PCB, and Ref. 24).



Picture source: US Environmental Protection Agency

Figure 5 - 29 A mobile chemical treatment unit

Limitations Mainly applicable for contaminated water in dams, ponds, water supplies and small lakes.

5.4 Chemicals that sink to the bottom

Combating chemical spills that sink to the bottom (Figure 1-13, Method C4)

General actions should be taken according to Subchapter 1.2.

Discharges of chemicals that sink to the bottom can heavily contaminate the impacted bottom sediments. Careful planning should be done, on such occasions, for the decontamination work. A sophisticated system may be needed to take care of and clean the contaminated sediments (Ref. 23 and Ref. 31, cf. also Annex 3 “Testbank”).

Sunken spills on the bottom can be recovered by different kinds of dredging techniques and there are various types of suitable **dredges** (Ref. 32, Ref. 33, Ref. 34, Ref. 35, Ref. 36 and Ref. 37). Different dredges are more or less suitable for removal of chemicals from the bottom. There are three main types of dredges according to Figure 5 - 30, of which airlift pneumatic dredges should be mentioned as successful examples used in well-documented accidents (Ref. 23 and Ref. 38, cf. also Annex 3 “Testbank”).

Type	Examples	
Mechanical dredges	Bucket Ladder, Clamshell, Dipper	
Hydraulic dredges	Plain Suction Dustpan Cutterhead	Hopper Mudcat PIJESP (Peripheral Injector Jet Suction Pump)
Pneumatic dredges	Pneuma, Airlift	

Figure 5 - 30

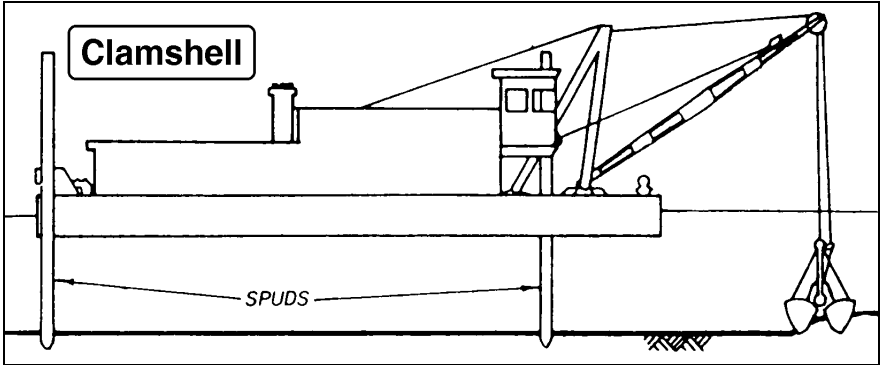
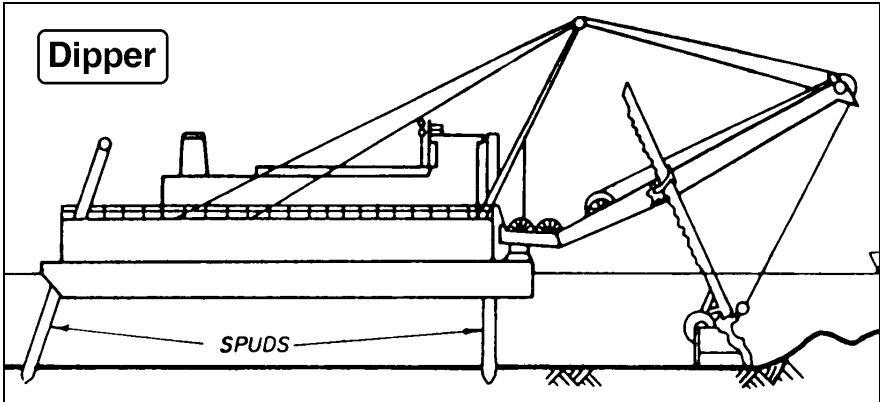
Appropriate safety precautions should always be taken in all dredging operations of sunken hazardous materials. Divers surveying the operation should be aware of the risk of chemicals as well as mechanical hazards. Personnel working at the surface must wear relevant personal protective gear. Recovered hazardous materials or contaminated mud may pose severe hazard and should be treated with great precaution with regard to the properties of the chemicals involved. If the recovered material is transferred to barges it may be necessary to cover the barges tightly in order to protect human and the environment.

Some dredges have storage tanks of their own. Such tanks should only be used for contaminated mud under the following conditions:

- ♦ If the storage tank is approved for the chemical(s) involved (the same rules as for a chemical tankers)
- ♦ If a monitoring system is installed
- ♦ If the accommodation is sheltered or gas-tight
- ♦ If fast evacuation of crew is possible
- ♦ If the crew wear appropriate Personal Protective Equipment (PPE) during the operation

Recovery of sunken spills from the seabed using mechanical dredging systems

(Figure 1-13, Method C4)

Method	Dredging
Application	Solid or semi-solid chemicals which are heavier than water (sink to bottom) e.g. phenol, sulphur, creosote, coal tar, tall oil resin and some biocides (danger of scattering of biocides) (Group S and SD).
Description	<p>Clamshell and Dipper dredges (Figure 5 - 31 and Figure 5 - 32) are the most unsophisticated types of equipment that can be used in shallow waters with the machinery placed on a barge, or nearby quay or shore. Such an equipment was used in 1973 in Gothenburg, Sweden, to dredge sunken phenol from the bottom of the harbour dock (cf. Annex 3, accident Phenol).</p> <p>Figure 5 - 31 Mechanical dredge of Clamshell type</p>  <p style="text-align: right;"><small>Picture source: Hand et al. 1978</small></p> <p>Figure 5 - 32 Mechanical dredge of Dipper type</p>  <p style="text-align: right;"><small>Picture source: Hand et al. 1978</small></p> <p>Other types of mechanical dredges (e.g. Bucket Ladder) are normally not suitable for removal of sunken chemicals. They cause too much turbulence and run the risk of spreading the spill over larger areas.</p>
Advantages	Rather simple equipment to handle. Often easily available.
Limitations	Feasible in shallow water only. There is a great risk of scattering the sunken chemical over larger areas.

Recovery of sunken spills from the seabed using hydraulic dredging systems

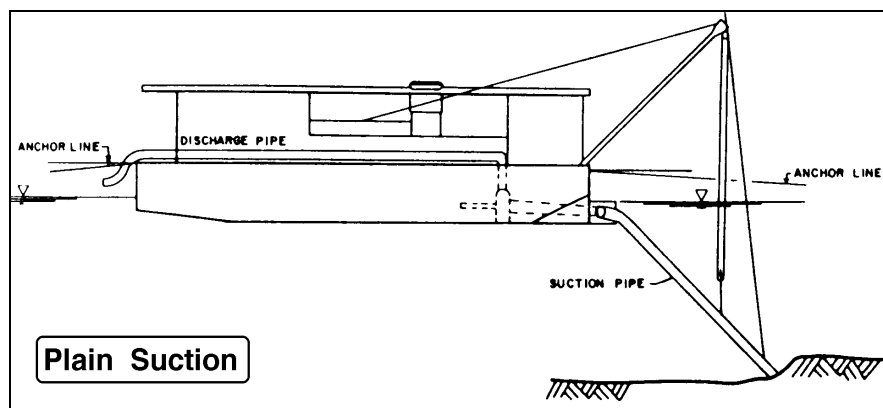
(Figure 1-13, Method C4)

Method Dredging

Application Chemicals which are insoluble or sparingly soluble in water, and heavier than water (sink to bottom) e.g. carbon tetrachloride, carbon disulphide, ethylene dichloride, ethyl chloride, tetramethyl lead (Group S and SD).

Description Hydraulic dredges are often suitable for recovery of sunken chemicals from the bottom where care should be taken not to scatter the spill over larger bottom areas during the dredging operation.

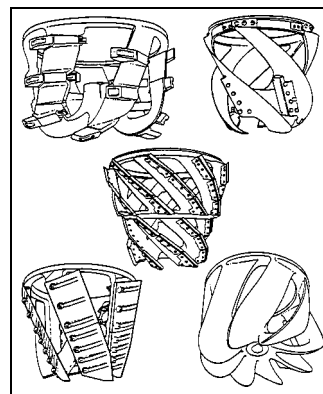
Figure 5 - 33
Hydraulic dredge of Plain Suction type



Picture source: Hand et al. 1978

A common type of hydraulic dredge is shown in Figure 5 - 33.

Some types of hydraulic dredges are equipped with so called cutterheads (Figure 5 - 34) in order to facilitate the work when deepening channels, etc. When such dredges are used for removal of sunken chemicals, the cutterheads should be dismantled, as they, like buckets on mechanical dredges, cause strong bottom turbulence that tend to scatter the spill.



Picture source: Hand et al. 1978

Figure 5 - 34 Various shapes of cutterheads

Limitations Feasible in shallow water only.

Recovery of sunken spills from shallow water using special dredging systems

(Figure 1-13, Method C4)

Method Dredging

Application Chemicals which are insoluble or sparingly soluble in water, and heavier than water (sink to bottom) e.g. carbon tetrachloride, carbon disulphide, ethylene dichloride, ethyl chloride, tetramethyl lead (Group S and SD).

Description Special hydraulic or mechanical-hydraulic dredges are sometimes convenient for recovery of sunken chemicals in shallow waters (Ref. 39).

Figure 5 - 35

A simple hydraulic dredge that is designed as a catamaran-based suction pump for dredging at depths of about one to three metres. The pump head can be swung down, between the hulls, to the bottom. Dredged material is pumped backwards to an adjacent storage container. The bottom suction pump has been manufactured under the name of "Crisafulli Sludge Handling System (Ref. 58).

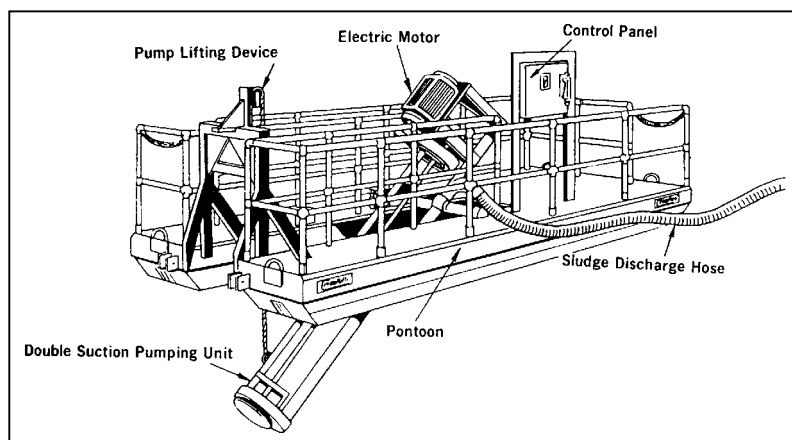
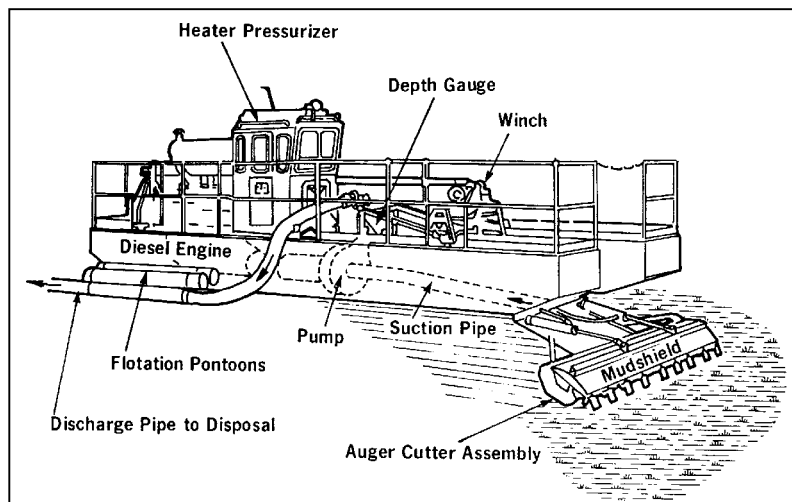


Figure 5 - 35 and Figure 5 - 36: Picture source: Environment Canada

Figure 5 - 36

A simple mechanical-hydraulic dredge for shallow water. It is built as a catamaran barge equipped with a suction pump connected to a rotating and cutting device that dredges the bottom materials. The system can operate down to 5 m. The system has been manufactured under the name of "Mudcat Auger Dredging Unit" (Ref. 59).



Limitations Designed for shallow water only

Recovery of sunken spills from the seabed using a simple suction system

(Figure 1-13, Method C4)

Method Dredging by a suction pump system (Peripheral Injector Jet Suction Pump PIJESP)**Application** Chemicals which are insoluble or sparingly soluble in water, and heavier than water (sink to bottom) e.g. carbon tetrachloride, carbon disulphide, ethylene dichloride, ethyl chloride, tetramethyl lead (Group S and SD). This system is especially suitable if the spill is scattered over the seabed and the suction head must be held and manoeuvred by a diver.**Description**

Figure 5 - 37, Figure 5 - 38 and Figure 5 - 39 shows a PIJESP which has been supplemented, inside the head, by nozzles pointing inwards. With this system it is possible to add e.g. pressurized hot-water to facilitate dredging of lumpy or high viscous chemicals. It has been used under winter conditions for removal of sunken oil after an accident.

Figure 5 - 37
A PIJESP which can be operated by divers

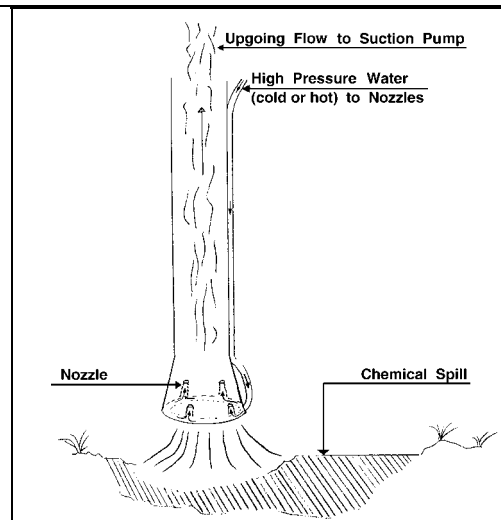


Figure 5 - 38
A diver holding a PIJESP

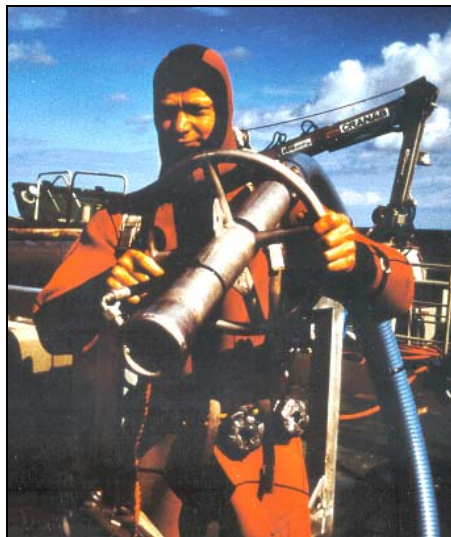


Figure 5 - 39 A close-up view of the PIJESP's suction head showing the nozzles mounted inside the mouth pointing inwards.

Limitations The divers' full protective equipment may interfere with the manoeuvring of the PIJESP when recovering a sunken hazardous material spill.

Recovery of sunken spills from the seabed using a pneumatic dredge

(Figure 1-13, Method C4)

Method Dredging by a pneumatic dredge.

Application Chemicals which are insoluble or sparingly soluble in water, and heavier than water (sink to bottom) e.g. carbon tetrachloride, carbon disulphide, ethylene dichloride, ethyl chloride, tetramethyl lead (Group S and SD).

Description Figure 5 - 40 shows a pneumatic dredge that operates with a submersible air-driven pump which is supplied with air from a compressor on the barge. The pump is designed with three cylinders that alternately fills, by the hydrostatic pressure, with sediment during the dredging operation. The sediment is then forced upwards to the surface by the compressed air. The advantage of this technique, compared to hydraulic dredging, is that 1) the mud does not need to be fluid but may contain up to 70 % dry matter, and 2) the method has no limitation regarding working depth. The type of pneumatic dredge showed in Figure 5 - 40 was used, on one occasion, in an American river for removing sunken PCB at a depth of 15 m. A smaller pneumatic dredge is shown in Figure 5 - 41 and Figure 5 - 42.

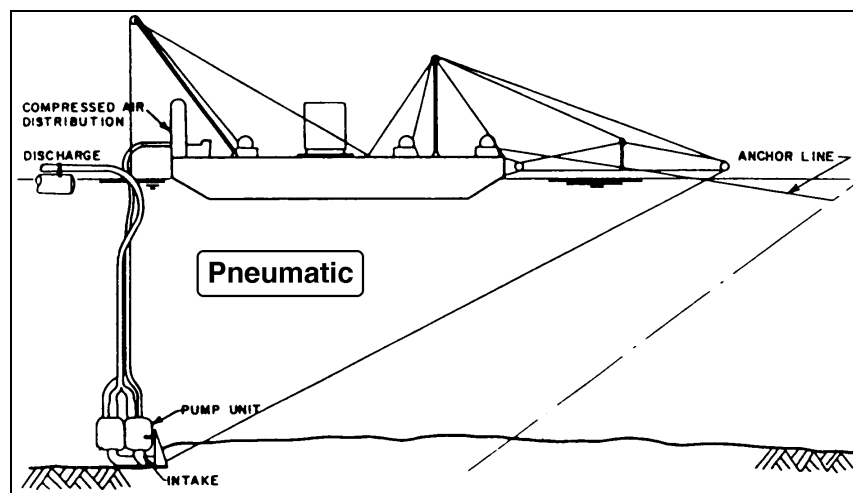


Figure 5 - 40 Pneumatic dredge of "Pneuma" type

Picture source: Hand et al.

Limitations Pneumatic dredges have in theory no depth limitations but the strong suction force at great depths (> 50 m) cause violent dredge mouth movements which obstruct proper dredging and pose great risks for divers working close.

Recovery of sunken spills from the seabed using a simple pneumatic dredge (Airlift)

(Figure 1-13, Method C4)

Method Dredging by a pneumatic dredge (Airlift)

Application Chemicals which are insoluble or sparingly soluble in water, and heavier than water (sink to bottom) e.g. carbon tetrachloride, carbon disulphide, ethylene dichloride, ethyl chloride, tetramethyl lead (Group S and SD).

Airlift has turned out to be a very useful type of dredge for recovery of sunken chemicals in water depths down to 10-20 metres. The system has no theoretical depth limitation. The dredging efficiency is better the deeper the water is. Airlifts are sometimes used in the North Sea for dredging stones down to depths of 60 - 70 m. But it is unlikely that airlifts could be used operationally at such depths for dredging sunken chemicals.

Description

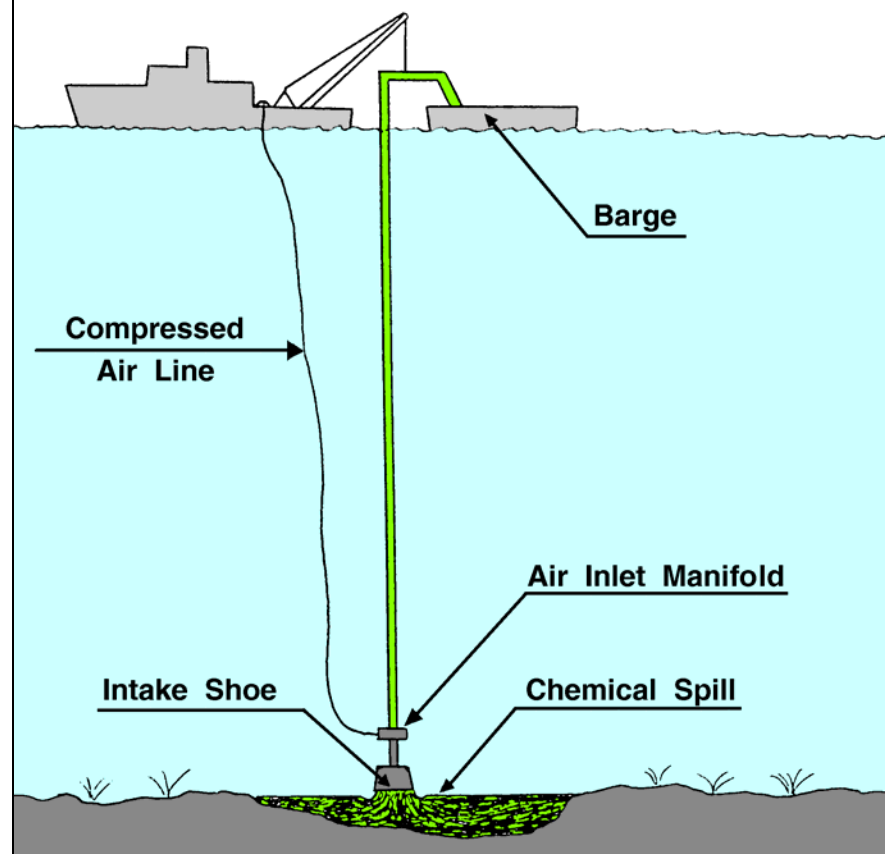


Figure 5 - 41

A small pneumatic dredge (airlift)

Airlift is a simple pneumatic dredge which, in principle, is just a tube extending from the support vessel down to the bottom (Figure 5 - 41). A compressor on the support vessel transfers compressed air, in a separate hose, either down to the head of the main tube, or to an inlet manifold, placed somewhere on the tube. The rising air expands

and causes a strong current in the tube which is stronger the greater the working depth is.

Practical arrangement

Figure 5 - 42 shows a suitable system for practical operation of an airlift system. A surface vessel (barge etc.) is positioned above the dredging site and an air compressor on board the vessel supplies the diver with compressed air at the airlift mouth. The barge can also receive the dredged material in built-in tanks or in separate containers on board.

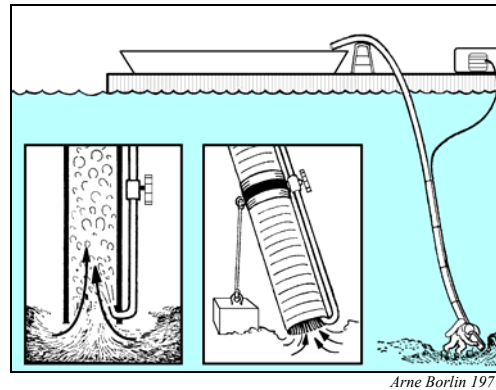


Figure 5 - 42 Practical arrangement for operating an airlift system. To achieve greater mobility the diver can work with a flexible hose attached to the airlift mouth.

The diver operates the airlift tube, which is stabilized by a weight to neutralize the strong lateral movements that strengthen with increasing working depth. The diver can also adjust the compressed air flow by a knob on the tube.

Limitations

A practical limiting factor is the compressor which has to be bigger (and more expensive) the greater the depth is. Furthermore, the tube is more difficult to manoeuvre at great depths (> 20 m), as the lateral forces become stronger. The risks for divers are also greater at increasing depths because of the enormous suction forces close to the airlift head.

The divers' full protective equipment may interfere with the manoeuvring of the Airlift when recovering a sunken hazardous material spill.

Experiences

An airlift was used with success after a ship accident in 1980 where 16 tonnes of pentachlorophenol (PCP) was dredged from the bottom of Mississippi River (Ref. 23; also cf. Annex 3 "Testbank").

Controlled evacuation of cargo from a sunken barge using a simple pneumatic pump (Airlift)

Method Cargo pumping by a pneumatic dredge (Airlift)

Application A special application of an airlift system was demonstrated in the Mississippi River in 1988 (cf. Annex 3, "Sunken barge") at a response operation where a sunken barge with sulphuric acid was emptied (Figure 5 - 43) (Ref. 38).

Description An air-lift tube is lowered into the barge (cf. Figure 5 - 43) and compressed air is delivered by an air compressor. By letting the air bubble upwards through the acid inside the tube the acid is drawn from the tank and slowly discharged into the water. The rate of the discharge is easily controlled by altering the rate of introduced air in the system.

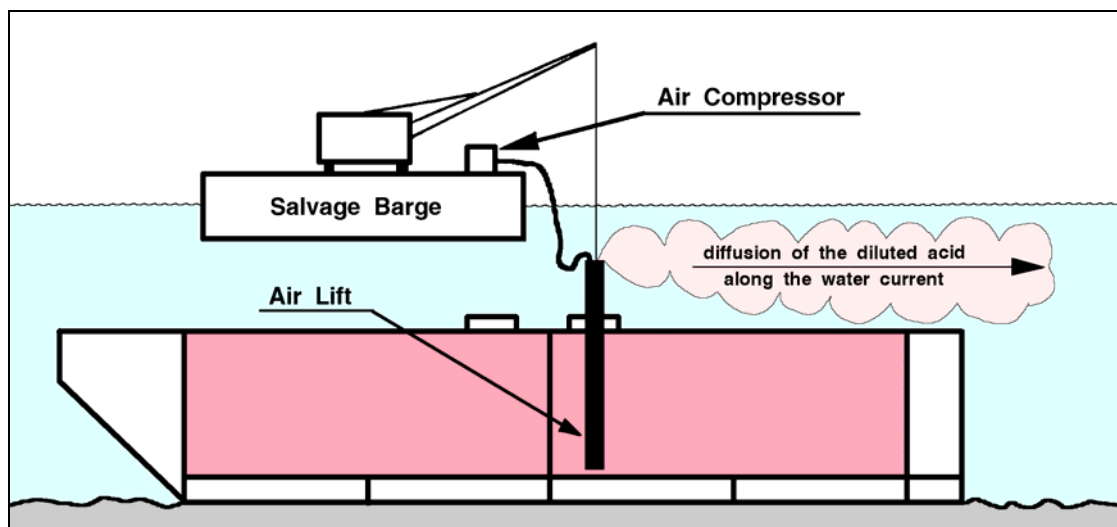


Figure 5 - 43 A sunken barge with a cargo of concentrated sulphuric acid was emptied by an airlift dredge and the acid was very slowly released into the Mississippi River under **strict supervision** of downstream pH-levels.

Limitations Feasible for soluble chemicals only.

Using an underwater drilling system to enable evacuation of contents from sunken tanks and vessels

Method Drilling holes in sunken containers and vessels.

Application Sunken containers and vessels containing liquid substances.

Description

DOLS, Diving Oil Lightering System, is an underwater system for drilling holes in ship hulls and lightering oil from sunken vessels. The DOLS equipment has been designed, as regards size and weight, so as to facilitate its handling by the divers (see Figure 5 - 45).

A hydraulic punching drill is attached (see Figure 5 - 44) by a magnet to the ship plate where the hole is to be made. After the drilling operation the hole is fitted with a special flange which is adapted to the lightering hose.

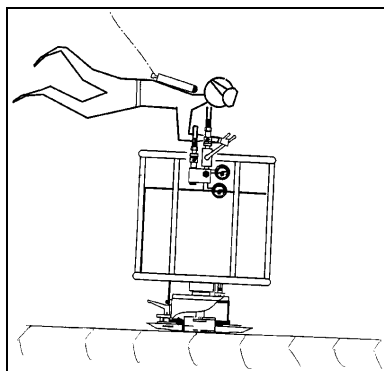


Figure 5 - 44

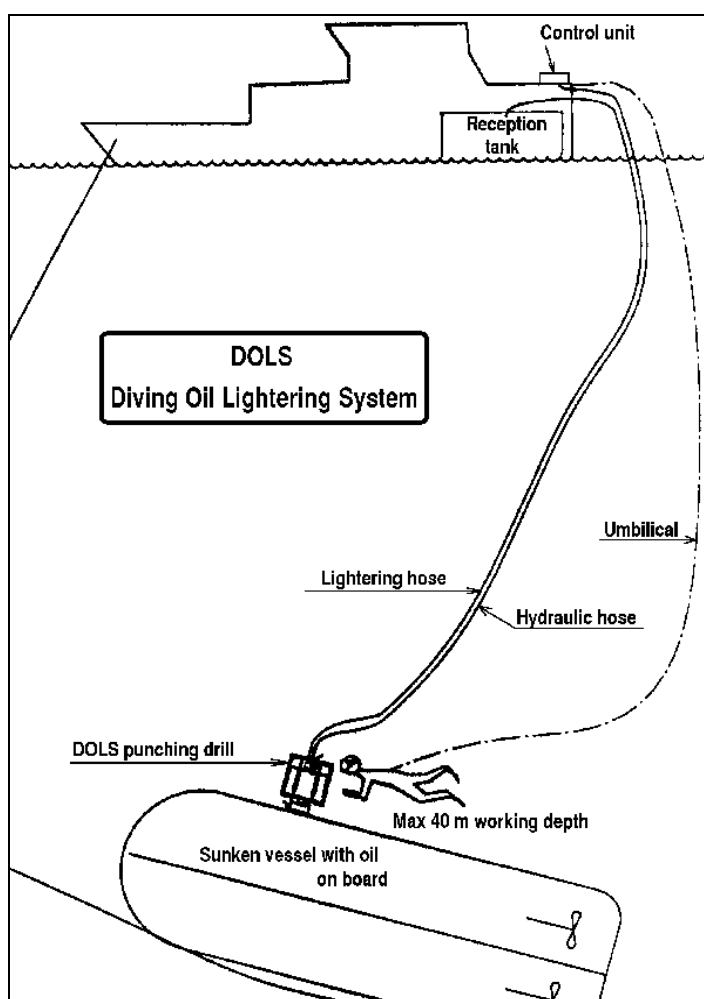


Figure 5 - 45

Limitations Feasible only in water depths less than 40 m.

5.5 Chemicals that react with water

General actions should be taken according to Subchapter 1.2. Details on some reactive chemicals are given in Section 1.3.2. It is impossible to give general guidance on how to respond to chemicals that react with water. The response must be planned from case to case with extreme consideration to the reactivity of the substance.

5.6 Miscellaneous disposal methods

General

Disposal processes include methods by which chemicals and chemical-contaminated wastes are disposed of or finally eliminated. Such methods are normally applied after the response phase. A few techniques are utilized at the site of accident, but most of them are practised at special facilities after transportation of the hazardous materials. Main groups of disposal methods are briefly discussed below.

In situ burning (controlled burning)

Many substances emit highly toxic vapours when burning. This method is therefore used in exceptional cases only, and approval is generally required from appropriate authorities. Floating spills on the water surface are normally difficult to ignite and usually require special ignition techniques like incendiary bombs containing thermite, flame throwers or air curtains.

Incineration

High-temperature burning in a special combustion chamber gives complete oxidation if the burning is performed under carefully controlled conditions. There are various types of incinerator systems based on either fixed or moving bed designs. Generally speaking, incineration is a very efficient technique to dispose of a wide range of substances where the process gives minimum pollution.

Wet air oxidation

Wet air oxidation of chemicals under moderate temperatures and elevated pressure with proper combinations of temperature, pressure and reaction time can give complete oxidation of substances in a specially designed equipment. The process is energy conserving with a proper chemical feed and the oxidation reaction is thermally self-sustaining once started.

Pyrolysis

A combustion process in two steps based on insufficient oxygen supply. It is aimed for complex waste mixtures that are converted by heat to solid easy-to-handle char in a pyrolyzing chamber with no oxygen. The volatile fractions are given off to a fume incinerator.

Landfill

Burial of chemical waste in ground cavities or excavated trenches. The material should be pre-treated according to applicable regulations in order to reduce contents of certain components. Many states prohibit landfill of certain chemicals.

Deep-well storage

Underground storage require selection of a geologic formation and drilling a well to a appropriate depth. The method is often strictly regulated and surround by requirements regarding low seismic activity, low site value as a resource, careful geologic investigation and perfect encapsulation technique.

6 Techniques for corrective response to accidents involving lost packaged dangerous goods in the marine environment

6.1 Introduction

6.1.1 The International Maritime Dangerous Goods Code (IMDG Code)

The IMDG Code (Ref. 40) contains information on several thousands of substances, materials and articles. Figure 6 - 1 reviews the main properties for each of the IMDG Code classes that should be considered when assessing risks to man and to the environment. When responding to accidents involving packaged dangerous goods it is crucial to identify and recognize the IMDG Code Labels, Marks and Signs on the packages (cf. Annex 6). Reference is made to the IMDG Code regarding their exact meanings.

Class	Types of substances and articles	Properties to be considered	Examples
1	Explosives	Risk for explosion <i>en masse</i> , hazardous gases or projection, sensitivity to water or impact	ammonium nitrate detonators
2	Gases compressed, liquefied, or dissolved under pressure	Flammability, toxicity, oxidizing effects, corrosiveness	oxygen LPG acetylene
3	Flammable liquids	Flash point, toxicity, corrosiveness, solubility in water	ethyl alcohol kerosene
4	Flammable solids	Sensitivity to drying, carbon dioxide or water	sulphur calcium carbide
5	Oxidizing substances	Risk for explosion, type of packaging	hydrogen peroxide sodium chlorate
6	Poisonous substances, repugnant and infectious substances	Type of toxicity, flammability, sensitivity to water	phenol, TML, TEL dung dead animals
7	Radioactive substances and articles	Level of activity, package design	tritium radium
8	Corrosives	Level of corrosiveness, flammability, flash point	sulphuric acid sodium hydroxide
9	Miscellaneous substances and articles		asbestos, PCB transformers containing PCB

Figure 6 - 1

6.1.2 Approval of packagings for transport of dangerous goods

All packagings for transport of dangerous goods must be type approved. This also applies to outer packagings (e.g. salvage drums) for containment and transport of damaged drums or similar containers.

Testing and type approval of packagings for dangerous goods are performed by authorized institutes in each country and the approvals are valid internationally.

Type approved packagings are always marked according to a template system. For a tight head steel drum the marking is shown in Figure 6 - 2 and for a removable head steel salvage drum the marking is shown in Figure 6 - 5.

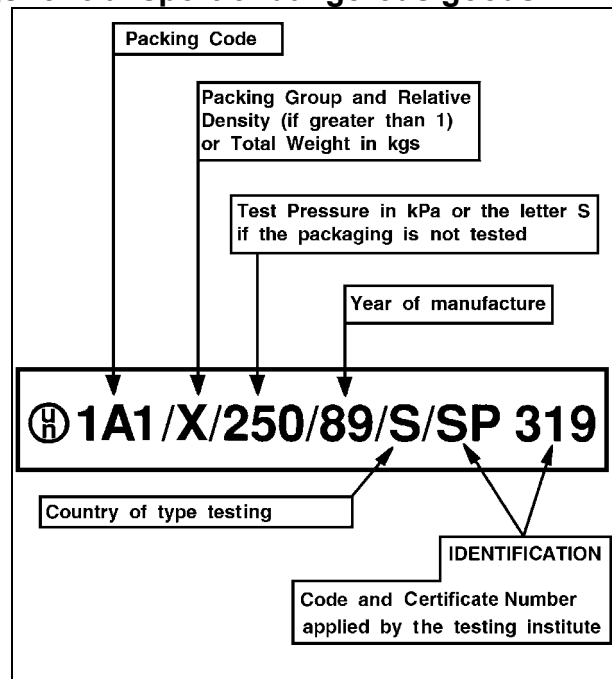


Figure 6 - 2

Template for a type approved steel drum.

6.2 Examples of packagings and containers

6.2.1 General

A great variety of packagings are used for transportation of dangerous goods, e.g. sacks, boxes, carboys, drums, jerricans and steel cylinders. These types of small packages are usually stowed in freight containers. Portable tanks, road and rail vehicles, freight containers, large packagings (LP:s) intermediate bulk containers (IBC:s) and nuclear fuel flasks are also regarded as packagings in this context.

6.2.2.1 Small and intermediate size packagings

Salvage drums

The IMDG Code, 2000 Edition, 1.2.1 Definitions, states the following:

"*Salvage packagings* means special packagings conforming to the applicable provisions of this Code into which damaged, defective or leaking dangerous goods packages, or dangerous goods that have spilled or leaked are placed, for the purpose of transport, recovery or disposal".

A salvage drum is always larger than the inner package allowing the latter to be placed inside the salvage drum for safe shipment to a disposal or treatment facility.

The construction material of the salvage drum must be compatible with the substance in the inner package. Salvage drums are usually made of steel or polyethylene.

Salvage drums must pass, at a minimum, standard UN performance requirements and shall be marked with the appropriate UN approval (cf. Figure 6 - 5).



Picture source: Environment Canada

Figure 6 - 3



Picture source: UltraTech International, Inc.

Figure 6 - 4

Figure 6 - 5 (right)

Example of type approval marking for a removable head steel salvage drum (cf. also Sections 4.8.3 and 6.1.2).



Meaning of marking codes in Figure 6 - 5:

- u
n The United Nations packaging symbol.
 - 1 Type of packaging (1 = drum).
 - A Type of packaging material (A = steel).
 - 2 Removable head
 - Y Tested for packing groups II and III
 - 300 Leakproofness hydraulic test pressure, kPa
 - S Intended for the transport of solids or inner packagings or, for packagings (other than combination packagings) intended to contain liquids, the hydraulic test pressure which the packaging was shown to withstand in kPa, rounded down to the nearest 10 kPa.
 - 94 Year of packaging manufacture.
- USA The State authorizing the allocation of the mark, indicated by the distinguishing sign for motor vehicles in international traffic.
- abc The name of the manufacturer or other identification of the packaging specified by the competent authority.

The terms “salvage packagings” and “salvage drums” are more and more being reserved for approved packagings for transportation of leaking or damaged dangerous goods, while other terms like “overpacks”, “overdrums”, “cover drums” and “recovery drums” are used for cover packagings which are intended for undamaged dangerous goods and which therefore do not need to be approved as salvage packagings.

Steel and plastic drums

Drums for hazardous materials range from 15 to 250 litres and are generally made of steel, plastic or fibre. They are most often stowed in freight containers where they sometimes are carried on pallets. Smaller drums are most often placed on pallets wrapped in

polyethylene sheets. Around 80 or 160 large drums (~ 200 litres) can be stowed in a 20-foot resp. 40-foot box container.

The traditional **steel drums** are very common as containers for both chemicals and petroleum products. Two main types are used: With **tight heads** (non-removable heads) for liquids and with **open heads** (removable heads) for solids. The heads on the latter type are fastened by locking rings. This type has often also a plastic bag as an inner packaging.

Figure 6 - 6

Common characteristics of steel drums		
External volume (litres)	Tare (kg)	Volume of contents (litres)
225	15-20	200-210
120	12-15	110
60	4-6	55
30	2.5-4	27

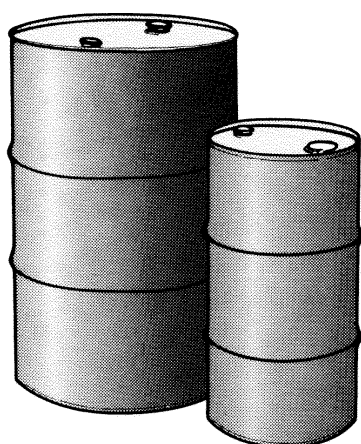
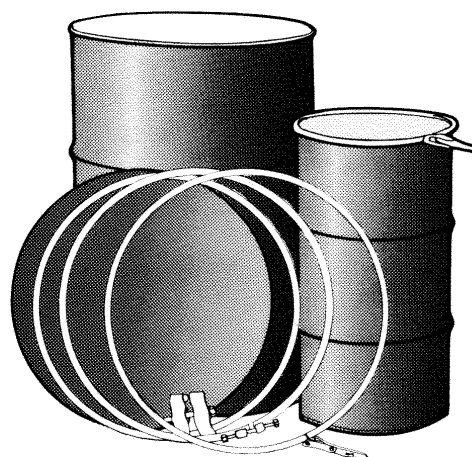


Figure 6 - 7 Tight head or non-removable head drums for liquids



Picture source: Van Leer Sweden

Figure 6 - 8 Open head or removable head drums for solids

Drums are most often carried in dry freight containers where a 20-foot container can take between 78 and 82 pieces of 225 litre-drums. Drums may also be stowed and strapped on loading pallets and wrapped in polyethylene sheets. An empty loading pallet weighs between 7 and 10 kg.

Drums as well as many other types of packagings are now often made of **plastics**. Also plastic drums are manufactured in the two forms: With tight heads (non-removable heads) for liquids and with open heads (removable heads) for solids.

Figure 6 - 9 (down)

Common characteristics of plastic drums			
External volume (litres)	Tare (kg)	Volume of contents (litres)	No. of drums per pallet
215-225	8-10.5	200	4
125-130	3.5-4.5	120	5
65-68	2-3.5	60	8
32-33	1-1.6	30	12



Picture source: Hazardous Cargo Bulletin

Figure 6 - 10 Drums and other types of plastic packagings for dangerous goods

Fibre drums

Normal sizes of fibre drums are 60-220 litres. They are only manufactured with open heads (removable heads) for solids. They are either made of kraft liner throughout or kraft liner reinforced by layers of plastics and/or aluminium. The kraft liner layer can also be treated with paraffin wax or silicone. Heads and bottoms of fibre drums may also be reinforced by steel rings.



Picture source: Hannels Industrier, Sweden

Figure 6 - 11

Examples
of fibre
drums.



Picture source: Van Leer, Sweden

Figure 6 - 12

Fibre drums lose their mechanical strength in contact with seawater – already after one hour as regards those made of kraft liner throughout. Reinforced fibre drums keep watertight but also lose their strength after some time in seawater. This should be observed during response actions as fibre drums may easily rupture when handled by pick-up devices.

Large packagings, LP (in the 2001 IMDG Code)

An LP consists of an outer packaging with contents of either articles or smaller packagings. It exceeds 400 kg net mass or 450 litres capacity but have a volume of not more than three cubic metres. The LP approval encompasses the outer packaging together with its contents as an integrated unit. Examples of use: Objects with explosives, clinical waste, etc.

Figure 6 - 13 shows an example of a Large Packaging LP made of plywood (1.4 x 1.1 x 1.4 m) approved for explosives on an inner specialized pallet.



Picture source: Peter Blomgren, SP, Sweden

Figure 6 - 13

Intermediate Bulk Containers, IBC

Approved containers for transport of chemicals of sizes between normal drums and freight containers.

IBC sizes

1-3 m³, 1-3 tons

IBC construction materials

Metals (steel, aluminium etc)

Plastics, composites

Wood, wooden materials

Textiles, Paper

Figure 6 - 14

An IBC made of textile

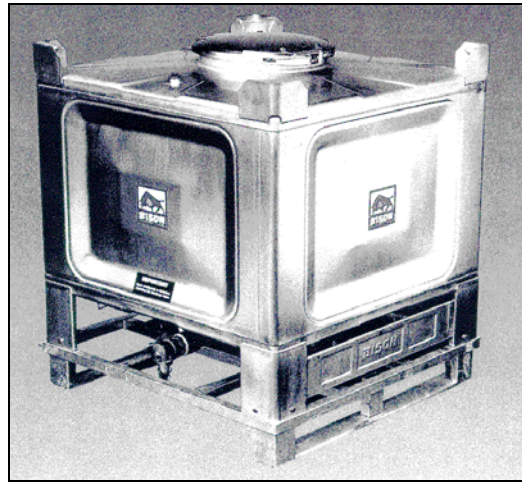


Picture source: Hazardous Cargo Bulletin



Picture source: Van Leer, Sweden

Figure 6 - 15
An IBC made of plastic

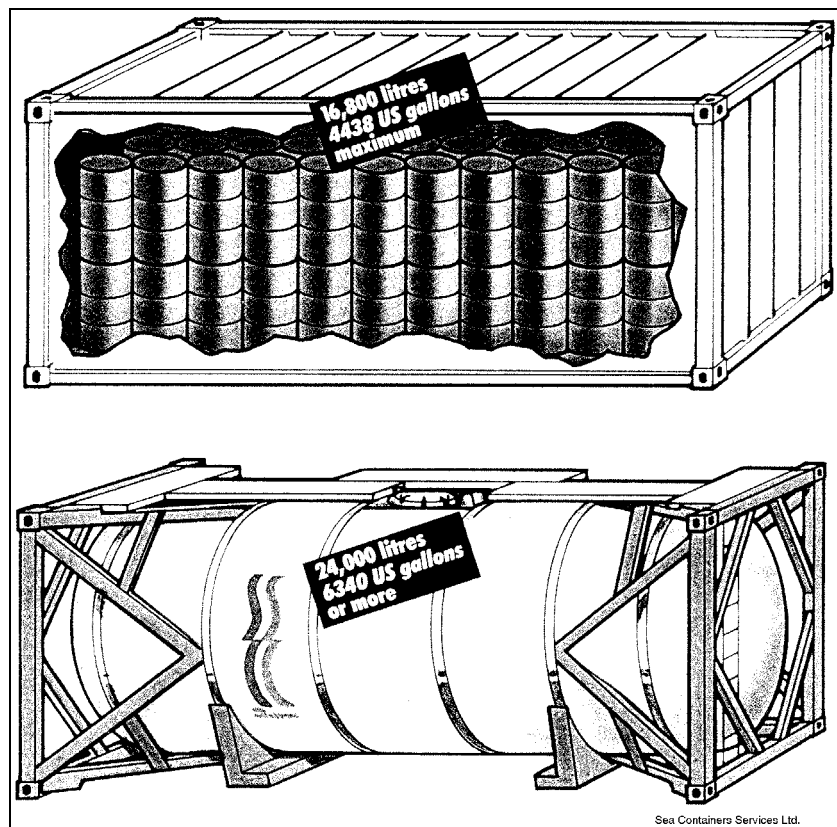


Picture source: Bison Containers, Norway

Figure 6 - 16
An IBC made of metal

6.2.3 Sea freight containers

Standard dry freight containers and tank containers are often used for transport of chemicals and dangerous goods at land, at sea and on inland waterways. They are internationally standardised. Standard dry freight containers are normally 20 feet or 40 feet in length and tank containers are 20 feet. Figure 6 - 17 from a tank container manufacturer illustrates that a tank container can hold more liquid than a dry freight container of the same size stowed with drums.



Sea Containers Services Ltd.

Picture source: Sea Containers Services Ltd.

Figure 6 - 17 A tank container can take 43 % more liquid than a dry freight container of the same external dimension.

Common types of dry freight 20-foot and 40-foot containers

Standard containers	For general purpose/normal cargo
High cube containers	Specifically for light, voluminous cargo or those of excessive height (up to 2.67 m)
Hardtop containers	With removable steel roof; For heavy lifts, cargo of excessive height, or loading from above or door end
Open top containers	With removable tarpaulin for loading of cargo of excessive height from above or door end
Flat racks	For heavy lifts and excessively wide cargo Can be positioned side by side for non-containerisable cargo
Platforms	For heavy lifts and extra large cargo Can be positioned side by side for non-containerisable cargo
Ventilated containers	For cargo requiring ventilation
Insulated containers	For sensitive cargo requiring constant temperature Temperature control via the ship's refrigeration plant, terminal refrigeration plant or a "clip-on" refrigeration unit
Reefer containers	For cargo requiring a constant (low or high) temperature With integrated refrigeration or heating unit
Bulk containers	For loose/bulk cargo

Figure 6 - 18

Approximate data for general-purpose dry freight containers

	Dimensions			Cubic capacity	Maximum payload
	Length	Width	Height		
20' (20-foot)	6 m	2.4 m	2.4 m	33 cbm	22 tons
40' (40-foot)	12 m	2.4 m	2.4 m	67 cbm	27 tons

Figure 6 - 19

Tank containers

Tank containers (always 20-foot) are used for transport of liquids or gases. They are constructed with two basic components - the tank itself and the outer framework. Weight, volume and construction details of a tank container vary considerably due to the properties of the transported substance.

IMO define 5 different types of tank containers where the following two types are significant for chemicals:

IMO 1 tanks for the highly flammable, toxic and corrosive liquids.

IMO 2 tanks for medium hazard products such as flammable liquids, herbicides, resins and insecticides.

6.3 Labelling and marking of dangerous goods

The IMDG (International Maritime Dangerous Goods) Code (Ref. 40) contains provisions on how packaged dangerous goods should be labelled. These provisions are valid for all types of transported packages that might be inspected on any occasion in order to determine their contents. The IMDG Code contains all details on how dangerous goods must be labelled. The labels are shown in Annex 6.

If the substance in the package besides the main hazard (e.g. toxic) also exhibits an extra so called “subsidiary risk” (e.g. corrosive) this must also be shown by extra labels (see Figure 6 - 26).

The contents of the package must be given on the exterior of the packaging by substance’s proper shipping name (correct technical name). The proper shipping name is the name of the substance under which it is listed in the IMDG Code. The proper shipping name must also be supplemented by a chemical name of the substance and by the UN number (cf. Figure 6 - 22 and Figure 6 - 27).

The substance’s name may be given in the national language for domestic transport, but most countries require English for international transport.

The packaging must be approved for transport of dangerous goods (cf. Section 6.1.2), and this approval must be marked on the packaging (cf. the drum’s head in Figure 6 - 22).

Labels and inscriptions must be clearly readable after three months in seawater. The labels’ sizes should be 100 mm x 100 mm for smaller packages (drums, boxes, etc.) and 250 mm x 250 mm for freight containers and dangerous goods on pallets.

The US National Fire Protection Association (NFPA) has a marking system ("the NFPA fire diamond", Figure 6 - 20) that indicates the dangers associated with various hazardous materials (cf. Annex 6). The system is intended for use on fixed installations, like storage containers, storage rooms and warehouses, entrances to laboratories, and chemical processing equipment. The system is designed for the benefit of emergency responders. Though the system is not required in transportation it is often seen on transported dangerous goods all over the world. (See Annex 6)



Figure 6 - 20

Tank cars and tank containers running by road under international ADR regulations will carry a two- or three-digit code, referred to as the Hazard Identification Number (HIN) or the Kemler Code. This code gives information about the hazards involved in dealing with the material. If the digits are preceded by an X (as in Figure 6 - 21) it indicates that the substance reacts dangerously with water. The number below the Kemler Code is the UN number for the substance. (See Annex 6)



Figure 6 - 21

The so called **Hazchem Codes** are used in the UK only. They are shown on vehicles carrying dangerous by road in UK national journeys and are therefore not dealt with here.

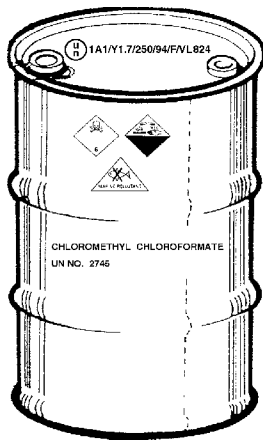


Figure 6 - 22
A drum with labels, proper shipping name of contents and approval marking.



Figure 6 - 23
A pallet with sacks of an oxidizing substance.

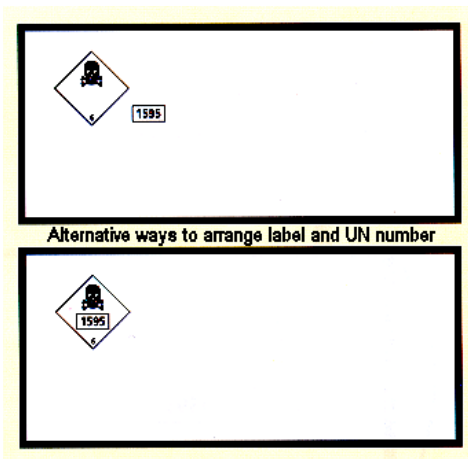


Figure 6 - 24
An example of a dry freight container with packages of a single dangerous substance.

Figure 6 - 25
Both sides and both ends of a dry freight container or a tank container must carry a placard or placards corresponding to the appropriate labels.

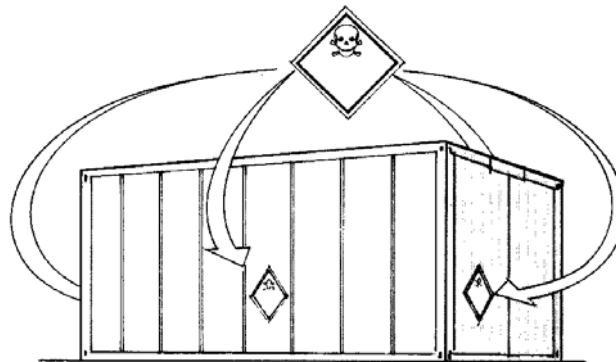


Figure 6 - 26
An example of a container containing packages of dangerous substances belonging to different classes. Only placards have to be affixed.

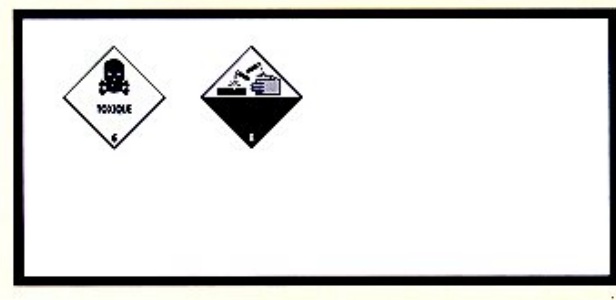
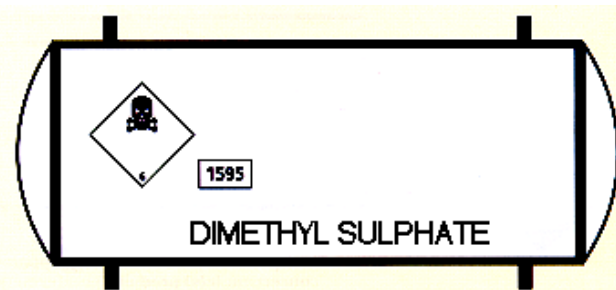


Figure 6 - 27
An example of a portable tank (tank container). As well as the placards and the UN number, the proper shipping name must be marked on at least the two sides.



6.4 Behaviour of packages in seawater

6.4.1 General

Many properties of the packagings influence their short-term and long-term behaviour when lost at sea. Such properties are for instance:

- Gross weight, gross volume, buoyancy.
- The packaging's appearance and shape (dry freight container, tank container, intermediate bulk container (IBC), large packaging (LP), drum, box, steel cylinder, can, bottle, sack, etc.).
- Combination of outer and inner packaging, e.g.
 - smaller packagings packed or stowed in dry freight containers
 - smaller packagings enveloped in outer safety covers
 - many small packaging held together by outer wrappings
- Packaging material (iron, stainless steel, aluminium, wood, plastics, composite, glass, textile, paper, etc.).

6.4.2 Grouping of packages according to their buoyancy in water

It is difficult to develop a sophisticated classification system for packages of dangerous goods based on their buoyancy in water. There are actually only the two alternatives float or sink on the assumption that the package is not punctured. On rare occasions the package's bulk density might be very close to that of the surrounding water. Then the package may float just below the water surface (is waterlogged) or may slowly sink to the bottom. In turbulent water the package may of course whirl round in the water body and neither reach the surface nor the bottom.

In the so called European Classification System (Annex 4) emphasis is laid on 12 Property Groups (G, GD, E, ED, etc.) for substances. But also three Groups for packages (PF, PI and PS) are included in a flow chart which defines the Classification System (see Figure a4-1 in Annex 4). The latter three groups are also defined in Figure 6 - 28.

PF	PI	PS
Package Floater	Package Immersed	Package Sinker
The package floats	The package has the same bulk density as water and is waterlogged*	The package sinks
$w/v < ds - 0,01$	$w/v = ds \pm 0,01$	$w/v > ds + 0,01$
w = the package's gross weight, grams v = the package's gross volume, millilitres ds = water's density, grams/millilitre		

Figure 6 - 28 (cf. Annex 4)

**A waterlogged package may, due to the intensity of water currents, tumble around in the water column at varying depth.*

6.4.3 Buoyancy of freight containers

Many types of packages may float in water owing to internal empty spaces or low density of the contents. Even dry freight containers are often observed floating at sea or washed ashore. Sometimes even tank containers may float.



Picture source: CEDRE

Figure 6 - 29

A floating dry freight container.

Based on calculations alone it is not possible to predict the buoyancy of a freight container or its resistance to mechanical and environmental impact. Its behaviour under the initial impact depends on which part of the container that first touches the water surface. The corners, edges and floor will withstand impacts while the sides and the roof may be torn open and allow the contents (e.g. smaller packages) to escape.

General-purpose freight containers (dry freight containers) are not watertight. For example an undamaged empty freight container fallen into the sea will be slowly filled with water and sink after a while.

Tank containers, on the other hand, are watertight and, if they sink, the valves (safety valve and decompression valve) will balance the external and internal pressures.

6.4.4 Buoyancy of drums

Many liquid chemicals are transported in 200-litre steel drums. Figure 6 - 30 shows the typical data for such drums that can be used when calculating the buoyancy in water when filled with various chemical liquids. Figure 6 - 31 and Figure 6 - 32 show results from such calculations and indicate when drums might float or sink.

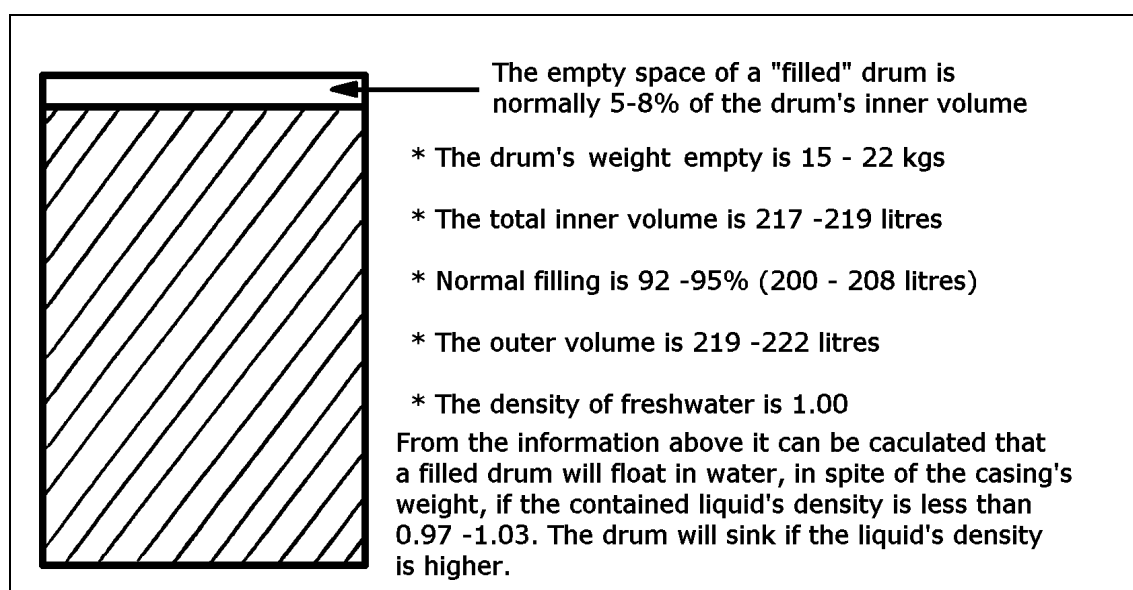


Figure 6 - 30 Buoyancy calculation for steel drums filled with liquid chemicals

Figure 6 - 31 gives examples of low density liquid chemicals which are often carried in 200-litre steel drums, and which due to their density will cause the drums to float in water.

Types of chemicals	Examples
Hydrocarbons	hexane, benzene, toluene, xylene
Alcohols	methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol
Ketones	acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone, cyclohexanone, methyl cyclohexanone
Ethers	diethyl ether, ethyl butyl ether
Esters	methyl acetate, ethyl acetate, butyl acetate
Amines	monoethylamine, diethylamine, ethylene diamine, diethylene triamine, diethylene tetramine
Aldehydes	formaldehyde, acetaldehyde, butyraldehyde, acrolein

Figure 6 - 31

Figure 6 - 32 gives examples of high density liquid chemicals which are often carried in 200-litre steel drums, and which due to their density will cause the drums to sink in water.

Types of chemicals	Examples
Acids	acetic acid, acrylic acid, formic acid, phosphoric acid, sulphuric acid
Bases	sodium hydroxide solution, potassium hydroxide solution
Glykols	ethylene glycol, diethylene glycol, propylene glycol
Chlorinated hydrocarbons	carbon tetrachloride, trichloroethylene, tetrachloroethylene, methylene chloride, ethylene dichloride, trichloroethane
Miscellaneous	carbon disulphide, toluene diisocyanate, tetramethyl lead, tetraethyl lead

Figure 6 - 32

NB: Cans and drums filled with solid chemicals will always sink in water.

An accident involving drums of propionic acid (cf. Annex 3, accident "Propionic acid")
On several occasions around 8-10 January, 1975, approximately 30 very rusty drums of propionic acid were washed ashore on the Swedish West Coast about 100 km north of Gothenburg. It was not possible to judge how long time the drums had been moved by the sea and exposed to marine water. Propionic acid is chemically closely related to acetic acid. Drums with acetic acid would sink in fresh water but the slightly lower density of propionic acid (0.99) than acetic acid (1.05) together with the better buoyancy in marine water explain that the drums in this case floated and were washed ashore.

6.4.5 Resistance of drums to mechanical and environmental impact

Type of drum		Drop	Pressure	Corrosion	Wettability
Steel drums	Tight-head	+	+	++	n/a
	Removable-head	-	-	++	n/a
HD polyethyl-ene drums*	Tight-head	++	++	n/a*	n/a
	Removable-head	+	-	n/a*	n/a
Fibre drums	Removable-head	+	--	n/a	-

Figure 6 - 33 Durability of drums

*Plastic materials may loose its strength when exposed to the sun's UV-light

n/a = not applicable			
++	very strong	-	may be damaged
+	strong	--	easily damaged

An accident involving steel cylinders of chlorine

(See Annex 3, accident "Sindbad"; See also Section 5.1.1)

*In 1979 a ship lost her deck cargo of 51 steel cylinders containing **chlorine** gas off the Dutch coast. Five years later Dutch responsible authorities started an extensive re-sponse operation. The cylinders were, however, so corroded that no attempts were made to salve the cylinders. Instead, divers placed explosives under each cylinder, which then was blasted under strict control.*

6.5 Safety precautions

6.5.1 IMO manuals

Many aspects on safety precautions are addressed by International Maritime Organization (IMO) in the Manual on Chemical Pollution (Ref. 1), Section 1 on "Problem Assessment and Response Arrangement" and Section 2 on "Search and Recovery of Packaged Goods Lost at Sea".

6.5.2 General observations

The packaging properties and the development of events will be determining for the choice and design of response actions. Floating packages require quite different actions compared to accidents involving sinking packages. The packages' sizes and weights will be decisive for the choice of salvage equipment. The packages' appearance and the packaging material have a bearing on how they should be handled. The planning of the whole operation depends on whether the packages are damaged or leaking.

Before starting a salvage operation against packages lost at sea it is important to predict their behaviour in order to assess the risks to response personnel, population on land, seafarers, and to the environment. The following questions should be asked:

- Is there a risk that the contents of the packages will escape?
- Will the package float or sink?
- To where will floating packages move?
- Will sunken packages stay or move on the seabed?

Mechanical damage of the packages during the accident may cause stress to the packaging material and increase the risk of ruptures.

6.5.3 General checklist

- ♦ Always observe the greatest caution when starting to inspect and salvage a package which is suspected to contain chemicals. A package with unknown contents and with no interpretable information on its cover must be considered dangerous until clarity is achieved. Always act on a worst possible case basis.
- ♦ All relevant information should first be gathered about the chemicals as well as the properties of the packaging.
- ♦ Adjust the level of the personnel protection to the contents of the package (if known) as well as package size and appearance (damage, leakage)
- ♦ Observe the uttermost caution if the contents and the appearance of the package are unknown.
- ♦ Unprotected personnel must be directed to the windward side of packages with unknown contents or packages with hazardous leakage.
- ♦ Use appropriate personnel safety equipment if there is any risk for the packagings to be damaged during the salvage.
- ♦ Observe the greatest caution when working close to crane lift operations, especially when loaded freight containers are involved.
- ♦ With due consideration to safety, mark as soon as possible large containers with appropriate devices (buoys and/or radio/radar beacons, reflectors or transmitters). See also Section 6.7.4.
- ♦ Take samples of the contents of damaged (and leaking) packages. Sampling of intact packages should be avoided.

The packaging material's weather resistance will significantly influence the safety precautions during the response action. E.g. paper and wood fibre exhibit short marine environmental durability while casings of e.g. iron may resist several years before they are penetrated by rust (Ref. 41, Ref. 42 and Ref. 43).

Recovered packages containing chemicals and dangerous goods should always be treated with greatest caution during the salvage action as damaged packagings might leak. Smaller packages that are adversely affected by the marine environment should by safety reasons always be transferred into salvage drums (cf. Figure 6 - 3) before other actions and transport. Note that these salvage drums must be approved for transport of dangerous goods.

6.6 Salvage of floating packaged goods

Salvage of floating drums

Method Salvage by collection nets

Application Mainly floating drums containing certain short-chain hydrocarbons, alcohols, ethers, ketones, amines, acetates, aldehydes. Also other types of floating packages containing dangerous goods.

Description Small packages (like drums) floating on the water surface can most easily be salvaged by a special heavy-duty designed collection nets.

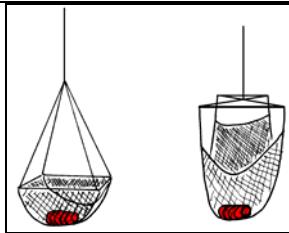


Figure 6 - 34
Collection bag nets for salvage of packaged dangerous goods on the water surface.

Figure 6 - 35

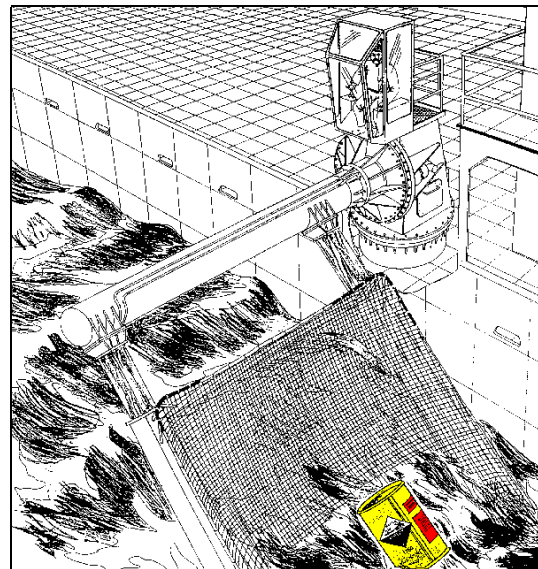
The net device should be manoeuvred with appropriate considerations of safety precautions as the package may be damaged during the operation.



Picture source: CEDRE

Figure 6 - 36

There are also specially constructed, more sophisticated and robust systems for salvage of items on the sea surface like this "Sealift".



Picture source: SMV Engineering A.S., Norway

Limitations Operational wave height maximum 2 m.

Salvage of floating freight containers

Method Lifting by crane.

Application A floating container may be recovered on board a salvage ship by lifting it to the stern using slings attached to the corners of the container.

Description

Large containers, e.g. freight containers, must be salvaged by means of arrangements which are adjusted from case to case with regard to the circumstances and to the available salvage equipment.

Specially designed slings for hooking on freight containers (cf. Figure 6 - 37) should be available on board the salvage vessel. These slings are fitted with two hooks (ABK or CROSBY) having a carrying capacity of at least 20 tonnes (each sling has a length 5 metres and a breaking point of 50 tons).

Procedure

- If possible start to recover part of the container's contents already when it is still waterlogged.
- Clear the deck of the salvage vessel and prepare for use of personal protective gear if necessary.
- Reel out 100 m wire cable with attached buoys to make it float. Carry four slings by a workboat to the floating container.
- Handled the slings one by one at each of the container-corners held by a buoy in the water.
- Hook the slings onto the corners. Use lower corners if they are judged to be of better strength.
- Manoeuvre the salvage vessel in such a position as to lift the container in the safest way (if possible with the container doors facing the vessel).
- Start winching as soon as the container is raised by a wave.
- Control the cable tension during lifting (a 20-foot container $\frac{3}{4}$ filled with water has a weight of nearly 30 tons).
- If necessary (and if possible) puncture and drain the container at the start of the lifting operation.
- Fasten the container as soon as it is keeping balance on the vessel's deck. It can later be moved to a safer place.

Limitations A salvage vessel with heavy lifting capacity must be available for the operation as the weight of the container may increase considerably due to penetration of water and mud. The weather must be calm enough to allow attaching the container to a crane hook. No attempts should be made to recover the container if its contents is unknown (it should however be buoyed).



Picture source: CEDRE

Figure 6 - 37



Picture source: CEDRE

Figure 6 - 38



Picture source: IMO

Figure 6 - 39

Salvage of floating freight containers	
Method	Towing to a safe haven.
Application	A towline is attached to one or more of the container corners and the container is towed to a haven where it can be safely taken care of.
Description	<p>Experience has shown that a floating freight container during a towing operation (cf. Annex 3, accident Perintis) may be accidentally lost and unable to be found again. It is therefore important <i>prior</i> to the towage operation to equip the container with</p> <ol style="list-style-type: none">1) a large buoyant device (floatation boom or collar) with buoyancy enough to keep the container afloat, and2) a tracing device e.g. radio transmitter, transponder, radar reflector or optical blinker. <p>It is recommended that four propylene ropes are attached asymmetrically to the corners of one of the short sides of the container. Two by two of the ropes should be of equal length. The length of two of the ropes should be double or threefold the length of the shorter ones. The ropes of equal lengths should be attached in the corners of the same perpendicular.</p> <p>In such a way one of the edges of the short side of the container will plough through the water like the stem of a ship. The resistance of the water during such a towage is considerably reduced compared to if the ropes would be attached in a symmetric way to the container.</p> <p>The ropes could be difficult to attach even in a slight sea swell and sometimes it might be judged to be enough with two hooks (one submerged) at each end of a vertical edge.</p> <p>If the sea is too rough for a fastening the hook on a submerged corner it might be sufficient to attach a single rope to one of the available hooks above the water surface.</p>
Limitations	Towage of a container with potentially hazardous leaking content must be planned carefully in order to avoid vulnerable coastal sites. The safe haven for the container as well as all safety precautions must be carefully selected and planned with appropriate regard to the operation against the container.

6.7 Salvage operations involving sunken packaged goods

6.7.1 General

Specialist resources must often be used in connection with activities described below.

- ♦ Searches, especially over large sea bottom areas, are best done by using side scan sonar.
- ♦ Selection of echoes is performed by interpretation of imageries from a sides can sonar.
- ♦ Locating and positioning of echoes can be done by a system consisting of a hydroacoustic transmitter on board a search vessel and transponders which are set out on the bottom within the search area.
- ♦ Sorting out insignificant echoes can to some extent be made by colour coded sector scanning sonars.
- ♦ Identification of remaining "hot" echoes could preferably be done by submersibles to ascertain which of the echoes originate from intended items.
- ♦ Close inspection of found items should be done by submersibles or divers in order to find out their physical appearance, i.e. if they are leaking, how they should be salvaged, etc.
- ♦ Salvage of goods on the seabed.

6.7.2 Locating packages on the seabed

When lost packages have sunk to the seabed it will normally be necessary to search for them over a large area. When targets are spotted, they should be inspected more closely, in order either to discard them as false, or to identify them as the lost packages.

The work to find packages on the seabed may comprise the following phases, which all also include special routines for precision navigation:

- Large bottom area search
- Checks on obtained echoes
- Inspection of found goods
- Salvage of goods

Locating packages on the seabed may be very difficult and will depend on the situation. When organizing and performing a search for lost packages, the most important information is the position report and an indication of its accuracy. The water depth and the topography of the sea floor will highly influence the complexity of the search operation. Other important factors affecting the search are package type, size and shape, packing material, as well as sea currents and sea state.

Currents may also move packages from the known position or cover them with bottom sediments. Their position may also be affected by fishermen's trawling.

Precision navigation systems

On many occasions during search operations at sea, it is necessary to utilize specific navigational systems to be able to manoeuvre vessels in a precise manner and make accurate map plots of the search area.

Whichever system is used to locate the lost packages, the prime requirement is that the system must be very accurate so that the echoes can be easily found again after the general large area plotting.

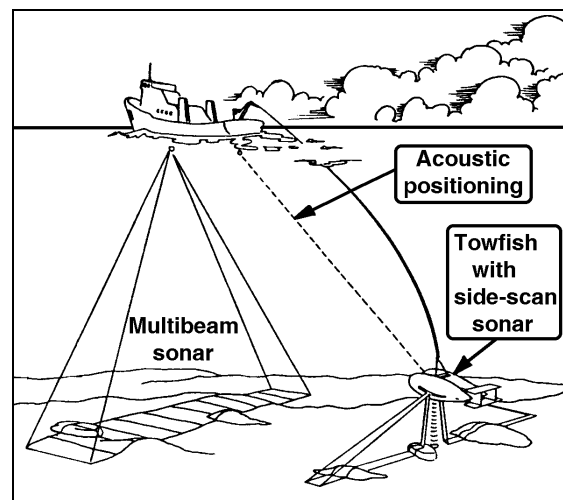
A prerequisite for a successful large area search is a well-equipped platform. The brain of the platform is a **survey computer** that can

- be pre-programmed with reference lines and target points
- calculate the ship's position continuously
- furnish the control system with position coordinates continuously
- guide a large area search system with position reference data
- collect position reference data from different sources, e.g.:
 - radio positioning system
 - conventional GPS
 - differential GPS
 - hydro-acoustic positioning system.

Searching large bottom areas

An underwater search for sunken items usually starts with searches over large areas by sonar systems (hull-mounted, towfish-mounted or ROV-mounted) sometimes in combination with magnetometers. A major factor in the success of modern side-scan sonar systems is that they are towed near the bottom rather than hull mounted. Proximity to the bottom allows much more detailed, higher resolution records. When a number unidentified echoes have been registered and positioned they have to be more closely inspected and identified by certain high-resolution sonars, underwater camera systems and/or divers.

A side-scan sonar is a tool by which it is possible to survey large undersea areas. A side-scan sonar system utilize a towed device (towfish or "fish") which emits high frequency, high intensity pulses of sound to either side of a moving vessel. Objects and features on the seafloor reflect the pulses (give echoes) and return them to the towfish. The pulses are the converted to electrical signals which are sent up the tow cable to a graphic recorder that makes a continuous strip chart recording of the echoes. The record generally shows the bottom directly below the ship as well as the terrain on either side of the ship.



Picture source: Swedish National Defence Research Institute

Figure 6 - 40 Large bottom area search by hull- and towfish-mounted sonars.

6.7.3 Underwater techniques using submersibles for actions against sunken packages

General

By means of various submersibles it is possible to perform a variety of underwater work, e.g. inspection and identification of packages on the seabed. However, it is difficult to accomplish salvage of cargo from the seabed utilizing solely submersibles. Some submersibles have manipulator arms that can be used to touch and turn items. More sophisticated submersibles are equipped with gear that can grab and salvage single items. Some submersibles are even manned and may thus be more versatile.

Inspection and identification of sunken packages

If it is not judged to be safe to use divers in underwater operations, the use of submersibles equipped with TV cameras is recommended.

Conventional TV or low-light-level TV (LLLTV) cameras may be used, if necessary combined with a light source. Simple sleds carrying TV cameras may be towed or trailed by an umbilical cord.

Most submersibles use TV cameras for inspection of targets on the seabed. The image is transferred through the wire, or wireless, to a TV monitor located on board the surface vessel from which the submersible is controlled.

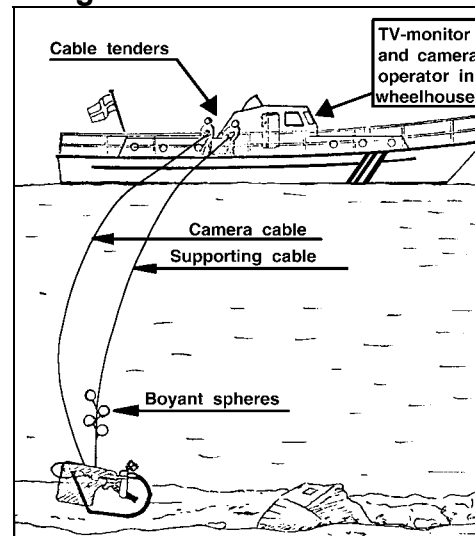


Figure 6 - 41

Figure 6 - 42 More sophisticated submersibles with their own propulsion systems and obtaining their energy and commands through an umbilical cord are so-called remotely operated vehicles, or ROV:s. The ROV should also be equipped with a positioning system so that the finds are documented on sea charts.

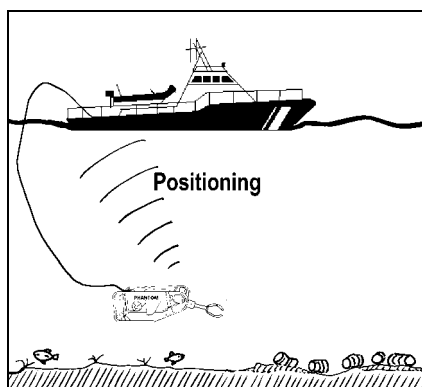
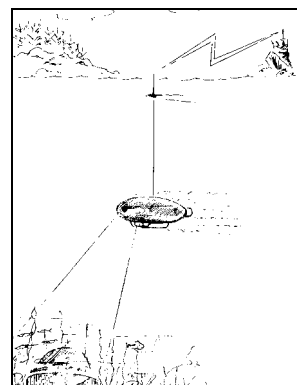


Figure 6 - 43 Autonomous remotely operated vehicles, AROV:s, have their energy supply on board and are controlled by signals through thin wires or by hydro-acoustic (wireless) techniques. Such thin control wires can either be electrical or fibreoptic and may be expendable according to the operational needs.



If the identity of the contents is known (e.g. if the labelling is intact), the hazards can readily be assessed. If not, identification of the contents and assessment of the hazards should be obtained before recovery is attempted. If the presence of radioactive material is suspected, measurement of the radiation level should be carried out before any other actions.

It may be possible to use detection equipment (monitoring instruments) in the field to assist in these processes. A chemical laboratory may be necessary to identify samples where the use of detection equipment is insufficient.

6.7.4 Providing sunken goods with pingers and buoyant bags

Pingers

When sunken items have been found and identified it is necessary to mark them in order to facilitate for response personnel to find them afterwards. Acoustic transmitters (pingers) can be used. They send ultrasonic pulses of certain frequencies which easily propagate long distances in water. With receiving (homing) systems the source can afterwards be located. The choice of frequency is of vital importance as low frequency (10 kHz) sound is transmitted longer but more difficult to locate exactly than a high frequency (40 kHz) sound.

Acoustic transmitters are normally very reliable but they should not be attached directly to the item on the seabed as masking effects may restrain the sound transmission in certain directions. The pinger should instead be attached firmly to the item by means of a 20 m long floating rope. Such a buoyant pinger reduces the risk of masking.

Buoyant bags

In some cases it may be beneficial to raise the item found on the seabed to the surface by attaching buoyant bags to it.

6.7.5 Underwater techniques using divers for actions against sunken packages

General

Response actions against sunken packages can be accomplished by trained divers or by other means.

The prime three diving techniques are the following:

- | |
|---|
| <ul style="list-style-type: none">- SCUBA diving- Saturation diving- Atmospheric diving |
|---|

Divers working with leaking packages should take particular care as the diver's suit may be torn and his skin may be exposed to the leaking substance. Therefore the divers should wear protective gear appropriate to the hazard involved to avoid skin contact with the surrounding water. The best solution is normally acquired by dry diving suits which are certified for the specific chemicals involved.

Packages up to the size of drums may be transferred by means of a transfer crane to a large container which is lifted to the surface when filled. Larger packages may be attached one by one to a line and lifted to the surface. These methods can be used for packages on the seabed or in a sunken ship. In the latter case the ship's hull may need to be opened in order to reach the packages inside the ship, possibly causing the packages to float free.

Bounce diving

A bounce dive is a dive of relatively short duration and generally less than 10 minutes. Sometimes a bounce dive is characterized as a relatively deep dive with a short bottom time (with a long surface interval to eliminate gas bubble formation in blood and tissues).

In recreational diving the concept of bounce dives usually means going straight down and, immediately after reaching the bottom, coming straight back up, without stops. In commercial and military diving, any dive not involving decompression from saturation would usually be regarded as a bounce dive, even if it involved a long decompression.

"Bell bounce diving technique" means a diving procedure whereby a diving bell or diving submersible is used to transport divers who are under atmospheric pressure or pressures greater than atmospheric pressure to a work site and subsequently to transport the divers under pressures greater than atmospheric pressure from an underwater work site, but does not include saturation diving techniques.

SCUBA diving

Inspection of packages in shallow water and sometimes even recovery may be carried out by trained SCUBA (Self-Contained Underwater Breathing Apparatus) divers, i.e. air divers in light suits. If necessary, the divers should wear outer safety suits. In some situations, it may be convenient to use tethered divers. SCUBA divers normally work down to maximum 40 m.

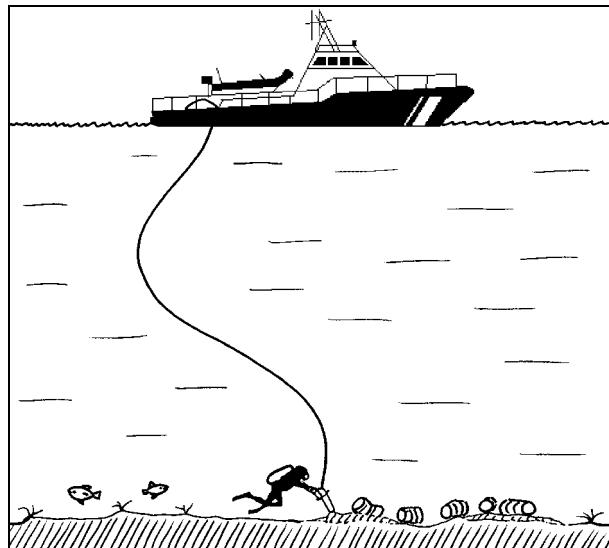


Figure 6 - 44

Saturation diving

General cargoes composed of numerous packages can be recovered by applying a special deep-diving technique called "saturation diving" or "closed bell diving", which has now been used for many years by the offshore industry. Saturation diving techniques generally require a team of divers. When not diving, they stay in a pressure chamber in order to avoid the need for decompression every day. The divers breathe a mixture of helium and oxygen, which reduces the decompression time required following the completion of the dive.

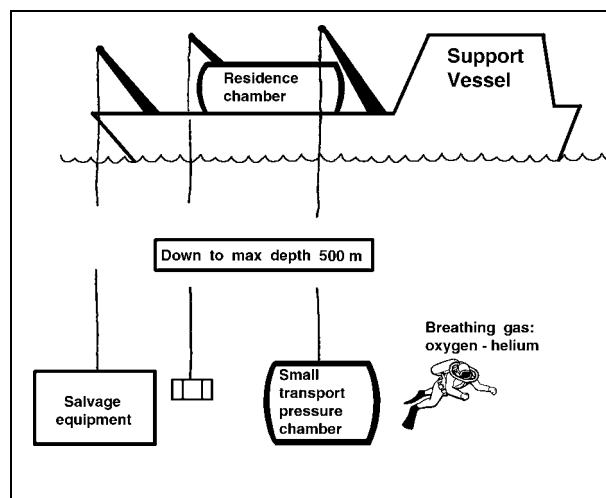


Figure 6 - 45 A closed bell diving system

Atmospheric diving

For deep water work "atmospheric diving" or "JIM diving" is an alternative to saturation diving. It can be utilized at depths beyond the range of conventional saturation diving. In atmospheric diving, a bulky, high-pressure resistant diving suit is used by the diver, who breathes air at normal pressure. An atmospheric diver needs no decompression time when resurfacing.

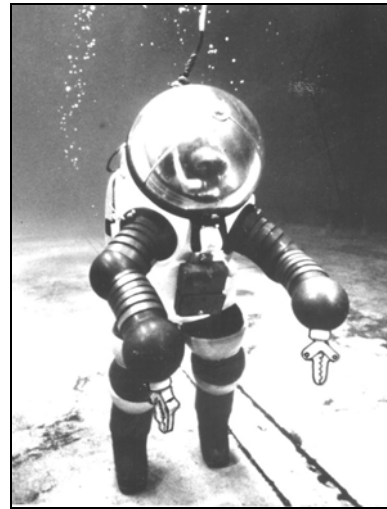


Figure 6 - 46
Underwater diving work in
an atmospheric diving suit

Picture source: Oceaneering

6.7.6 Methods for recovery of sunken goods.

It is often not advisable to drag or trawl the seabed for sunken dangerous goods. Such actions may often damage the packages so that their contents are scattered over the seabed. However, on occasions when the situation is completely under control as regards the packaging's construction, depth conditions, etc., trawling has sometimes been successful.

It is also possible to pick up sunken goods by means of bucket-like devices on grabbing-cranes. But it is advisable to supervise the seabed operation in order to hit the target and avoid to damage it. The supervision can be performed by means of TV-cameras or divers wearing protective suits.

Salvage of sunken drums**Method** Bottom package picker**Application** Drums containing dangerous solids or drums containing certain liquid acids, bases, glycols, chlorinated hydrocarbons, organolead compounds, or organosulphur compounds.

Description An operation involving recovery of sunken packages must be planned in consideration of their sizes, scattering, appearance as well as the properties of their contents. Small packages in not too deep waters can be recovered by means of a hydraulic driven "bottom picker". This should be equipped with a video camera to facilitate the catching of goods on the seabed. If the packages are sunken in greater depths they may first be transferred under guidance and assistance by divers to large containers kept on the seabed. During salvage of large containers (e.g. freight containers) the risk must always be assessed that their contents might escape to the environment during the operation.

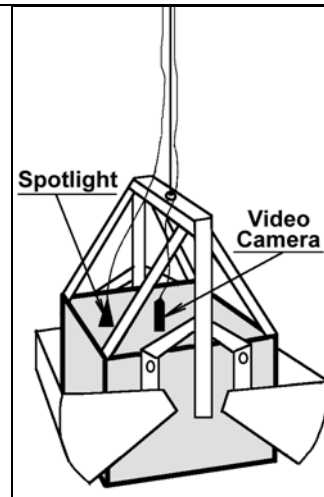


Figure 6 - 47
A so called "bottom picker" equipped with a video camera (ref.: Oy Kart Ab, Finland, and Finnish Environment Institute)

Recovered packages with potential contents of hazardous materials should by safety reasons always be transferred into salvage drums (cf. Figure 6 - 3) before further actions and transport.

Limitations Aimed for relatively small packages (sizes up to drums).
Applicable under calm weather conditions.

Salvage of sunken drums

Method Use of Remotely Operated Vehicles (ROV:s) and racks to hold the drums.

Application Drums that may be damaged and leaking substances which are so dangerous that diver operations should be avoided.

Description Remotely Operated Vehicles (ROV:s) equipped with manipulator arms transfer the drums into outer salvage drums and the thus obtained packages into racks taking e.g. up to 20 packages.

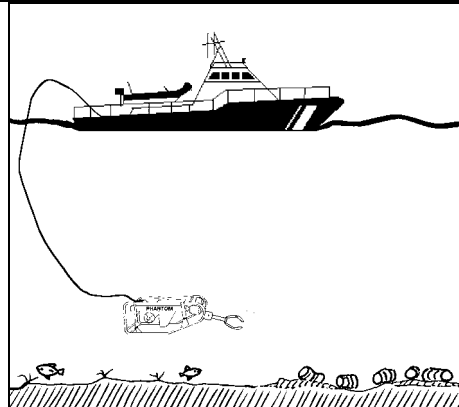


Figure 6 - 48

The filled racks are hoisted to salvage barges by means of pontoon cranes (cf. Annex 3, accident "Santa Clara").



Picture source: US Coast Guard

Figure 6 - 49

Limitations A sophisticated and accomplished technique and equipment must be available in order to perform such an operation.

A careful decontamination of the equipment may be difficult and time-consuming to perform.

Salvage of packages from depths down to 500-600 m

Method Bell diving system with saturation divers

Application A demolished vessel on the seabed cannot be salvaged together with its cargo by pontoon cranes. On such an occasion the operation must be planned in consideration of the cargo's distribution within and outside the wreck. Divers must probably be utilized in an appropriate manner to handle the goods manually before it can be salvaged.

Whether demolished or not packages may have to be recovered from inside or outside the sunken ship on the seabed.

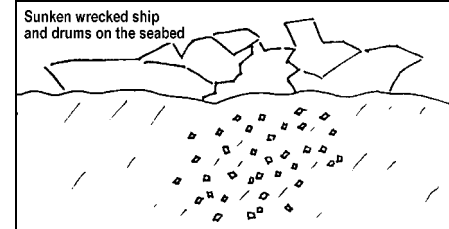
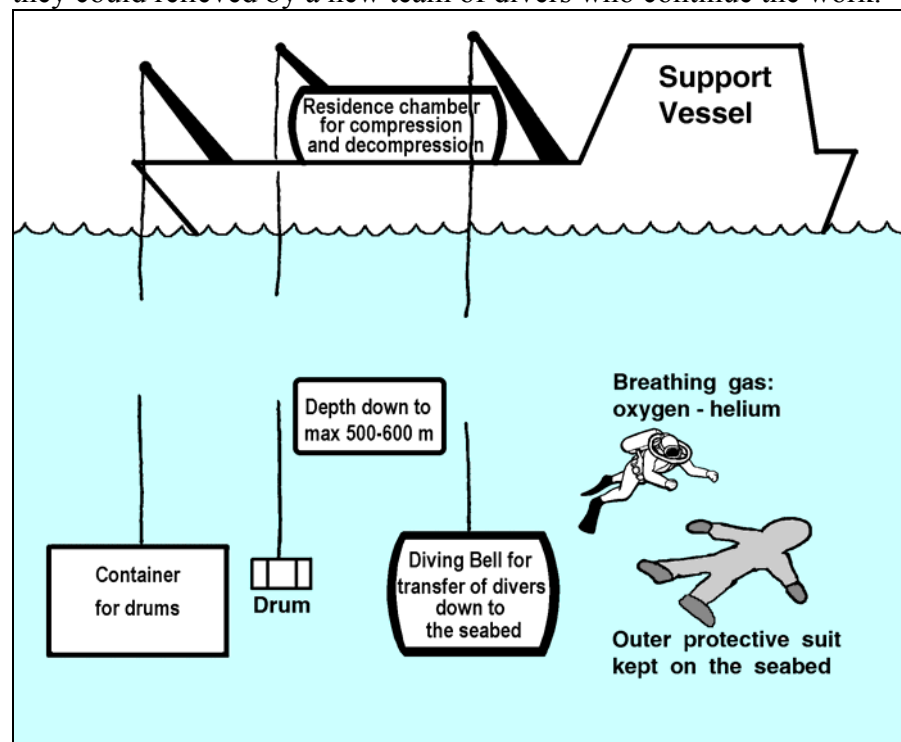


Figure 6 - 50

Description The work on the seafloor should be carried out by alternating teams of divers breathing a mixture of oxygen and helium. The divers work at the seafloor e.g. for 8 hours per day and stay until next morning in a pressure chamber placed on the supply vessel's deck. After days or weeks of work under continuous pressure the divers are slowly decompressed in the deck pressure chamber for some days where after they could be relieved by a new team of divers who continue the work.

Figure 6 - 51
A closed bell diving system



Limitations Very expensive operations with costly breathing gases and complicated decontamination procedures for divers and equipment.

Divers should not work in waters showing dangerous concentrations of hazardous substances.

6.7.7 Miscellaneous methods

Although recovery of sunken packages is the most natural way of response, other techniques must be considered on some occasions.

If the water is very deep or the goods is scattered over large areas the option of **no response** may be the only reasonable alternative because of enormous costs that cannot be justified.

Intentional release of packaged chemicals may sometimes be suitable for substances whose hazard can be reduced by mixing with water and where, for some reason, recovery would be more hazardous. Prior to undertaking any intentional release, careful consideration needs to be given to the proximity of the release to any sensitive marine resources and to currents or other factors which may influence the rate of dilution or transport of the released material.

The release may be performed by puncturing the package, by remote control if necessary, and monitoring the mixing and dispersion. Puncturing can be made by a cutting tool, a sledge or even gunfire. One case is documented where a large amount of small containers were punctured by firemen's axes before dumping into the sea (cf. Annex 3, accident Rio Neuquen) (Ref. 47).

Momentary river releases of acids and bases have earlier turned out to be devastating for the aquatic life. The spill moves downstream like a "cloud" in the river water and kills all organisms in the river down to the river outlet (Ref. 45 in Norwegian, and Ref. 46).

Intentional continuous release from a sunken container

Method Pumping substance into the surrounding water.

Application Examples are corrosive substances such as sodium hydroxide, sulphuric acid and phosphoric acid, or certain soluble flammable liquids like methanol and ethanol.

Description Figure 6 - 52 shows how an air lift system can be used for controlled underwater discharge of a water-soluble chemical. This method has been used once with success for emptying a sunken barge with sulphuric acid in the Upper Mississippi River. (Annex 3, accident "Sunken barge") (Ref. 38).

The pH values were continuously carefully checked a short distance downstream so that they didn't exceed values harmful to the aquatic life in the river. This was performed during the whole operation (a few days).

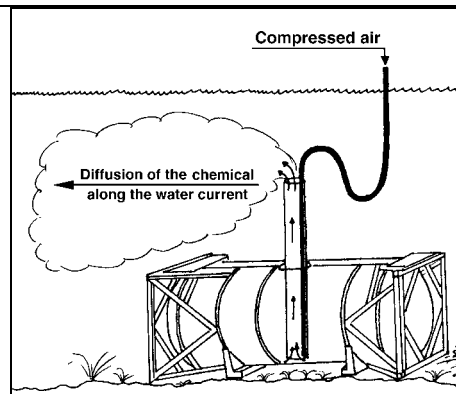


Figure 6 - 52 Use of an airlift dredge for controlled discharge of a liquid chemical into the surrounding water.

Limitations Mainly for soluble, relatively non-toxic substances.
Not for stagnant waters.

Intentional momentary release of gas from a sunken container

Method Breaking containers by explosives.

Application Corroded metal containers of a sparingly soluble hazardous gas, which might rupture during normal recovery operations.

Description

Figure 6 - 53 shows an example of using explosives after an accident off the coast of the Netherlands. (Annex 3, accident Sindbad) (Ref. 44).

Sunken steel cylinders containing chlorine were broken by explosives and the gas escaped through the water column into the air.

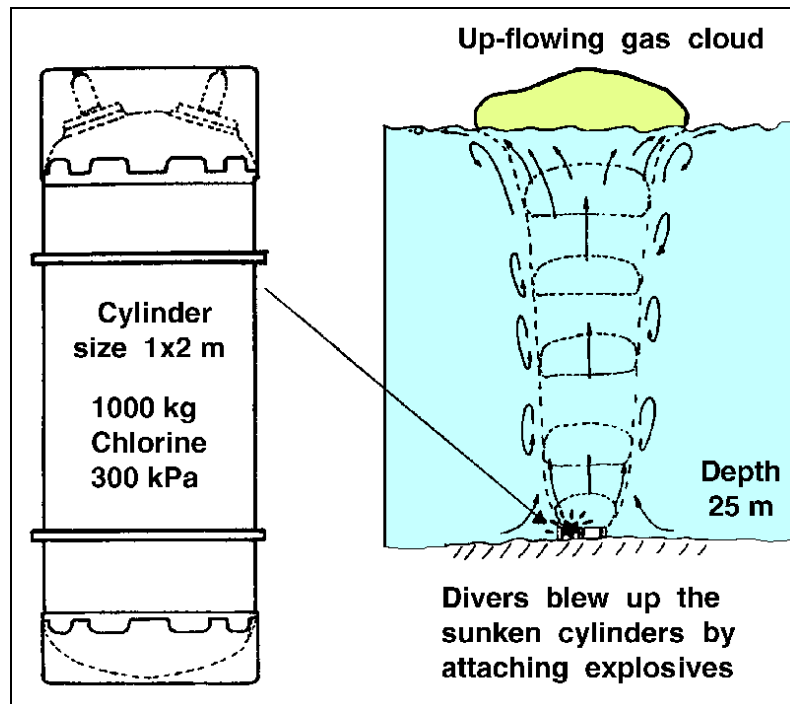


Figure 6 - 53

The rising chlorine gas cloud was strictly supervised by fully protected personnel. An exclusion zone was established (Figure 6 - 54) and patrolled by ships, helicopters and aircraft.

Ammonia gas was released upwind as an indicator gas that seeded the chlorine gas cloud and made it clearly visible as a white smoke over a large area.

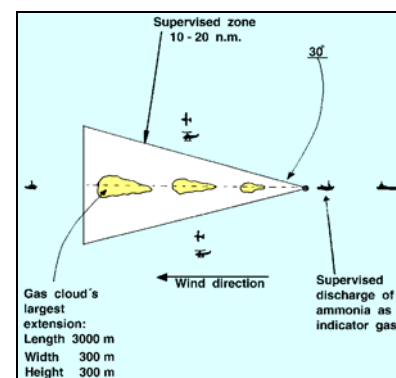
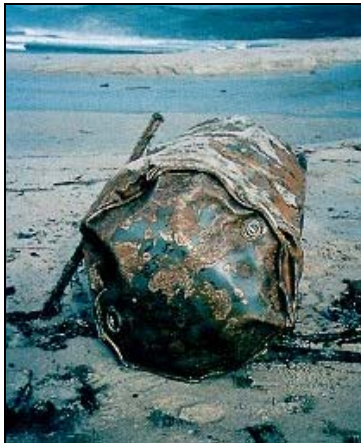


Figure 6 - 54

Limitations Very careful planning is necessary as regards safety for divers and crews of participating craft, as well as for seafarers and populated areas.

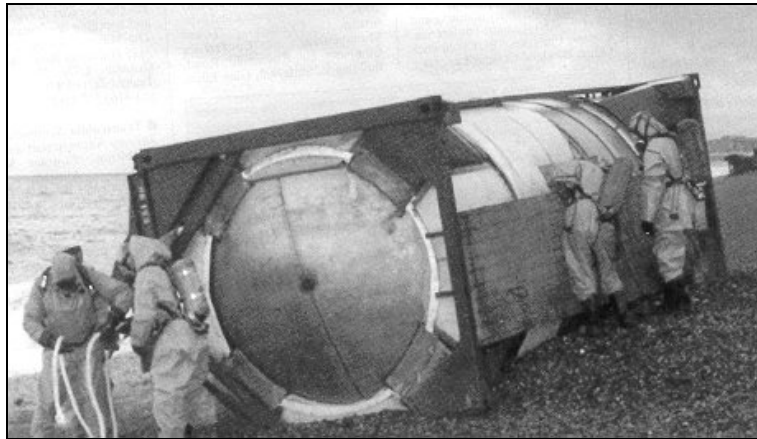
Not applicable to sunken containers in deep water.

6.8 Packages washed ashore



Picture source: IMO

Figure 6 - 55



Picture source: Hazardous Cargo Bulletin

Figure 6 - 56

Packages lost at sea may eventually be washed ashore. Upon impact with the shore, they may be damaged and may start leaking, particularly on rocky or stony shorelines. People may come in contact with packages on shore and may be injured by leaking substances. The public should be advised never to approach such packages.

Special care must be taken when inspecting packages washed ashore. The packagings may have been damaged on impact with the shore and may be leaking, contaminating the surrounding area. Inspection of the packages should be carried out by trained experts only.

If the contents is known (e.g. if the labelling is intact), the hazards can readily be assessed. If not, identification of the contents and assessment of the hazards should be obtained before recovery is attempted. If the presence of radioactive material is suspected, measurement of the radiation level should be carried out before any other actions.

It may be possible to use detection equipment in the field to assist in these processes. A chemical laboratory may be necessary to identify samples where this is insufficient.

Drums washed ashore (Figure 6 - 55) should always be contained in salvage drums (Figure 6 - 57) before transportation or further handling.

The requirement for packaging approval for transport of dangerous goods is also valid for cover drums (cf. Section 6.1.2).

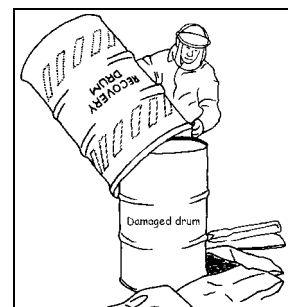


Figure 6 - 57

Salvage drum

Freight containers washed ashore (Figure 6 - 56) should if possible be emptied before any actions to move them. The off-loading (evacuation) must be performed under strict safety precautions.

6.9 Salvage of packages from sunken craft

6.9.1 General

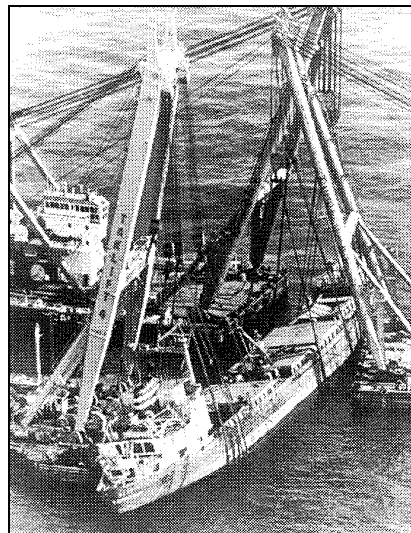
As a result of a collision, heavy weather or an explosion on board a ship, damage to the ship may be so severe that she will sink with all or part of her cargo on board. Due to the initial incident or to the impact with the seabed, the ship may be more or less demolished. In such cases, part of the cargo may escape from the ship while part may remain on board. On some occasions, the ship will lie intact on the seabed with all her cargo remaining on board.

6.9.2 Salvage of whole craft

A sunken ship with a cargo of chemicals that lies intact on the seabed may be leaking substances into the bottom water. On such an occasion it is important to monitor the surrounding water in order to establish the limits of the polluted area.

Under certain circumstances, with the ship intact, it may be possible to salvage the whole ship by lifting it with large pontoon-carried cranes. It is also possible to lift the ship by attaching buoyant objects inside or outside the hull.

The sunken German vessel Viggo Hinrichsen loaded with chromium compounds was salvaged in 1973 by means of pontoon cranes (cf. Figure 6 - 58) from a depth of 17 m one nautical mile north of the Swedish island of Öland in the Baltic Sea (cf. Annex 3, accident "Viggo Hinrichsen").



Picture source: Hazardous Cargo Bulletin

Figure 6 - 58

6.10 Chemical warfare agents

6.10.1 Background

After World War II large quantities of war ammunition were dumped in both the North Sea and the Baltic Sea. Some of this ammunition contained various types of weapons for chemical warfare. War gas ammunition was dumped within areas shown in Figure 6 - 59. Amongst these weapons especially mustard gas bombs have proven to be a particular risk for fishermen.

Two areas in the Baltic Sea have during the decades after the War been involved in numerous fishing incidents. These areas are marked out in Figure 6 - 59 about 15 nautical miles east of the Danish island of Christiansoe and about 40 nautical miles southeast of the southern point of the Swedish island of Gotland. The ammunition (mainly mustard gas bombs) in these areas is not contained in sunken ships. It lies openly on the seabed at such depths as to be dangerous for fishermen. Mustard gas bombs may also be found in positions outside these areas.

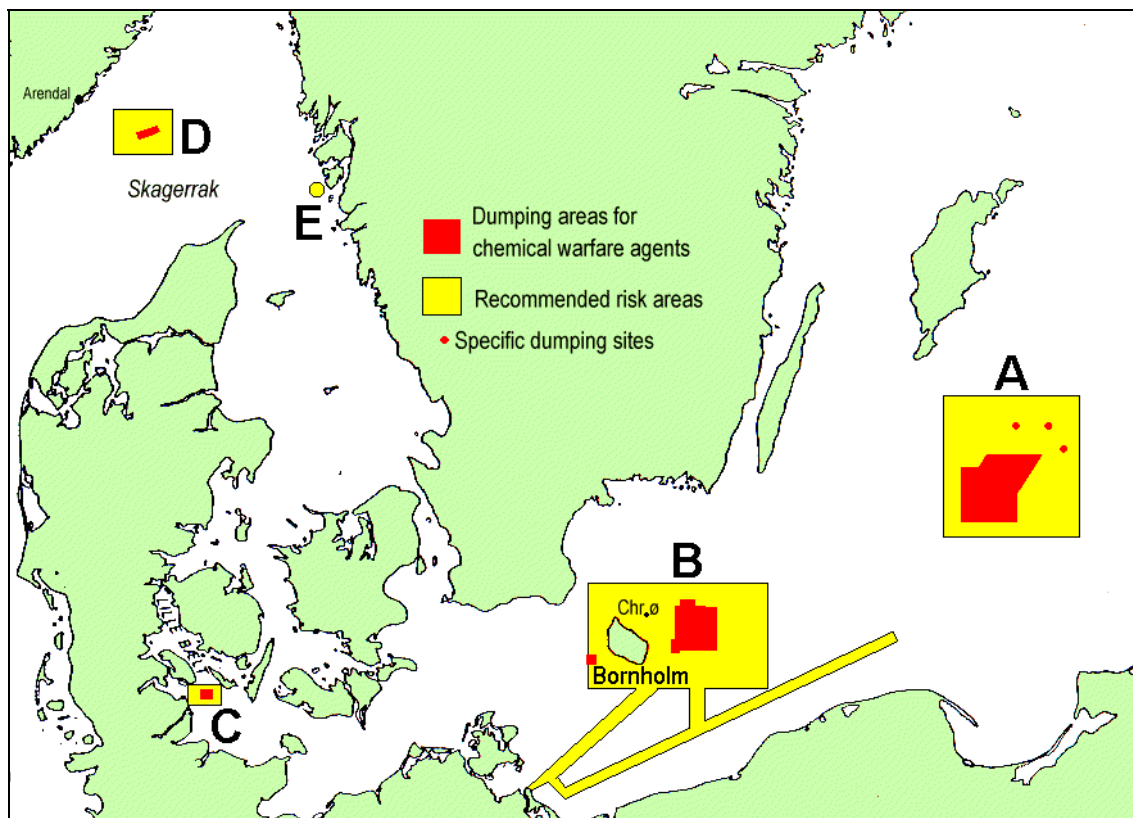


Figure 6 - 59 Dumping areas and recommended risk areas for chemical warfare agents

Five dumping areas A - E are marked out in the map above (Figure 6 - 59). In these areas the following types of items were dumped (as far is known):

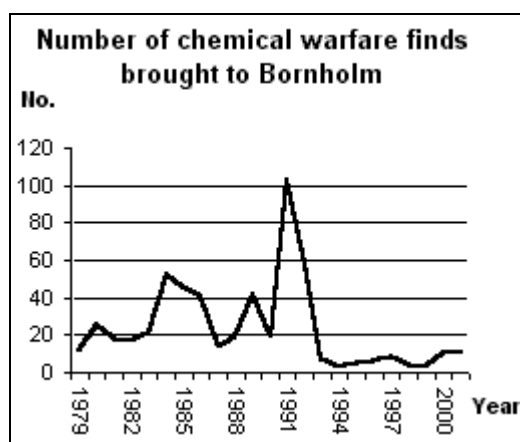
A and B:	Gas bombs - most of them containing mustard gas, but also a fewer number of sternutators (sneezing gases), lachrymators (tear gases) and suffocating gases.
C:	Gas bombs containing nerve gases and suffocating gases.

D:	Sunken ships (at great depths) with ammunition containing mustard gas and suffocating gases.
E:	Sunken ships probably containing ammunition with mustard gas as well as other warfare agents.

Of nearly 300 discarded Danish fish catches during 1968-84 about 90 % were contaminated by mustard gas and the rest by sneezing gas (sternutator) or tear gas (lachrymator). Approximately the same ratios have been reported during 2000-2002 though the total numbers of finds have decreased considerably (cf. Figure 6 - 60).

Since 1966 almost 700 finds of chemical warfare ammunition have been brought to Bornholm. Figure 6 - 60 shows the numbers of chemical warfare finds brought to Bornholm each year during 1979-2001.

Figure 6 - 60
The number of finds of chemical warfare agents brought to the Danish island of Bornholm during 1979-2001.



Source: Bornholms Marinedistrikt

6.10.2 Appearance of chemical warfare bombs

Chemical warfare agents were originally most often contained in two types of aerial bombs (cf. Figure 6 - 61). One of them Type KC 250 (cf. Figure 6 - 62) is 160 centimetres long and has four fins in the rear. The other is 100 centimetres and has no fins. Both types are 34-36 centimetres in diameter and have cone-shaped front parts.

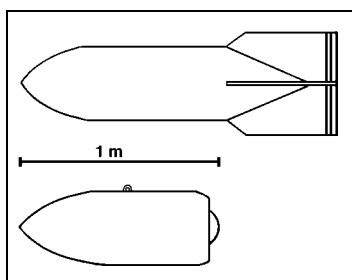


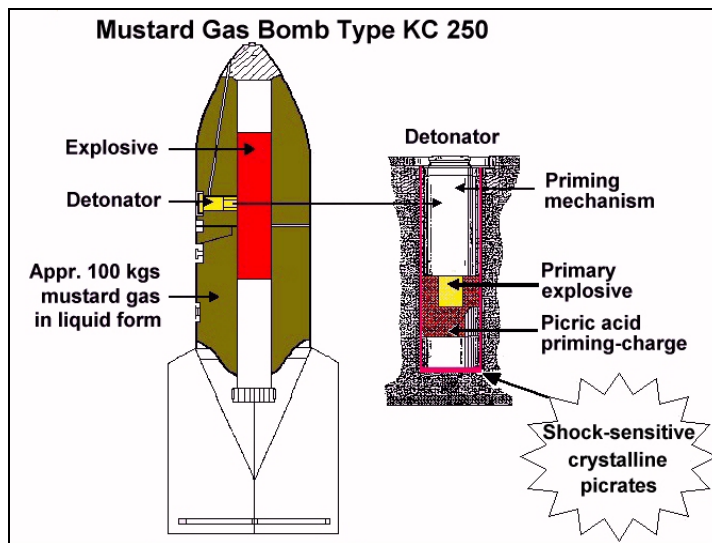
Figure 6 - 61
Two types of aerial bombs



Picture source: Bornholms Marinedistrikt

Figure 6 - 62
An aerial mustard gas bomb of type KC 250

Figure 6 - 64 shows the design of Type KC 250 with explosive (TNT), detonator and liquid mustard gas. Figure 6 - 63 shows a central explosive core and tailcone dismounted from such a bomb.



Picture source: Bornholms Marinedistrikt

Figure 6 - 64 The design of Type KC 250 bomb



Picture source: Bornholms Marinedistrikt

Figure 6 - 63
Central explosive core and tailcone dismounted from such a KC 250 bomb



Picture source: Bornholms Marinedistrikt

Figure 6 - 65



Picture source: Bornholms Marinedistrikt

Figure 6 - 66

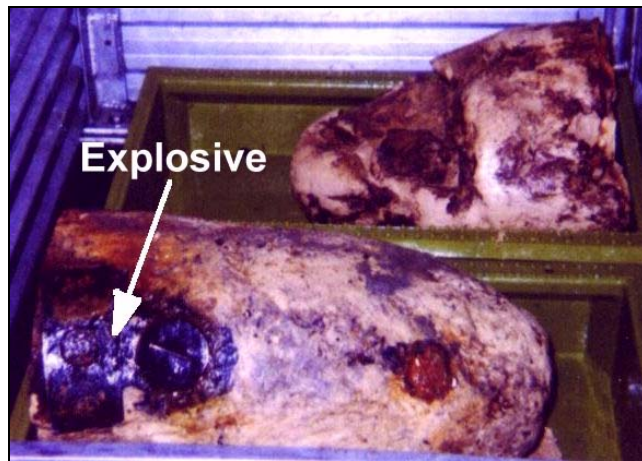
The bomb shells are made of thin material and have now often completely corroded away. Finds of whole bombs as in Figure 6 - 65 and Figure 6 - 66 are nowadays getting more and more rare.

When dumping the bombs after WW 2 they were, by natural reason, not armed i.e. not provided with detonators. But the finds often contain both priming and bursting charges (see Figure 6 - 67 and Figure 6 - 68). As far is known, no explosion has happened in actions against finds of chemical warfare bombs in the Baltic Sea Area, but due safety precautions are yet always taken on such occasions.



Picture source: Bornholms Marinedistrikt

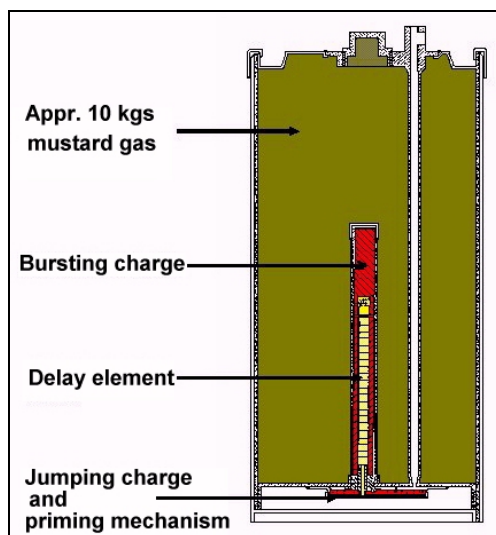
Figure 6 - 67



Picture source: Bornholms Marinedistrikt

Figure 6 - 68

Among chemical warfare finds in the Baltic Sea, bombs of Type KC 250 (or their remains) are the most common. But also other types of ammunition occur but more seldom. Figure 6 - 69 shows the construction of a so called “jumping mine” and Figure 6 - 70 shows a find of a weathered lump of mustard gas from such a mine. A jumping mine is designed to be dug down. It is trip-wire released and is then thrown 10-15 m upwards where it detonates and distributes mustard gas over appr. 150 square metres.



Picture source: Bornholms Marinedistrikt

Figure 6 - 69 Construction of a jumping mine with mustard gas



Picture source: Bornholms Marinedistrikt

Figure 6 - 70 A weathered mustard gas lump from a jumping mine

Danish information documents aimed for fishermen also contain brief data on war gas artillery shells (diam. 10.5 cm, length 35-50 cm, cf. Figure 6 - 71).



Picture source: Bornholms Marinedistrikt

Figure 6 - 71 A war gas artillery shell

Fishermen in the Baltic Sea sometimes get mustard gas in their fish catch. The recent finds of mustard gas sometimes resemble clay. They could also be solid, dark yellow/brown lumps as in Figure 6 - 72, Figure 6 - 73 and Figure 6 - 74. Such lumps vary in size up to 80 kgs. On some occasions they may easily fall apart in pieces and may

expose a high viscosity liquid from the inner parts where the mustard gas is still un-weathered and extremely hazardous and can pose severe injuries.

Weathered (hydrolized and oxidized) lumps of mustard gas



Picture source: Bornholms Marinedistrikt

Figure 6 - 72



Picture source: Bornholms Marinedistrikt

Figure 6 - 73



Picture source: Bornholms Marinedistrikt

Figure 6 - 74

Sternutators (sneezing gases) have never been found in weapons in the Baltic Sea, but only in storage wooden cases. These cases have been decayed by now and finds of sneezing gases show up as lumps (cf. Figure 6 - 75).



Picture source: Bornholms Marinedistrikt

Figure 6 - 75 Sneezing gas

6.10.3 Properties of chemical warfare agents

Appearance and behaviour of mustard gas

Consistency	In spite of its name, mustard gas is not a gas. In the mustard gas bombs a more or less viscous fluid or sludge is found which may have the consistency of oil, mush, Vaseline or lumps of jelly. When exposed to the environment mustard gas oxidize and solidify.
Colour	Yellow to brown or dark-brown (sometimes almost black).
Odour	Sharp, sweet odour which may resemble cress, garlic, horseradish or mustard. The agent is insidious since sense of smell may be fatigued and fail to give warning of dangerous concentrations.
Behaviour	Mustard gas often contains special additives which makes it easily stick to skin, clothing and gear. Mustard gas in liquid state will penetrate rapidly through fabric and leather. Ordinary rubber and many types of plastic provide short-time protection.

Medical effects of mustard gas

Mustard gas is very hazardous to health both when exposed to the liquid and its vapour. Mustard gas penetrates easily into the body via the skin, mucous membranes and respi-

ratory tract. Symptoms do not show immediately. Often the injuries do not appear until several hours after the exposure. In mustard gas accidents it is very important to start first aid as soon as possible because injuries caused by mustard gas can take a very long time to heal.

Skin	Even minor amounts of mustard gas cause itching and burning red spots, or even shooting pain, a few hours after exposure to the skin. After another few hours large liquid-filled blisters may develop. If the blisters break, slow-healing wounds are formed which can easily be infected. Therefore the blisters should be prevented from breaking in every way.
Eyes	When exposed to vapours of mustard gas, the victim at first feels the eyes itching and smarting. After increasing smarting pain and reddening of the eyes a copious flow of tears will arise as well as sensitivity for light, temporary blindness, and a heavy swelling of the eyelids. If the eyes are exposed to liquid mustard gas they will be injured with a severe risk of blindness.
Lungs	The risk of injuries by mustard gas vapours is highest in warm weather, stationary air and confined spaces. Inhalation of hazardous concentrations of mustard gas vapours gives rise to nasal catarrh (runny nose), hoarseness, sore throat and coughing. The coughing may become painful, the power of speech may be lost and the breathing may be deteriorated. The result may be serious injuries to the windpipe and lungs.

In severe cases of skin in exposure or inhalation, a general poisoning will develop in the body after some hours, besides the above mentioned symptoms. In these cases the victim may be affected by general sickness, lethargy, loss of appetite, nausea, fever, vomiting and bloody diarrhoea in combination with severe pains in the chest and stomach.

Lachrymators (tear gases) are volatile substances which affect the mucous membrane of the eyes and cause watery painful eyes. They may irritate the skin and cause local injuries. The effects do not last very long after the affected person has been removed from the gas.

Sternutators (sneezing gases) affect the mucous membranes of the nose, throat and respiratory passages and causes sneezing, coughing, a runny nose and watery eyes. These effects can last from 15 minutes to a couple of hours after the affected person has moved away from the gas to fresh air.

Nerve agent of the tabun type is, in its pure form, a transparent and odourless glycerine-like substance. However, impurities sometimes make the liquid dark and give it a fruity smell, and any additives to it may also affect its smell.

Nerve agents are easily absorbed through the skin, respiratory organs, eyes and the gastro-intestinal tract. Nerve agents in liquid and vaporised form easily penetrate all textiles and leather. Ordinary rubber and many types of plastic only provide brief protection.

A small dose of nerve agent will cause headaches, painful eyes, blurred vision, pupil contractions, a running nose and a feeling of weight on the chest.

A large dose will cause the above symptoms followed by cramps, difficulty in breathing, a slow pulse, and may be fatal as a result of respiratory or cardiac arrest. If a person is exposed to a large dose, the entire poisoning process is very quick. usually between 5 and 10 minutes, unless the patient is treated.

Suffocating agents. A typical suffocating agent is phosgene, which is a colourless gas. Phosgene is a liquid below 8°C,. In low concentrations it has a rather sweet, not unpleasant smell, which is reminiscent of newly cut hay.

In high concentrations the smell becomes sharper and irritating. The fumes are heavier than air. The substance is very insidious, and harmful quantities can be inhaled without the person noticing anything.

For the first few hours after a person has been exposed to phosgene fumes, the only effect is irritation of the mucous membranes in the respiratory passages. The symptoms of poisoning are difficulty in breathing, coughing, a feeling of suffocation, thirst, vomiting, pain in the chest, lips turning blue, foaming at the mouth, extreme weakness, mental disturbances followed by unconsciousness. The reason for this is that phosgene causes pulmonary oedema and prevents oxygen absorption because of damage to the lung tissue.

The mucous membranes of the eyes are also affected by phosgene, which can result in permanent eye damage, even though there are no symptoms of this at the start.

Smoke-generating agents contain often phosphorous compounds. A mixture of sulphur trioxide and chlorosulphonic acid is another powerful smoke generator. In its liquid form it is extremely corrosive on contact with the skin. In its vaporised form, it consists of small particles of hydrochloric acid and sulphuric acid, which irritate the skin, eyes and respiratory organs.

Phosphorous is found in smoke ammunition where the whole charge or part of it consists of yellow (white) phosphorous. When phosphorous is taken out of the-water and comes into contact with the oxygen in the air, it ignites. Phosphorous sores heal very slowly.

The information above does not deal with the possible chronic adverse effects of the poisons.

6.10.4 Actions in incidents involving finds of chemical warfare agents

First steps

1. Responsible bodies are alerted according to pre-arranged plans. If the find is suspected to contain explosives it must not be moved until it has been examined by appropriate expertise.
2. A vessel is commissioned for a first action involving transport of personnel, warning of seafarers and necessary assistance to involved fishing vessels.
3. If the affected fishing vessel can run by its own engines it is primarily directed

to a suitable decontamination anchorage where environmental response vessels are utilized for decontamination actions.

4. Vessels are commanded for transport of disarming personnel and safety equipment. The vessels carry safety equipment for own personnel.
5. Chemical warfare finds, contaminated waste, discarded catch etc. is brought to land and taken care of according to local regulations.

Immediate on-site decontamination of personnel contaminated by mustard gas

It is very important that contaminated skin and eyes are immediately cleaned before the mustard gas has penetrated into the body. Every minute's delay will increase the risk of injuries. If both the skin and eyes are contaminated, assistance should be received from someone not injured so that the first actions can be taken simultaneously according to the guidance below. Do not touch the face and eyes with contaminated hands. Get medical aid as soon as possible.

N.B.!

Stay in the open air on deck if the clothes are contaminated. It is important that not to scatter the mustard gas to clean spaces on the vessel.

Skin

First take off all contaminated garments as well as rings, watches etc. There must be a full certainty that no contaminated garments or objects remain on the body. Act rapidly but cautiously so that the face and eyes do not become contaminated.

Remove quickly the (sometimes sticky) mustard gas which can be scraped from the skin with a knife or similar. Act cautiously and avoid rubbing it into the skin or to spread it. Low viscous mustard gas should be "tweaked" away with an absorbent material in order to prevent spreading on the skin. Also this must be done quickly.

Use thereafter a special decontamination agent for mustard gas, if available on board. Observe carefully the instructions which apply for the agent. Wash decontaminated skin areas with usual soap or soft soap and water. Observe that mucous membranes and the lower abdomen are especially sensitive to mustard gas. Finish up by careful washing of all the body with soap and water.

Apply wet bandages on injured skin areas. Blisters should not be broken.

Wash immediately contaminated eyes with a soft spray of clean and preferably lukewarm fresh water for at least 15 minutes. Keep the eyelids widely apart during washing. Use an eye wash station if available on board. Then close the eyelids and clean the surrounding skin parts cautiously with soap and water. Do not use any kind of eye ointment, decontamination agent or bandage.

Decontamination of vessel and equipment which are contaminated by mustard gas

- ♦ On first hand an area of at least 30 m radius should be cordoned off.
- ♦ Continuously monitor the air outside the cordon. The cordon must be expanded if any instrument indication is obtained or suspected smell is noticed.
- ♦ The following apply for decontamination of vessel and equipment:
 - Indicating equipment is used to judge the need for decontamination as well as to check for any remaining contaminants after decontamination actions.
 - The personnel must wear full personal protective equipment including self-contained breathing apparatus.

Below are 6 different decontamination methods and agents described that have to be used depending on the properties of the contaminated surface. A reference to a detailed report on destruction methods for chemical weapons is given in Ref. 61.

Mustard gas (and other chemical warfare agents) penetrate rapidly through porous materials like wood, fabrics, rubber, etc. It is therefore difficult to decontaminate such materials and it has to be performed by means of penetrating decontaminants or methods like DS2 or boiling. DS2 is a mixture of diethylenetriamine (70%), sodium hydroxide (2%) and ethylene glycol monomethyl ether (28%).

These decontamination methods can have unwanted effects on the materials' properties. Hard surfaces are not so difficult to decontaminate as they don't imbibe mustard gas and other chemical warfare agents. Feasible methods are high-pressure steam or hotwater spraying, or treatment with DS2 or chloride of lime.

DS2 or chloride of lime should be distributed over the contaminated items and should act for 15-30 minutes before flushing with high-pressure water.

Decontamination equipment like deck brushes, buckets, cotton waste, etc. as well as well as equipment that is difficult to decontaminate should be regarded and treated as contaminated waste.

1. *Airing*
Gaseous mustard gas in the air of closed spaces is remove by violent airing.
2. *Washing*
Contaminated items are washed with cotton waste soaked with hot soap or detergent solution, or soaked with light diesel fuel oil, kerosene, etc. Alternatively the items are flushed with hot soap solution during simultaneous working with a brush. Discarded cotton waste etc., soaked with kerosene or diesel fuel oil, used for washing should be collected in tin containers as these solvents might affect plastic containers.

3. *High-pressure water spraying*

Spraying with water (preferably heated) under high pressure. The angle between the jet and the item's surface should not exceed 30°.

4. *High-pressure steam or hotwater spraying*

Treatment of contaminated items with steam or hotwater under pressure (preferably high pressure).

5. *Decontamination with chloride of lime*

A slurry of chloride of lime (sodium hypochlorite can also be used) in at least 3 parts of water is distributed over the contaminated item's surface. The slurry is worked into the surface with a brush and should act for 15-30 minutes before careful washing or flushing.

N.B.: Chloride of lime and sodium hypochlorite are corrosive for eyes and skin. Both agents corrode metals and may damage fabrics etc. Dry chloride of lime may ignite upon contact with mustard gas.

6. *Decontamination with DS2*

DS2 is distributed on the contaminated item's surface (0.05 – 0.1 litre/m²) and should act for 15-30 minutes before careful washing or flushing.

N.B.: DS2 is harmful to breathe and is corrosive to eyes and skin. It is alkaline and corrosive to certain metals (e.g. light metals) and may damage certain other materials. DS2 may react violently (fire or explosion) when mixed with chloride of lime or hypochlorites and if ignited by sparks or fire.

First response actions in chemical accidents

A. Organisation chart for Emergency Responders and their command

An OSC should be appointed who is especially trained for maritime accident involving chemicals and dangerous goods. The OSC should supervise both own Emergency Responders **and** all supporting outside groups of Emergency Responders (cf. Figure a1 - 1).

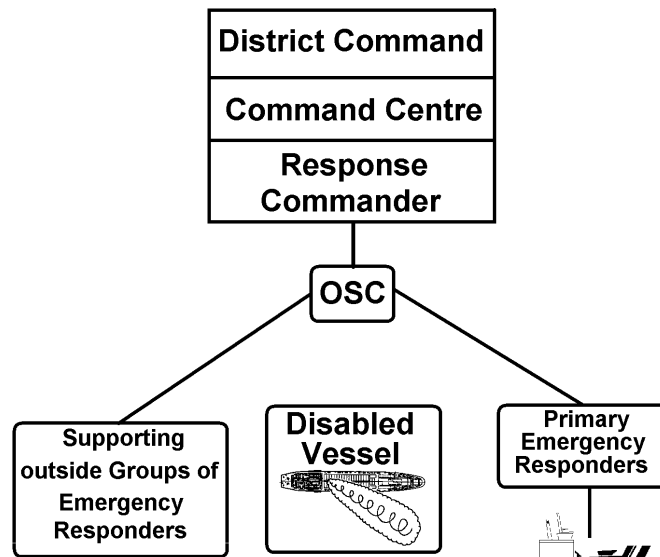


Figure a1 - 1

B. Threatening picture

The actual **risk environment** is crucial when judging the necessary extent and safety of a Emergency Responder action. The risk level vary considerably depending on the target of operation and the type of work needed. Furthermore due consideration should be given to the character and scope of the emergency.

For practical reasons the design of the responder action should be based on one of two levels of priority for the risk environment:

High risk work area with any one of the following properties:

- Action site (e.g. on board a ship) with longer penetration than the length of a life line.
- Bad sight.
- Risk for closed lines of retreat for responders.
- Risk for special difficulties depending on the ship's construction or the type of target.

Other risk areas than a high risk environment is such an environment that could not be clearly classified as a high risk environment.

Actions on board ships involved in chemical accidents should always be carried out by Emergency Responders.

C. Classifying the actual accident and evaluating the risks and resource needs for response

Type of accident

◆Grounding - cargo - life - release - fire	◆Collision - cargo - life - release - fire	◆Fire on board - cargo - life - gas - explosion	◆Sunken vessel - cargo - depth	◆Lost goods - freight container - type of packaging
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Risk information

◆Weather condition - wind - water current - temperature - spread forecast	◆Substances - very flammable liquid - misc. flammable liquid - corrosive substance - toxic substance - toxic & flammable subst.	- oxidizing substance - toxic gas - toxic & corrosive gas - combustible gas - combustible & toxic gas	◆Misc. - contaminated areas - tanks - pressure vessels
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Resource needs (examples)

◆Ships/Aircraft - environmental response vessels - surveillance aircraft - other agencies - lightering vessels	◆Personnel - environmental response teams - Emergency Responders - misc. personnel - expertise personnel	◆Decon-tamination - decon basins - decon hand showers - decon cabin showers - containers for contaminated clothing	◆Medical care - medical personnel - medical emergency cases - ship's dispensaries - responders medical backpacks - Oxy-boxes
◆Personal protection equipment - full protection suits - fire (protection) suits - chemical protective - chemical coveralls - personal protection transport boxes	◆Search equipment - ROVs - shipborne sensors - airborne sensors	◆Recovery equipment - salvage drums (recovery drums, overpacks) - Peripheral Injector Jet Suction Pump PIJESP - airlifts - skimmers - dredgers - lightering drills for sunken vessels	
◆Containment equipment - water - booms - expander wedges - misc. types of wedges - recondensing equipment - treating agents		◆Monitoring instruments - trace gas monitoring instruments - explosive meters - oxygen-deficient air monitoring instruments - monitoring instruments for chemical warfare agents - radioactive meters	

Figure a1 - 2

D. Exclusion areas in major accidents

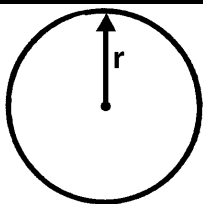
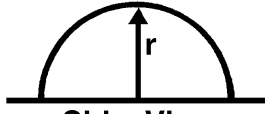
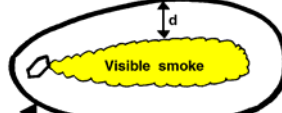
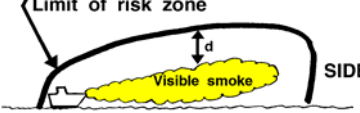
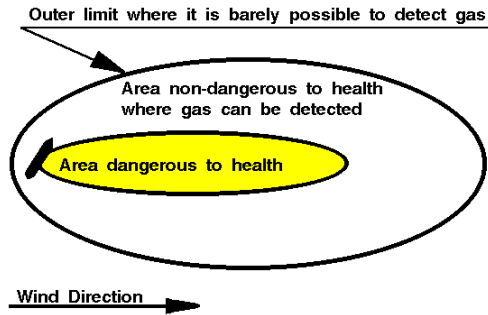
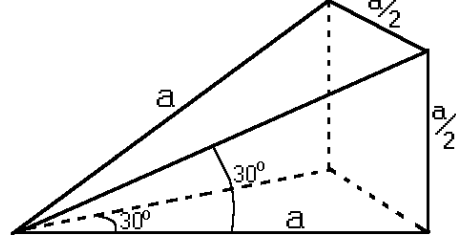
Incident type	Examples of substances	Shape and size of area																
Risk of violent fire	Acetone Acrylonitrile Gasoline Cyclohexane Hexane Methyl alcohol Methyl ethyl ketone Vinyl acetate	Semisphere Radius 100 m	 Top View															
	Risk of explosion	LPG (propane, butane) Ethylene Propylene Butadiene Explosives Mixtures of oxygen-containing and combustible substances	Semisphere Radius 1000 m	 Side View														
Fires in substances composed of carbon, hydrogen and oxygen (produce normal smoke)	Acetone Acrylonitrile Cyclohexane Gasoline Hexane Methyl alcohol Methyl ethyl ketone Vinyl acetate	Area with a limit of 100 m from all the visible parts of the smoke	 TOP VIEW															
Fires in substances containing halogens, e.g. chlorine, or nitrogen (produce often very toxic smoke)	Chlorinated hydrocarbons E.g.: Ethyl chloride, Chlorobenzene Dichloropropane Vinyl chloride Ethylene dichloride Ethanolamine Some plastics	Area with a limit of 500 m from all the visible parts of the smoke	 SIDE VIEW															
A spill or a penetrated container that gives off hazardous vapours	Benzene Steam cracked naphtha Light crude oil Benzene/toluene/ xylene mixture (prolysis gasoline)	The limit of the risk zone is where it is barely possible to detect gas by trace gas analyzing devices	 Wind Direction															
A spill or a penetrated container (containing liquefied gases) that gives off hazardous vapours	GROUP I Ammonia Vinyl chloride GROUP II Propane Butane LPG Ethylene Propylene Butadiene GROUP III Ethyl chloride Chlorine	<table><tr><th rowspan="2">Spill tons</th><th colspan="2">Health hazard</th><th rowspan="2">Fire/explosion hazard</th></tr><tr><th>I</th><th>II</th></tr><tr><td>a</td><td>a</td><td>a</td><td>a</td></tr><tr><td>km</td><td>km</td><td>km</td><td>km</td></tr></table>	Spill tons	Health hazard		Fire/explosion hazard	I	II	a	a	a	a	km	km	km	km		
Spill tons	Health hazard			Fire/explosion hazard														
	I	II																
a	a	a	a															
km	km	km	km															

Figure a1 - 3

E. Order of priority for actions

- | | |
|---|---|
| <ol style="list-style-type: none">1. Life saving:<ul style="list-style-type: none">- Search for victims- Carriage of victims from the risk area- First aid- Decontamination of victims- Transportation of victims | <ol style="list-style-type: none">2. Stop, limit and combat discharges
(e.g. collect, neutralize, wash overboard)3. Reduce damage
(Fight fire, cool goods, move goods) |
|---|---|

F. Personal protection equipment for Emergency Responders

The decision on choice of personal protection equipment should be taken by the Responder OSC considering check lists and actual threatening picture (risk environment). The personal protection equipment could be e.g. a) fire protection suit with self-contained breathing apparatus, b) fire suit with a cover and breathing equipment, or c) chemical coverall with breathing equipment.

G. To enter a ship involved in a chemical accident

General tactics considering the wind direction

At a chemical accident on board a ship a hazardous clouds (visible or invisible) may be generated and moved by the wind. In such a case the ship should be moved so that the cloud moves obliquely from the crew's accommodations (cf. Figure a1 - 4).

Boarding and accident response should also be performed from the opposite side of the cloud.

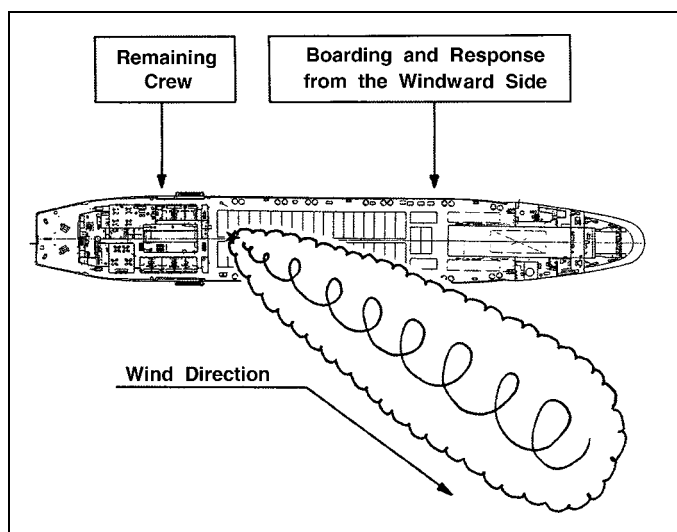


Figure a1 - 4 Boarding and accident response from the opposite side of the hazardous cloud.

Safety precautions

Emergency Responders who board a ship in actions against accidents shall bring:

- ♦ Appropriate personal protection equipment (cf. Annex 5 "Body protection levels")
- ♦ Appropriate monitoring devices (e.g. for toxic, flammable and radioactive environment)
- ♦ Appropriate safety equipment (e.g. for communication, decontamination and life saving)
- ♦ Appropriate response equipment (e.g. for fire fighting, cooling and neutralizing)

Important safety measures:

- ♦ Safe return spaces with clean areas shall be prepared on board
- ♦ First response backup teams shall be readily available and appropriately equipped
- ♦ A safe number of extra air bottles shall be easily available close to the responders

H. Alternative ways of transport to and from the disabled ship

	Advantages	Disadvantages
By response vessel	Good work platform Contains work equipment Well-known working environment	Slow Boarding is difficult Weather dependant
By helicopter	Rapid Easy to deploy responders independent of weather	Limited flight time Limited load capacity Special safety regulations (e.g. adverse weather)

I. To board a disabled ship

The disabled ship's type and construction determine the available practical alternatives for boarding (cf. Figure a1 - 5).

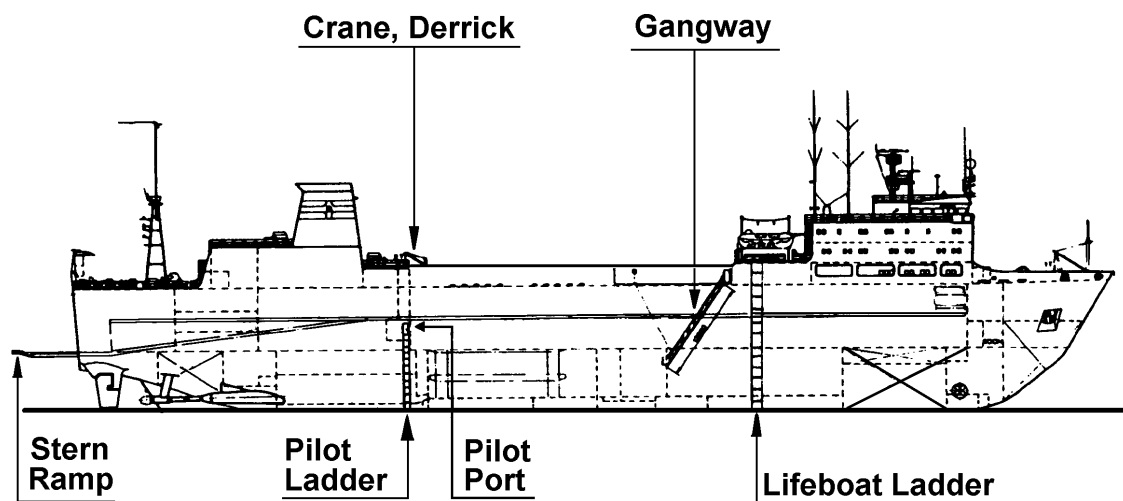


Figure a1 - 5 Examples of alternatives for boarding

Depending on the ship's available crew and power supply at the moment of boarding the following three alternative situations appear.

1. The ship is manned and the power supply is intact

- | | | |
|-------------------|-------------------------|-------------------|
| * Pilot ladder | * Bunker and food ports | * Ramps |
| * Lifeboat ladder | * Gangway | * Helicopter |
| * Pilot ports | * Derricks | * Direct boarding |
| * Pilot elevator | | |

2. The ship is manned but the power supply is out of order

- | | | |
|-------------------|------------------------|-------------------|
| * Pilot ladder | * Gangway | * Helicopter |
| * Lifeboat ladder | * Bunker or food ports | * Direct boarding |
| * Pilot ports | | |

3. The ship is unmanned

- | | |
|-------------------|---------------------------------|
| * Direct boarding | * Boarding vessel's own derrick |
| * Helicopter | * Already lowered ladder |

J. The site of accident on board a disabled ship

The hot zone on board must be restricted for access by Emergency Responders only. These responders must wear full protective suits.

The response action always starts from the limit of the hot zone where also a decontamination station is placed. In actions on board ships it is not always possible to follow these rules especially when the wind speed is not enough to safely blow away hazardous gases.

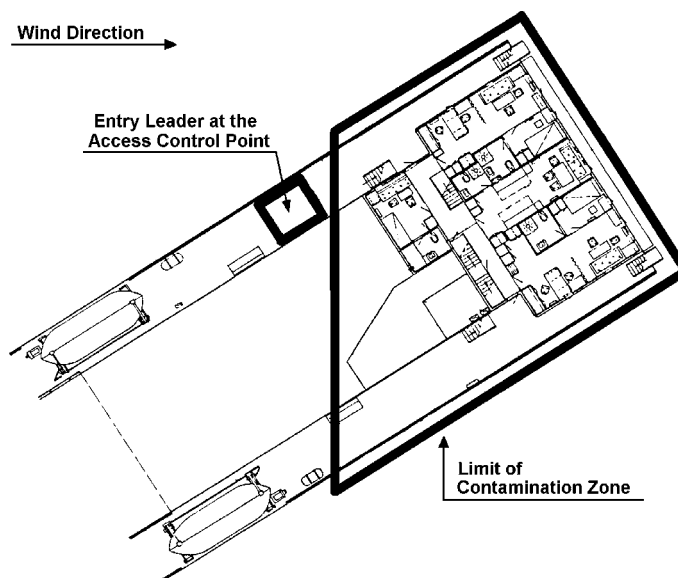


Figure a1 - 6 The restricted hot zone on board a ship disabled by a chemical accident

The decontamination station may on such occasions be located on board a response vessel which then also is the base for response. Figure a1 - 6 shows an example of a cordoned off hot zone with a decontamination station.

K. Example of a checklist

In an operation at sea against a chemical accident it is valuable to follow a checklist where the steps could be ticked off, one by one, during the course of operation. The list below might earn as an example. It is established by the National Strike Force of the United States Coast Guard and is called **Hazardous Chemical Emergency Response Checklist**.

1. Risk assessment completed.....	<input type="checkbox"/>
2. PPE* selection completed.....	<input type="checkbox"/>
3. Emergency Response Procedures completed.....	<input type="checkbox"/>
4. Work zones established	<input type="checkbox"/>
5. PPE* checks completed	<input type="checkbox"/>
6. Decontamination line assembly completed	<input type="checkbox"/>
7. Instruments calibrated.....	<input type="checkbox"/>
8. Communication plan completed	<input type="checkbox"/>
9. Pre-entry medical monitoring completed.....	<input type="checkbox"/>
10. Initial entry objectives established.....	<input type="checkbox"/>
11. Action levels established.....	<input type="checkbox"/>
12. Sampling plan completed.....	<input type="checkbox"/>
13. Pre-entry brief completed	<input type="checkbox"/>
14. Practice run through decontamination line	<input type="checkbox"/>
15. Communications check.....	<input type="checkbox"/>
16. Authorization for entry	<input type="checkbox"/>
17. Post-entry medical monitoring completed.....	<input type="checkbox"/>
18. Entry team debrief completed.....	<input type="checkbox"/>
19. Emergency Response and Site Safety Plan modifications.....	<input type="checkbox"/>
20. Equipment decontamination/inventory completed	<input type="checkbox"/>
21. Contaminated materials disposed	<input type="checkbox"/>
22. Potential Exposure Record forms completed.....	<input type="checkbox"/>
23. Debrief conducted with OSC.....	<input type="checkbox"/>

Figure a1 - 7

**PPE = Personal Protection Equipment*

Chemical resistance of materials

In actions against chemical accidents involving solvents or aggressive chemicals it is crucial to be aware, during the response operation, of the risk for deterioration of chemical protection clothing as well as response equipment and devices (booms, skimmers, containers, pumps, hoses, etc.).

Figure a2 - 1 and Figure a2 - 2 below can be used as a rough tool in assessing the chemical resistance of various materials to aggressive chemicals.

The letters at the top of the Figure a2 - 2 columns relate to chemicals and chemical groups (examples within brackets) in Figure a2 - 1.

<i>(examples within brackets)</i>		<i>(examples within brackets)</i>	
A	Chlorine	K	Chlorinated hydrocarbons (carbon tetrachloride)
B	Sulphur dioxide	L	Alcohols (isopropanol)
C	Ammonia	M	Ketones (acetone)
D	Oxidizing substances (hydrogen peroxide)	N	Ethers (diethyl ether)
E	Salt solutions (sodium chloride solution)	O	Esters (ethyl acetate)
F	Alkalis, lye (sodium hydroxide solution)	P	Nitriles (acrylonitrile)
G	Inorganic acids (sulphuric acid)	Q	Amines (triethanolamine)
H	Organic acids (formic acid)	R	Amides (dimethylformamide)
I	Aliphatic hydrocarbons (n-hexane)	S	Aldehydes (formaldehyde)
J	Aromatic hydrocarbons (toluene)		

Figure a2 - 1

Source: Finnish Emergency Services College

N.B.

The chemicals in Figure a2 - 1 refer to pure substances. Their aggressive effects on materials may be considerably increased if they are contaminated or mixed with other substances. These effects may also be enhanced by increased temperature and concentration.

The properties and aggressive effects of substances in the same chemical group may differ from substance to substance. By this reason the information in Figure a2 - 1 and Figure a2 - 2 should be regarded as indicative. If possible the deleterious effects of a chemical to a material should be checked by consulting sources with information specific for the chemical and material in question.

Besides the chemical resistivity of materials also the mechanical durability should be considered. For example, a plastic container which is chemical durable against volatile liquids may not be suitable as a pressure vessel because it may not withstand the vapour pressure of the enclosed liquids, especially on certain occasions of elevated temperature e.g. when exposed to sunlight.

When using hoses, containers, etc. made of plastic or rubber appropriate safety precautions must always be taken to eliminate any charges of static electricity with grounded arrangements.

Materials	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
Polyethylene (HDPE, LDPE, PE-X)	0	2	2	2	2	2	1	1	2	0	1	2	0	0	2	0	2	0	2
Polypropylene (PP)	2	2	2		2	2	1	2	1	1	0	2	1	0	2				2
Polyvinyl Chloride (PVC)	1	0	2	2	2	2	1	1	1	0	0	2	0	0	0	0	2	0	2
Polytetra Fluoroethylene; Teflon (PTFE)	2		2		2	2	2	2	2	2	2	2	2	2	2	1		2	2
Polyvinyl Alcohol (PVAL)			0	0		0	0	0	2	2	2	0	0	2	2	0	2	0	0
Polystyrene (PS)	0	1	2		2	1	0	1	1	0	0	2	2	0	0				0
Polyvinylidene Fluoride; Kynar (PVDF)		2	2	2	2	2	2	2	2	2	2	2	1	2	2		0		2
Polycarbonate (PC)	1	0	0		2	0	0	0	2	0	0	2	0	0	0		0		2
Polymethyl Methacrylate; Plexiglas (PMMA)	1	2	2		2	1	0	0	2	0	0	0	0	0	0		1		2
Acrylonitrile-Butadiene-Styrene (ABS)	2	0	1		2	2	0	0	1	0	0	2	0	0	0				2
Perfluoroethylene Propylene (FEP)	2		2		2	2	2	2	2	2	2	2	2	2	2	1		2	2
Perfluoroalcoxy Alcane (PFA)	2		2		2	2	2	2	2	2	2	2	2	2	2	1		2	2
Polychlorotrifluoroethylene (PCTFE)	0				2	2	2	2	2	2	0	2							
Ethylene Chlorotrifluoroethylene (ECTFE)	0				2	2	2	2	2	2	0	2							
Ethylenetetrafluoroethylene (ETFE)					2	2	2	2	2	2		2							
Polyamide; Nylon (PA)	0	0	2		2	2	0	0	2	2	2	2	2	2	2				2
Polyacetal (POM)	0	0	2		2	2	0	0	2	2	2	2	2	2	2				2
Polyethylene Terephthalate (PETP)					2	2	0	0	2	2				2	2				2
Polyphenylene Oxide (PPO)	2	2	2		2	2	2	2	0	0	0	2	0	0	0				2
Polyphenylene Sulphide (PPS)	1	2	2		2	2	0	2	2	2	2	2	2	2	2				2
Styrene-Acrylonitrile (SAN)	0	1	2		2	1	0	1	1	0	0	2	2	0	0				0
Polysulphone (PSU)	1	1	2		2	2	1	2	1	0	1	0	1	1	0				2
Phenol-Formaldehyde (PF)	0	2	2		2	2	0	2	2	2	2	2	2	2	2				2
Epoxy (EP)	0	2	2		2	2	0	1	2	2	2	2	2	2	2				2
Unsatisfied polyester; reinforced plastic	2	2	2	1	2	0	1	1	2	0	0	2	0	0	0	0			2
Natural rubber (NR)	0	1	1	0	2	2	1	0	0	0	0	1	1	0	0	0	0	0	0
Isoprene; synthetic natural rubber (IR)	0	1	1	0	2	2	1	0	0	0	0	1	1	0	0	0	0	0	0
Chloroprene; neoprene (CR)	0	1	1	1	2	2	2	2	2	0	0	0	2	0	1	2	2	2	2
Nitrile rubber NBR)	0	0	2	0	2	2	0	1	2	0	1	2	0	0	0	0	2	2	2
Styrene-Butadiene rubber (SBR)	0	2	2	2	2	2	2	2	0	0	0	2	2	0	0	0	1	1	2
Butyl rubber (IIR)	0	2	2	0	2	2	1	2	0	0	0	2	2	1	2	0	2	1	2
Chlorobutyl rubber (CIIR)					2					0	0		2	1	2		0		
Fluorine rubber; Viton (FEP or FKM)	2	2	2	2	2	1	2	0	2	2	2	2	0	0	0	0	0	0	2
Chlorosulphonated polyethylene; Hypalon (CSM)	0	2	2	0	2	2	2	1	2	0	0	2	0	1	1	1	2	1	2
Ethylene-Propylene rubber (EPDM)	0	1	2	1	2	2	2	1	0	0	0	2	2	0	2	0	2	2	2
Silicon rubber (VMQ,PVMQ,FMQ,FVMQ,etc)	0	1	2	2	2	0	0	2	0	0	0	2	2	0	0		2	1	2
Ordinary steel (carbon steel; e.g. Fe 37)	2	2	0	0	0	1	0	0		2	2	0	2	2	2	2	0	0	
Ordinary cast iron	2	2	0	0	0	1	0	0		2	2		2	2	2	2	0	0	
Silicon cast iron	2	2	0	0	0	1	2	1		2	2		2	2	2	2		0	
Stainless steel (e.g. AISI 304)	2	2	2	2	2	2	0	0		2	2	2	2	2	2	2	2	2	
Acid resistant steel (e.g. AISI 316)	2	2	2	2	2	2	1	1		2	2	2	2	2	2	2	2	2	
Aluminium	0		2	2	0	0	0	1	2	2	2	0	2	2	2	0	0	0	
Brass (Cu-Zn)	0	2	0	0	2	2	1	2	2	2	2	2	2	2	2	0	0	0	2
Tin bronze (Cu-Sn)	0	2	0	0	2	2	1	2	2	2	2	2	2	2	2	0	0	0	2
Aluminium bronze (Cu-Al)	0	2	0	0	2	2	1	2	2	2	2	2	2	2	2	0	0	0	2
Red brass (Cu-Sn-Zn/Pb)	0	1	0	0	1	1	1	2	2	2	2	2	2	2	2	0	0	0	2
Titanium	0	2	2		2	1	2	2	2	2	2	2	2	2	2	2	2	2	2
Lead	2	2			2	0	2	0		2	2	0	2	2	2				
Monel (Ni-Cu-Al/Mn)	2				2	2	1	2		2	2		2	2	2			0	
Hastalloy B (Ni-Mo)	2			0	2	2	2	2		2	2		2	2	2				
Hastalloy C (Ni-Cr-Mo)	2				2	2	2	2		2	2		2	2	2				

Figure a2 - 2

Source: Finnish Emergency Services College

2 durable
 1 limited durability
 0 non-durable
 not known

Case histories of marine chemical accidents

Contents

Document name	Vessel type or IMDG class	Chemical name	Vessel's name	Year
Alesandro Primo	3, 6 3	acrylonitrile ethylene dichloride	Alessandro Primo	1991
Anna Broere	3, 6	acrylonitrile	Anna Broere	1988
Ariadne	3, 5, 6, 8	miscellaneous	Ariadne	1985
Ascania	tanker	vinyl acetate	Ascania	1999
Burgenstein	5	sodium peroxide	Burgenstein	1977
Cason	4	sodium	Cason	1987
Cavtat	6	tetraalkyl lead	Cavtat	1974
Dinoseb 1	6	dinitrobutylphenol (DNBP, Dinoseb)	Dana Optima	1984
Dinoseb 2	6	- " -	(herbicide-treated parking lot)	1974
Finneagle	3	trimethyl phosphite	Finneagle	1980
Frank Michael	dry bulk carrier	fertilizer	Frank Michael	1993
Ievoli Sun	tanker	styrene methyl ethyl ketone isopropyl alcohol	Ievoli Sun	2000
Igloo Moon	gas carrier	butadiene	Igloo Moon	1996
Julie A	8	hydrochloric acid	Julie A	1989
Korsnäs Link	5	sodium chlorate	Korsnäs Link	1991
Martina	tanker	hydrochloric acid	Martina	2000
Mont Louis	7	uranium hexafluoride	Mont Louis	1984
Oostzee	6	epichlorohydrin	Oostzee	1989
PCB	9	polychlorinated biphenyl	(transformer)	1974
Perintis	6	lindane, permethrine, cypermethrine	Perintis	1989
Phenol	6	phenol	(cistern)	1973
Poona	5	Sodium chlorate	Poona	1975
Propionic acid	8	propionic acid	(drums washed ashore)	1975
Puerto Rican	tanker	caustic soda solution	Puerto Rican	1984
René 16	2, 8	ammonia	René 16	1976
Rio Neuquen	6	aluminium phosphide	Rio Neuquen	1984
Santa Clara	6	arsenic trioxide	Santa Clara I	1991
Sindbad	2	chlorine	Sindbad	1979
Stanislaw Dubois	4	calcium carbide	Stanislaw Dubois	1981
Styrene Barge	3	styrene	(barge)	1992
Sunken Barge	8	sulphuric acid	(barge)	1988
Testbank	6	pentachlorophenol	Testbank	1980
Val Rosandra	gas carrier	propylene	Val Rosandra	1990
Viggo Hinrichsen	5	chromium trioxide	Viggo Hinrichsen	1973

Alessandro Primo **Maritime Chemical Accident**

1991, February 1

Adriatic Sea, 16 n.m. north-east of Molfetta, Italy

Acrylonitrile (Class 3, 6) in tank containers; flammable liquid, toxic to both human and marine life, TLV 2 ppm (USA), IDLH 85 ppm (USA); **marine pollutant**
Ethylene dichloride (Class 3) in tank containers; oily liquid, flammable and toxic, **marine pollutant**

Summary: On February 1, 1991, the chemical carrier Alessandro Primo **sank** in the Adriatic Sea 16 miles off the coast of Italy. The **water depth was 110 m** and aboard the ship was a cargo of 550 tonnes of acrylonitrile and 3000 tonnes of ethylene dichloride. An **exclusion zone** of ten mile radius was set up around the wreck. During the following days water samples were taken around the wreck at various depths. Four days after the incident a trace of acrylonitrile was found 500 m from the wrecks position. Surveillance of the wreck with the aid of a ROV also showed evidence of an **acrylonitrile leak**. It was considered to be impossible to recover the entire ship which had been severely damaged when hitting the bottom. Diving at this depth also posed great difficulty. Three companies specialised in the area was hired to recover the cargo which threatened to pollute the area. The first step was to block the leaking of acrylonitrile and this was done by February 21. By the beginning of April the recovery operations started. With the aid of a large pontoon and a depot ship, the tanks of Alessandro Primo were emptied within less than a month. Many precautionary actions were taken during the hazardous operation, such as a helicopter standing by and emergency personnel present. Despite the difficulties and the great risks no injuries were encountered. All of the remaining cargo was taken care of, although most acrylonitrile had leaked out before the recovery operation started.

Cause of Accident: Not available.

Comments on Response: The incident was complicated due to many different circumstances, such as great depth and very dangerous chemicals. The handling of the situation was successful and very professionally done. The environmental impact of the incident was very small, especially regarding that two very pollutant chemicals were involved.

Source of Information: 1) Report on the Alessandro Primo accident from REMPEC by G. Tosco. 2) Report from EniChem, Milano, 1996. 3) Project documentation from Smit Tak, Rotterdam.
(Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Anna Broere**Maritime Chemical Accident**

1988, May 27

Off the coast, 60 n.m. west of IJmuiden, The Netherlands

Acrylonitrile (Class 3, 6) in tank containers; flammable liquid, toxic to both human and marine life, TLV 2 ppm (USA), IDLH 85 ppm (USA); **marine pollutant**

Summary: On May 27, 1988, the Dutch chemical carrier **Anna Broere**, on her way from Rotterdam to England, collided with the Swedish container ship Atlantic Compass. Atlantic Compass could continue its journey towards Antwerp while Anna Broere was severely damaged and sank in the shallow water. The cargo of Anna Broere consisted of 547 tonnes of **acrylonitrile** and 500 tonnes of **dodecyl benzene**, of which the latter is not regarded as a marine pollutant and was therefore left untreated. Acrylonitrile however is a very dangerous chemical, both to humans and as a marine pollutant. An **exclusion zone** with a radius of 10 km and a height of 300 m was therefore set up. Dutch authorities started an operation in order to recover the acrylonitrile with the help of a large **floating crane**. First the wreck was sawed in half so that the stern could be lifted separate from the leaking cargo tanks. Both parts of the ship were eventually lifted and about half of the acrylonitrile was recovered. The other half had leaked out and rather quickly dispersed into the sea. During the operation the concentrations of acrylonitrile in air and water was continuously monitored due to the safety of the personnel. Because of **hard weather** the operation was delayed several times. The operation lasted a total of 73 days, but only in 25 of those days salvage work could be carried out.

Cause of Accident: A collision with another ship caused severe damage to the hull and caused the ship to sink.

Comments on Response: The response operation was done properly and correct. The costs came to be much greater than expected, but this was mostly due to the bad weather conditions. It can be discussed however if the calculated impacts on the environment would have been that severe. The 200 tonnes of acrylonitrile that leaked out did cause damage to the marine biota, but not at all as much as it was believed. As the concentrations of the pollutant were continuously measured, no unnecessary risks were taken by the rescue personnel.

Source of Information: Incident report on the Anna Broere, Rijkswaterstaat North Sea Directorate, The Netherlands.
(Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Ariadne**Maritime Chemical Accident**

1985, August 24

Port of Mogadishu, Somalia

Chemicals involved in accident			
	Class		Class
Acetone	3	Methyl ethyl ketone	3
Butyl acetate	3	Toluene	3
Dipentene	3	Xylene	3
Ethyl acetate	3	Hydrogen peroxide	5
Hexane	3	Organchlorine pesticides	6
Hydrazine	3	Sodium pentachlorophenate	6
Isobutyl alcohol	3	Tetra ethyl lead	6
Isopropyl alcohol	3	Trichloroethylene	6
Methyl isobutyl ketone	3	Nitric acid	8

Summary: On August 24, 1985, the Panamanian registered container ship **Ariadne** grounded about 100 m off the port of Mogadishu in Somalia. The ship carried a cargo of 600 containers and around 100 of these contained **hazardous chemicals** of various types. The Somali government requested help and five countries sent teams of experts in areas like salvage, fire fighting, spill response, chemistry, and environmental assessment. A temporary fire aboard the ship forced a limited evacuation of the port area because of smoke and chemical fumes. For the population it was considered that fire or explosion in the wreck were the primary risks. Therefore efforts were made to refloat the ship which caused the ship to break and a portion of the deck collapsed. Subsequently the ship broke up and the cargo and bulk oil of the ship was released. Some 250 drums were **washed ashore** where they were taken care of during the following six weeks. The rest of the bunker oil was pumped out and most of the cargo was removed and taken care of. Four months later the front piece of the wreck was towed some 35 n.m. out to sea where it was sunk. Finally, after nine months, the last pieces of the wreck were removed by a salvage tug and a large floating crane. It is not clear in detail what happened with the most dangerous chemicals. It is known that some of the tetra ethyl lead, sodium pentachlorophenate, and trichloroethylene was never recovered.

Cause of Accident: Grounding due to broken towing equipment.

Comments on Response: The operational respond to this accident is a good example of the need for outside help within third world countries. Because many ships pass through these countries, it is necessary to have a way to find quick assistance when an accident of this kind takes place. In this specific event the respond from foreign countries was both fast and successful and the operation can be considered to have been handled in an efficient way. It is unacceptable however that all hazardous chemicals were not recovered, especially as the stealing of drums floating ashore was not stopped fast enough.

Source of Information: 1) Report on the Ariadne incident from the 1986 Hazardous Material Spills Conference, EPA, USA. 2) Mission report on Ariadne Incident, IMO. (Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Ascania**Maritime Chemical Accident**

1999, March 19

Pentland Firth, Great Britain

Vinyl acetate (Class 3) in cargo tanks; watery liquid, flammable and polymerisable
TLV 10 ppm (USA)

Summary: On March 19, 1999, the chemical tanker **Multitank Ascania** reported a **fire aboard** in the Pentland Firth. Multitank Ascania was carrying a cargo of 1800 tonnes of **vinyl acetate**, a flammable and polymerisable liquid. The fire had started in the machinery spaces where an oil leak from a thermal oil pump had ignited. The crew made unsuccessful attempts to settle the fire, first with portable extinguishers and then by flooding the machinery spaces with the fixed CO₂ system. When the rescuers arrived it was decided to airlift the crew off the ship due to the risk of explosion. However, the master stayed onboard in order to anchor the vessel. A tug attempted to tow the ship away from the shore but the tow parted. The master chose to **anchor the ship** and he was then evacuated. An **exclusion zone** with a radius of 5 km was set up and almost 600 local residents were evacuated. The ship was then examined by a thermal imaging camera from a helicopter. The fire seemed stable and two salvage personnel boarded the ship in order to get more accurate **temperature readings**. The fire was receding and it was decided to tow the ship to Scapa Flow in Orkney. By March 21, the responders were able to make a full assessment of the situation. The ship's machinery was severely damaged and the ship could not continue its journey. Therefore the cargo had to be transferred to another vessel, which was done by March 30. The Multitank Ascania was then taken under tow to Rotterdam.

Cause of Accident: A leak in a thermal oil pump.

Comments on Response: The response to this incident was fast and effective, much due to an exercise that had taken place only two days before the accident. The crew on the ship also proved to be professional and capable of handling the proper equipment.

Source of Information: 1) Press release 2000/0487 from the Department for Transport, Local Government and the Regions, UK. 2) "Exercise To Action - Fire Dramas On The High Seas", News release from Briggs Marine, UK.
(Abstracted July 2002 by Edvard Molitor, Swedish Coast Guard H.Q.)

Burgenstein**Maritime Chemical Accident**

1977, January 10

Port of Bremerhaven, Germany

Sodium peroxide (Class 5) in drums; solid that reacts violently with water and organic materials; powerful oxidizer that decomposes by heat to free oxygen and may cause fire and explosion in contact with combustibles

Sodium cyanide, potassium cyanide (Class 6) in drums; highly toxic solids that in contact with water, moisture, oxidants, or acids emit the extremely poisonous gas **hydrogen cyanide**, TLV 10 ppm (USA), IDLH 50 ppm (USA)

Summary: During loading of the German ship **Burgenstein**, a drum with **sodium peroxide** was damaged by a fork-lift truck and part of the content was spilled on plastic materials on deck. Water from a rainfall had penetrated the hold and water had reached the drums. A truck wheel spun in the spilled peroxide and the wet plastic. Bright yellow flames flared up. The fire spread rapidly to other spills of peroxide on deck and thereafter to the cargo followed by a violent blaze. A number of longshoremen succeeded to escape on a ladder from the burning hold, but three crew died in the fire. The fire brigade arrived and started the fighting with water and foam. The fire spread to other parts of the cargo. Explosions forced the fire fighters to withdraw temporarily. The fire fighting had to be carried out under great precaution due to the presence of **cyanides** in the cargo that could emit **hydrogen cyanide**. The port and a large area around was declared as a **safety zone** and people in parts of the city were told to keep doors and windows closed. After 5 hours, the fire fighters managed to control the fire and after another 4 hours it was extinguished.

Cause of Accident: Damage of sodium peroxide drums by a fork-lift truck during loading. Spill of peroxide reacted with wet plastic sheets under a spinning truck wheel. The resulting fire could spread rapidly around in the hold to other spills of peroxide.

Comments on Response: At the initial fire fighting, the fire brigade used water. This was a serious mistake considering the cargo of 1) **sodium peroxide** that reacts vigorously with water, and 2) **cyanides** that emit hydrogen cyanide when wet.

Source of Information: "The BURGENSTEIN Case", Waterways and Shipping Directorate North, Special Federal Unit for Marine Pollution Control, Deichstrasse 12, D-2190 Cuxhaven, Germany.

(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Cason**Maritime Chemical Accident**

1987, December 5

Off the coast of northwestern Spain

Sodium (Class 4) in drums; Sodium is a metal that floats and reacts violently with water or moisture to produce highly flammable **hydrogen** which may autoignite during the reaction. Sodium is corrosive to skin and eyes.

Summary: On a voyage from Antwerp to Shanghai, the cargo of the Panamanian container ship **Cason** caught fire. Cason first sent a distress message, and one hour later reported that the fire was out of control and that the ship was being abandoned. During the evacuation, 23 of her 31 crew died. Cason carried several different types of chemicals. But the fire probably started in one of the 11 containers of altogether 1430 drums of 126 tons of **sodium**. A tug tried to salvage Cason, but adverse weather and the fire on board stopped the operation, and Cason went aground 100 m from the shore. A **response team** started to unload ortho-cresol and formaldehyde drums. But bad weather stopped this work and caused more of the sodium drums to break and catch fire. Soon, the whole ship was on fire. Sodium drums that had fallen into the water were also burning. The fire could be seen far away at sea. Seven days after the initial fire, it was possible to enter the stranded wreck again. The cargo could successively be recovered from Cason and from the shores. The operation was delayed several times because of the weather and technical difficulties. After three weeks the recovery of dangerous goods was regarded as completed. No ecological damage was observed.

Cause of Accident: Fire broke out during adverse weather in a freight container with sodium drums, which probably were inappropriately stowed.

Comments on Response: The cargo of sodium made the whole operation very complex and dangerous. The **great hazard of sodium** made it impossible to carry out efficient response work before all the sodium had disappeared through reaction with water. Adverse weather, however, prevented response work also afterwards. Recovery of dangerous goods stowed under deck was difficult and delayed the operation. As a result of this accident, the opinion was raised that shipped sodium should be better packed and secured. Another result from the work was that the use of **trade names** is highly inappropriate as it causes identification problems. The international co-operation during the response to this accident proved very positive. This is specially valid for the co-operation and advice received from the Marine Environment Division of IMO and from the group of experts of the special "Task Force" created by EEC.

Source of Information: An anonymous and undated report titled "The CASON case, December 1987, Northwest Spain" obtained from EEC.
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Cavtat**Maritime Chemical Accident**

1974, July 14

The Strait of Otranto, off the coast of southern Italy

Tetraethyl lead and **tetramethyl lead** (Class 6) in drums; liquids that are poisonous if inhaled or if skin is exposed; VP 0.01 kPa (20°C), TLV 0.075 mg/m³ (USA), IDLH 40 mg/m³ (USA); **marine pollutants**

Summary: The Yugoslavian dry cargo ship **Cavtat** collided with the Panamanian bulk carrier **Lady Rita**. Cavtat, who sank in Italian territorial waters at the depth of 94 m four hours after the collision, carried 150 tons of **tetramethyl lead** (TML) in 500 drums on deck and 120 tons of **tetraethyl lead** (TEL) in 400 drums in the holds. The hull of Cavtat was split open at the collision and this made salvage of the whole vessel impossible. 400 drums of TML lay on the seabed around the vessel whereas the other drums remained on and within the damaged ship. Some drums became demolished at the accident. After more than two years of governmental discussions and media debate, the Italian Parliament granted financial support for salvage of the cargo. In April 1977 salvage of the drums started by the Italian offshore company Saipem. Teams of two **saturation divers** each performed the work inhaling a mixture of oxygen and helium. They worked 8 hours per day during 20 days, after which a three days decompression they were replaced by two new divers. The team spent 16 hours overnight in a **residence pressure chamber** on a salvage vessel's deck. In the mornings they crept over to a smaller chamber that was descended to a place close to the wreck where they took on outer protecting suits which were kept on the seabed. Through instructions over radio between the salvage vessel and the divers the drums were moved by a lifting device to a special container that could hold 14 drums. When this container had been filled, it was tightened gas-proof, lifted to the vessel and replaced by an empty container. The work was finalized after one year.

93% (250 tons) of the cargo was salvaged and 20 tons lost. Monitoring afterwards showed minor environmental effects. The cost of the operation was USD 16 million.

Cause of Accident: The northbound Cavtat suddenly sheered apart and the collision occurred with the southbound Lady Rita.

Comments on Response: The decision to salvage the cargo was very much delayed and was not taken until 2.5 years after the accident, after great pressure from scientists, politicians and mass media. When the work started it was performed in a professional way by an offshore company.

Source of Information: 1) Principally personal communication, 2) G. Tiravanti, G. Boari, 1979, "Potential Pollution of a Marine Environment by Lead Alkyls: The Cavtat Incident", Environmental Science & Technology, 13 No. 7, 849-854. (Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Dinoseb 1**Maritime Chemical Accident**

1984, January 13

North Sea, 150 n.m. east of Esbjerg, Denmark

Dinitrobutylphenol (DNBP, Dinoseb) (Class 6) in drums; extremely toxic solid pesticide; **marine pollutant**

Summary: The Danish container ship **Dana Optima** encountered a heavy storm in the North Sea on her way from North Shields in UK to Esbjerg in Denmark. On Friday 13, her main and auxiliary engines stopped which caused some of the deck cargo to fall overboard. One of the lost containers carried 80 drums (200 litres each) of the extremely toxic **pesticide** dinitrobutylphenol (also known as DNBP or Dinoseb). These drums sank to bottom at the depth of 40 m. An extensive search started by vessels from Denmark and Holland equipped with ordinary **sonars**, **sides can sonars**, **precision navigation equipment** and a **remotely operated vehicle** (ROV). Dutch trawlers found and recovered 13 drums during March 27-30. After a search grid had been established, a systematic search could start where different sides can sonars were used. A Dutch minehunter made the first finds of 40 drums on April 2. Danish vessels thereafter made further finds and performed also the final salvage. The salvage operation was carried out by divers under surveillance by laboratory personnel. Recovered drum were placed in **overpacks** and transported to a disposal plant. After 4 months, 72 of the lost 80 drums had been found and salvaged. The drums had been damaged by fishing and salvage gear as well as by the high water pressure. Yet, no environmental effects were observed, due to little pollution by the low-soluble Dinoseb. The cost of the operation for Denmark was 1 million USD.

Cause of Accident: Engine failure in heavy storm that caused the ship to list and deck cargo to fall overboard.

Comments on Response: Valuable experiences were gained from this case and a strategy was elaborated for such operations. A rough survey was first made by sector-scanning sonars of the types used by fishing vessels and mine hunters. "Hot" areas were then thoroughly searched by means of sides can sonars. After mapping these areas, all suspected items were identified and examined by a submersible (e.g. a ROV) equipped with a TV camera before salvage. Navigation and positioning must be carried out by means of a precision navigation system that has the required accuracy. In this operation a system called **ARGO** system showed best accuracy, while **PULSE/8** was preferred because of greater sturdiness.

Source of Information: 1) IMO document MEPC 21/INF.2, Loss and Salvage of Drums Containing DINOSEB, Submitted by Denmark. 2) "Dana Optima", a report on the incident (written in Danish), Submitted by the National Agency of Environmental Protection, Denmark.
(Abstracted April 1991 by Björn Looström, Swedish Coast Guard H.Q.)

Dinoseb 2**Maritime Chemical Accident**

1974, July 24

Allentown, Pennsylvania, USA

Dinitrobutylphenol (DNBP, Dinoseb) (Class 6) extremely toxic pesticide; **marine pollutant**

Summary: On July 24, 1974, there was a **heavy rainfall** in Allentown, Pennsylvania. Shortly thereafter the fish started dying in a lake which was a tributary to a public water supply. On August 9 the incident was reported to the authorities. It was found out that a parking lot close to the lake had been treated with the **herbicide** dinitrobutylphenol (also known as DNBP or Dinoseb) on July 21. This herbicide is extremely toxic and approved for use only in dilute amounts. However, the parking lot had been treated with undiluted product and held very high levels of the herbicide. The outlet from the lake was closed and different options discussed. According to the manufacturer the product would be persistent for at least nine months. By that time it might have contaminated both surrounding waters and the groundwater. It was therefore decided that the lake and the parking lot must be decontaminated. This was done with the help of a new **mobile hazardous spills treatment trailer**. This trailer was equipped with a self-contained water treatment system using activated carbon adsorption. The trailer arrived on August 12 and the treatment was started. The intake was placed right by the head of the lake where the highest concentrations of DNBP were found. At first the effluent was put back into the lake as the efficiency of the system was uncertain. Analytical data soon showed that the system was working properly and the effluent was therefore released downstream from the lake. Most of the gravel on the parking lot was removed and sent to a secure site. The parking lot was then hosed with water and the outflow was collected in a sump which had been dug for this purpose. The water in the sump was then treated in the trailer system. The lake and the parking lot were declared as decontaminated by August 22.

Cause of Accident: Improper use of an extremely toxic herbicide.

Comments on Response: The trailer system proved to be efficient and useful. The problem with this incident was that it took from July 24 to August 9 before anyone contacted the proper authority. This incident clearly shows the importance for people handling dangerous chemicals to be aware of the potential risks.

Source of Information: "Removal of spilled herbicide from a New Jersey lake", Article from the 1976 National Conference on Control of Hazardous Material Spills. (Abstracted July 2002 by Edvard Molitor, Swedish Coast Guard H.Q.)

Finneagle**Maritime Chemical Accident**

1980, October 1

North Sea, 30 n.m. west of Orkney Islands

Trimethyl phosphite (Class 3) in tank container; flammable liquid with high flash point (= low flammability, Class 3.3); reacts violently with acids under production of heat; burns under formation of dangerous **phosphorous pentoxide** in the smoke gases

Summary: On a voyage from New Orleans to Valhamn in Sweden, the Swedish ro-ro ship **Finneagle** encountered very hard weather that caused shifting of her cargo. A tank container with **trimethyl phosphite** started to move. It was secured by the crew but came loose again. It was damaged and started to leak. A fire broke out, soon followed by an explosion. The fire increased in ferocity. The **sprinkler system** was started with **light water** added and went on for one hour. A distress call was sent out. Finagle's life boats and liferafts were impossible to launch in the heavy seas. The fire, heat, and irritating and poisonous **smoke gases** developed to such a degree that the ship had to be abandoned. Two arriving helicopters were unable to start rescue work because of the weather. A third big helicopter, that arrived later, was able to send down a line and successively save all 22 persons on board, among them one wife and two small children. Still burning, the ship was later towed to Lerwick in the Shetland Islands. On October 4 the main seats of the fire had been extinguished.

Cause of Accident: The trimethyl phosphite container on tween deck was unsatisfactorily secured by chains and not placed on deck fittings. Leakage of a **rubber solution** made the deck slippery which together with the insufficient securing made the arrangement unstable. The trimethyl phosphite container struck repeatedly a refrigerated trailer. Thereby, the tank container was punctured and started to leak. The spill reacted with **leaking acid** from damaged batteries in the refrigerated trailer. The trimethyl phosphite was heated by the reaction and developed flammable vapours that ignited, probably by **sparks** from the damaged batteries.

Comments on Response: The function of the sprinkler system was unsatisfactory. It sprayed about 300 tons of **water** until it stopped after one hour due to a **pressure failure**. Foam or powder is recommended for trimethyl phosphite fire - water is not suitable. The crew worked rationally and efficiently under very difficult conditions. They checked the cargo and improved the lashings. Wearing breathing apparatus they fought the fire in the smoked-filled engine room. The master steered the ship by hand during the whole operation and was able to hold it against wind and sea, thus greatly contributing to the successful abandoning of the ship. The British Search and Rescue Service performed the helicopter rescue very efficiently in darkness and adverse weather.

Source of Information: "Fire on Cargo Deck in Swedish Ro-Ro Vessel Finneagle off the Orkneys, October 1, 1980", Marine Accident Report, February 23, 1982, Swedish Maritime Investigation Commission
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Frank Michael**Maritime Chemical Accident**

1993, October 10

North of the island of Gotland in the Baltic Sea

Chemical name: Monoammonium Phosphate (Ammonium Dihydrogen Phosphate) which is a non-toxic solid fertilizer; a nutrient for algae and thus a severe oxygen consumer.

Summary: The German dry bulk carrier Frank Michael grounded and obtained severe bottom damage. The cargo of 1,100 tons of fertilizer started to escape and dissolve in the surrounding water.

A discussion started among responsible Swedish agencies regarding the need for actions to save the cargo. The total yearly emission of similar chemicals into the Baltic Sea amounts to millions of tons, compared to the ship's cargo content of 1,100 tons. Furthermore, the time of the year and the favourable water turnover in the area reduced the risk for the environment. But a general view was that all possible actions should always be taken to reduce the release of oxygen consuming chemicals into the vulnerable Baltic Sea. One of the questions was how much resources were reasonable to devote to a salvage operation. One hint might be a comparison of the cost to take care of this amount of phosphates in a sewage purifying plant. This cost is about 3.5 million USD and the figure was put forward as a proposed target for response endeavours. But the responsible agencies did not judge that response efforts of this size would correspond to the environmental benefit. Thus no response actions were taken to stop the release of phosphate.

The weather got worse and the cargo content of phosphate escaped into the sea during a few weeks after the accident.

Cause of Accident: Grounding due to an navigational error.

Comments on Response: The ship's bunker oil was lightered, but no response actions were taken. to stop the release the cargo of phosphate.

Source of Information: Various memos by involved agencies.
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Ievoli Sun**Maritime Chemical Accident**

2000, October 30

English Channel, 45 n.m. north of Batz, France

Styrene (Class 3) in cargo tanks; flammable liquid
TLV 20 ppm (USA), IDLH 700 ppm (USA); **marine pollutant**

Methyl ethyl ketone (Class 3) in cargo tanks; flammable liquid, explosive when mixed with air, TLV 200 ppm (USA), IDLH 3,000 ppm (USA)

Isopropyl alcohol (Class 3) in cargo tanks; flammable liquid
TLV 400 ppm (USA), IDLH 2,000 ppm (USA)

Summary: At 4:30 a.m. on October 30, 2000, the Italian chemical tanker **Ievoli Sun** reported a **leak** in the bow section. The ship was carrying 4,000 tonnes of **styrene** and 1,000 tonnes each of **methyl ethyl ketone** and **isopropyl alcohol** in cargo tanks. After consideration of the gravity of the situation, the crew was evacuated by a helicopter. The risk of grounding was obvious and as this might lead to pollution of the nearby coastline, the favoured option was to tow the ship to shelter. The towing began at 5:15 p.m. to the North-East. On the morning of October 31, the Ievoli Sun **sank** at a **depth of 70 metres** during towing. The ship had then reached a position 12 n.m. from Alderney. General surveillance of the area was started due to the risk of pollution. The wreck was marked out with beacon buoys and maritime traffic was diverted. After a complete survey of the wreck had been done it was decided that the most appropriate solution would be to pump up the styrene and the heavy fuel. The methyl ethyl ketone and the isopropyl alcohol could be released if monitored closely. This was done by a hired salvage team in April-May 2001. The **release** of methyl ethyl ketone and the isopropyl alcohol showed no evidence of environmental impact. The styrene and the fuel was **pumped up** with the help of a **remote operated offloading system**. Both air and sea samples were taken throughout the area during the operation but tests showed no traces of a styrene leak. The operation was finished in May 2001.

Cause of Accident: A leak in the bow section double bottom.

Comments on Response: The response organisation worked well, probably much due to the Erika incident that happened less than a year before the Ievoli Sun. Both national and international co-ordination was trimmed during the Erika incident and one command centre was still operational. The technology used to salvage the styrene and the heavy fuel proved to be efficient.

Source of Information: Brief report from the French authority Cedre. Available at www.le-cedre.fr.
(Abstracted June 2002 by Edvard Molitor, Swedish Coast Guard H.Q.)

Igloo Moon**Maritime Chemical Accident**

1996, November 6

Key Biscane, Florida, USA

Butadiene (Class 2) in gas tanks; liquefied compressed gas, flammable, reactive
TLV 2 ppm (USA), IDLH 2,000 ppm (USA)

Summary: On November 6, 1996, the gas tanker **Igloo Moon** ran **aground** outside Key Biscayne in Florida. The vessel had a cargo of 6,589 tonnes of **butadiene**, which was compressed and liquefied. A **chemical inhibitor** was added to prevent polymerization. Butadiene is a potential carcinogen. The first step taken was lightering of the fuel which was completed by November 8. Many different scenarios were evaluated and a plan for public evacuations were set up in case anything would go wrong. The option of controlled release of the chemical through venting was considered to be unsafe. The certificate of the inhibitor was due to expire on November 9 and the stability of the cargo was of utmost importance. Fresh inhibitor was sent on-scene, but due to the risk of ruining the product they chose to test the cargo instead. Analysis showed that the inhibitor would be secure until December 1. Because of the shallow depth, the salvage operations were very complex. A complete hydrographic survey of the area was done in order to find the best way to bring another gas tanker alongside the Igloo Moon. There was also concern of the **ballast water** in the vessel which would have to be released. The area is part of a National Park and **invasive species** would therefore pose a threat. In order to avoid this the ballast tanks were treated with 50 ppm of calcium hypochlorite for a six hour period. This would be enough to kill any exotic species, but would not effect the area upon release. On November 20 the lightering vessel Selma Kosan made her way alongside the Igloo Moon and approximately 1,000 tonnes of butadiene were transferred. The Igloo Moon then released the ballast water and was refloated with the flood tide on November 21. No chemicals were released into the water.

Cause of Accident: Grounding due to an unknown reason.

Comments on Response: The response operations in this incident were very complex. The area being part of a national park made it even more important to ensure that no harm was done to the environment. It is interesting that even though the butadiene posed the greater threat to the people in the area, the ballast water might have been the greater threat to the environment.

Source of Information: Report from the National Oceanic and Atmospheric Administration, USA.

(Abstracted July 2002 by Edvard Molitor, Swedish Coast Guard H.Q.)

Julie A**Maritime Chemical Accident**

1989, November 4

Harbour of Århus, Denmark

Hydrochloric acid (Class 8) in cylindrical tanks; watery liquid, corrosive, reacts with sheet-iron forming flammable hydrogen gas
IDLH 50 ppm (USA)

Summary: On November 4, 1989, the dry cargo ship Julie A reported a **leaking tank** of hydrochloric acid on board. The ship was at this time moored in the harbour of Århus. The leaking tank was one out of three cylindrical tanks stored in a hold below deck. The leaking tank contained a total of 300 tonnes of **33% hydrochloric acid**, which is very corrosive. When hydrochloric acid reacts with sheet-iron, flammable hydrogen gas is formed. The engines of the ship were therefore shut down. When the responders entered the ship they had to wade through knee-deep hydrochloric acid and they had a visibility of only two metres. They found a 25 mm hole in the tank and they plugged this with a wooden wedge. The acid had eaten its way through the tank as the tank-coating was not strong enough. The acid on the floor had also spread into the ballast tank and threatened to reach through the bottom of the ship. After some trouble finding the appropriate equipment to pump the acid into tanks on-shore, the offloading of acid was initiated. However, quite soon the stability of the ship was decreased and it was therefore decided to move the ship to a dry dock. This was done the next day and after that the ship was dried from the acid through a drilled hole in the bottom of the ship. It was estimated that the total amount of hydrochloric acid spilled in the harbour was about 1-5 tonnes.

Cause of Accident: Inappropriate tank coating made of glass-fibre reinforced polyester which was corroded by the hydrochloric acid.

Comments on Response: Although the responders had trouble finding the right equipment, the operation can be considered a success. This incident shows how important it is to have knowledge of the chemicals transported. It is also extremely important to have the right kind of transporting equipment.

Source of Information: 1) Report 107/89 from "Stadsingeniørens kontor" in Århus.
2) An article from Brandværn 2'90 by Knud Aage Eriksen.
(Abstracted July 2002 by Edvard Molitor, Swedish Coast Guard H.Q.)

Korsnäs Link**Maritime Chemical Accident**

1991, November 5

Off the English coast, 10 n.m. east of Teeside, England

Sodium chlorate (Class 5) in a total of 40 one-tonne bags; solid powerful oxidiser that decomposes by heat to free oxygen and may cause fire and explosion in contact with combustibles

Summary: The Swedish ro-ro ferry **Stora Korsnäs Link I** was on a voyage from Sweden to Hartlepool in England when a **fire** started in the machine room. Attempts were made to extinguish the fire by filling the machine room with **CO₂**, but the attempts failed and the crew was forced to shut down the engines. The ship's crew alerted the authorities of the nearest port Teeside and requested help. Rescue vessels were sent to the scene and rescue personnel boarded the ship. Two tugs from a local salvage company arrived and towed the vessel further out to sea. The fire had now spread to the upper deck and the rescue personnel were unable to settle the fire. Eight hours later, the salvage company had contacted the owner of the cargo and found out that the ship did not only carry different forest products but also potentially explosive chemicals. On the lower deck 40 tonnes of **sodium chlorate** was stowed within two containers. When this was found out the ship was quickly abandoned. A one-mile **exclusion zone** was established and the salvage tugs left the scene. After sometime they decided however to make a new attempt to save the cargo and a vessel with firefighting equipment was sent to the scene. The started to pump water onto the exterior of the ship in order to achieve control of the fire. The attempt was unsuccessful and the fire spread to the other cargo decks during the following days. On November 8, an **explosion** occurred close to the containers with sodium chlorate and it blew out the side of the ship causing the ship to roll over and capsize. After a few hours the ship sank at a depth of 40 metres. The explosion caused no injuries but blew out two windows on the firefighting vessel.

Cause of Accident: A fire in the machine room which spread to the cargo decks.

Comments on Response: The cargo manifest did not have the proper information and this led to a very dangerous situation as the rescue personnel boarded the vessel and tried to fight the fire unaware of the explosion risk. The second attempt to settle the fire was very risky and it was fortunate that no one got injured.

Source of Information: 1) "Gap in the paper chain", Hazardous Cargo Bulletin, January 1992. 2) Report S 1992:5, Swedish Board of Accident Investigation. (Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Martina**Maritime Chemical Accident**

2000, March 28

Öresund, West of Kullen, Sweden

Hydrochloric acid (Class 8) in cargo tanks; watery liquid, irritating vapour, corrosive
IDLH 50 ppm (USA)

Summary: In the morning of March 28, 2000, the chemical tanker **Martina** collided with the cargo ship Werder Bremen in Northern Öresund. The **collision** caused Martina to break in two halves and the stern part **sank** immediately. The rest of the ship, with a cargo of 600 tonnes of 30% **hydrochloric acid**, sank after a few hours. The weather was hard, with strong winds and heavy snowfall. Two out of seven crew members were saved from the water. Unsuccessful attempts were made to contact possible survivors inside the bow part of the ship before it sank. Due to the weather it was impossible to reach the ship during the first two days. On March 30 both parts of the ship were localized with the help of **remotely operated vehicles**. The cargo seemed to be intact and there was no immediate risk for oil leakage from the bunker oil. A salvage company was hired to remove the cargo and the bunker oil. As the hydrochloric acid is not a marine pollutant and not harmful in low concentrations it was decided that a **monitored release** of the cargo was preferred. However, the ships bunker oil was considered as a threat to the marine environment and should therefore be pumped up. The operations were done on May 20-23, 2000, and were reported to have been successful. No harm was done by the released hydrochloric acid.

Cause of Accident: A collision in hard weather which broke the ship in halves.

Comments on Response: The hard weather made it difficult to locate the ship at first. It also made diving in the area difficult, which is why the remotely operated vehicles were preferred. The salvage of the bunker oil was successful and the release of the hydrochloric acid proved to be safe, as it had no impact on the marine environment.

Source of Information: The report "Redovisning av operation Martina" by the Swedish Coast Guard.
(Abstracted June 2002 by Edvard Molitor, Swedish Coast Guard H.Q.)

Mont Louis**Maritime Chemical Accident**

1984, August 25

North Sea, 7 n.m. off the Belgian coast

Uranium hexafluoride (Class 7) in steel cylinders; low-radioactive solid that reacts with water to form the highly corrosive and toxic gas/liquid **hydrogen fluoride**, Bp 20°C, VP 100 kPa (20°C), TLV 3 ppm (USA), IDLH 30 ppm (USA)

Summary: The French ro/ro ship **Mont Louis**, bound for Riga, collided with the car ferry Olau Britannia off the Belgian coast. Among her cargo, Mont Louis carried 30 cylinders with 15 tons each of solid nuclear fuel **uranium hexafluoride** (UF₆), loaded in Le Havre, France. The two ships became interlocked into each other and were drifting several hours towards the shore. After separation, Mont Louis sank in international waters at the depth of 15 metres, partly exposed at low tide. The responsible French charter company ordered the Dutch salvage company Smit Tak International to salvage the cargo. The Belgian government kept the operation under close continuous observation. The hull of Mont Louis was **cut open** and the cargo was, after some difficulties, located in the hull and salvaged. The work had to be interrupted at several times because of rough weather. The 30 cylinders were successively salvaged until October 4, 40 days after the accident. A few days after the accident an intensive work started to achieve information about the cargo. This turned out to be a tedious procedure that first resulted in incorrect information. Not until three weeks after the accident, the Belgian authorities got a full understanding of the contents of the cargo and the nature of its risks. The radioactivity of UF₆ is low. The main hazard is its **reactivity**, particularly in liquid form. It reacts with water to form uranyl fluoride and highly corrosive and toxic **hydrogen fluoride**.

Cause of Accident: Information not available.

Comments on Response: The Belgium authorities experienced great difficulties in searching for correct information about the cargo when contacting the ship's crew as well as French authorities. It was also difficult to achieve a full understanding of the hazards of the cargo and to identify the risks. Statements made by ill-informed specialists caused considerable confusion. Much time and effort must be devoted to disclaim false information. The contacts with the mass media were time-consuming and demanding. The news reports on the accident were often inaccurate. The recovery of the cargo took long time and was difficult because of adverse weather and the complexity of the operation when cutting the hull and searching for the cargo in the holds. The cylinders were unaffected by the accident and neither chemical nor radioactive pollution happened.

Source of Information: Proceedings of the Symposium on Oceanology, Brussels, Belgium, 4-6 March, 1985, Thierry G. Jacques, Scientific Evaluations of an Incident at Sea Involving a Sunken Ship Carrying a Dangerous Cargo.
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Oostzee**Maritime Chemical Accident**

1989, July 18

German Bight

Epichlorohydrin (Class 6) in drums; poisonous liquid that emits toxic vapours; VP 2 kPa (20EC), TLV 5 ppm (USA); potential human carcinogen

Summary: The Dutch cargo ship **Oostzee** ran into a storm en route from Rotterdam to Leningrad. 975 tons of **epichlorohydrin** in 3900 drums (250 kg per drum) was stowed in upright position, without proper lashings, on the smooth-surfaced tweendeck. Filled drums, stowed around empty drums, shifted in the storm and squeezed the empty ones, thus resulting in greater shift and damage. Leaking drums gave rise to **dangerous atmosphere** that caused inhalation **poisoning** among the crew. Oostzee was instructed by the German Shipping Administration to anchor at a place close to Cuxhaven. All 14 crew were hospitalised for 10 days. The cargo holds were found to contain highly toxic atmosphere and a great number of damaged and leaking drums mixed with general cargo. As a first step, part of the spilled epichlorohydrin was pumped up and transported to a disposal site. The ship was taken to a better equipped port in the River Elbe but was soon moved to a less populated port in the Elbe Estuary. Special care was first taken to reduce the **risk of explosion**. But later it was realised that the gas concentrations were far below the flammable limit (but yet highly toxic). The engine rooms and the cargo holds were ventilated with the object to reduce the concentration of epichlorohydrin vapours to 3 ppm. During this work a wide **safety zone** was established around the vessel (diameter 1000 m) as well as in the airspace above (height 2000 ft). Damaged drums were transferred to **overpacks** and transported to a chemical company for disposal. Also the general cargo was finally unloaded. 263 damaged drums and 2200 l of epichlorohydrin had been taken care of for disposal. 8100 l of epichlorohydrin had evaporated into the air during the operation.

Cause of accident: See above. Shifting of cargo in adverse weather owing to improper stowage.

Comments on response: In the beginning of the operation it was difficult to assess the hazard from the cargo and Oostzee had for safety reasons to be moved several times during the response operation. There were no tugboats available that had safety equipment for toxic gases. The epichlorohydrin vapours were found to be more dangerous than expected and 30 persons from the response organisation and mass media had to be medically examined. One person was irreversibly injured. In view of these incidents, the awareness and cautiousness regarding the toxic and carcinogenic properties of epichlorohydrin might be questioned.

Source of information: "The OOSTZEE Case July/August 1989", Waterways and Shipping Directorate North, Special Federal Unit for Marine Pollution Control, Deichstrasse 12, D-2190 Cuxhaven, Germany.

(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

PCB**Maritime Chemical Accident**

1974, September 13

Duwamish Waterway, Seattle, Washington, USA

Polychlorinated biphenyl (Class 9) in an electrical transformer; toxic, bioaccumulative and carcinogenic liquid; TLV 0.001-0.5 mg/m³ (USA)

Summary: An **electrical transformer** was dropped on the quay while being loaded by a crane onto a barge. The transformer was punctured and most of its content of 1 m³ **polychlorinated biphenyl** (PCP), used as cooling liquid, leaked out onto the quay and down into the Duwamish waterway. The Duwamish River is one of the many **anadromous** (= migrating up the river) fish runs in the area. The hazard of the spill was not realized until four days afterwards when laboratory personnel and divers arrived and examined the place. The divers could observe pools of free PCB on the bottom of the 8 m deep waterway. On October 9 a 50 ton heavy special **chemical treatment unit** arrived. The bottom area was dredged by a pipeline dredge handled by divers. During the dredging operation, the river level depth was checked by means of **fathometer** readings over a cross section of the spill area. The depth checks were made aboard a Coast Guard cutter that was in attendance throughout the operation. The perimeter of the contaminated river area was physically cordoned off by a **bubble air curtain** established by pumping air through a perforated fire hose lying on the bottom around the area. The purpose of the bubble screen was twofold - protect migrating fish and prevent PCB from spreading. 2300 m³ of sludge was handled by the treatment unit and purified through settling using **Nalco 634**, a polyelectrolyte. This settling agent was chosen after tests with several different agents. 215 drums of PCB-contaminated mud was collected and later carried to a disposal site. The cost of the operation was USD 150,000.

Cause of Accident: The transformer was packed in a wooden box and bolted to 4" x 4" "skids" or planks under the box. When hoisting the box, one or both of the skids broke at the point where they were bolted. The transformer fell to the quay and broke some of the "fins" on its metal case. Thereby the case was ruptured, permitting the PCB coolant to leak out.

Comments on Response: The transportable physical/chemical treatment unit with its staff proved to be a very sophisticated cleaning tool for this kind of projects. The unit is a mobile waste water treatment plant utilizing primary settling, mixed media pressure filters and activated carbon columns. Earlier it had been used successfully in pesticide spills. By settling the sludge in this unit, the PCB content in the return water could be sufficiently reduced to permit immediate discharge back to the waterway.

Source of Information: Proceedings of the 1976 National Conference on Control of Hazardous Material Spills, p. 351-355
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Perintis**Maritime Chemical Accident**

1989, March 13

English Channel, 35 n.m. south-east of Brixham, UK

Lindane (Class 6) in a freight container; extremely toxic solid pesticide, TLV 0.5 mg/m³ (USA), IDLH 1.000 mg/m³ (USA); **marine pollutant**

Permethrine (Class 6) and **Cypermethrine** (Class 6), both toxic solid pesticides

Summary: The Panamanian registered, Indonesian owned container ship **Perintis** capsized and sank on March 13, 1989, due to hard weather. The ship was en route from Antwerp to Indonesia and had reached the middle of the English Channel. In its cargo were 6 tonnes of the extremely toxic pesticide **lindane** and 1 tonne each of **permethrine** and **cypermethrine**, pesticides that are both toxic to the marine biota. The lindane was carried in 116 drums stowed in a freight container which was placed on deck. The other two substances were kept in a total of 32 drums in the hold of the ship. After all crew members had been rescued, the search started for the cargo manifest which revealed the presence of pesticides in the cargo. As several containers had been spotted **floating away** from the scene, a massive search started for the containers and drums with pesticides. Fishing was banned in the immediate area of the ship. The lindane container was found on March 15 and a French tug towed the container towards Cherbourg. During the following night the container was reported lost from the tug and sunk in an unknown position. The container remained unfound despite an extensive search. For a long period tests were done on water and fish in the area but they showed no evidence of pollution. It was decided that due to the **low solubility** of lindane, it was safe to leave it on the seabed. As for the other two pesticides, 28 of the 32 drums were located and taken care of after an extensive search in an area around the wreck and in an area closer to the position where the ship first capsized. The search for the last four drums was called off as the substances showed a very low solubility in sea water, which meant they would not pollute a large area in case of a leak from the drums.

Cause of Accident: The ship capsized and sank due to hard weather.

Comments on Response: The operations were successful as to finding most of the drums with permethrin and cypermethrin. As for the lindane container it might be questioned whether it was a wise decision to tow it towards the coast. Not only because the loss of the container, but also because of the greater risks for pollution closer to the coast. In general, the co-operation between UK and France was handled successfully.

Source of Information: The Perintis Incident, Report from the Department of Transport, UK, 1992.

(Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Phenol**Maritime Chemical Accident**

1973, January 13

Port of Gothenburg, Sweden

Phenol (Class 6) in a cistern; poisonous liquid or solid, melting point +55°C, TLV 5 ppm (USA), IDLH 250 ppm (USA)

Summary: On January 13, 1973, the German tank vessel **Amalie Essberger** was unloading **molten phenol** in the port of Gothenburg. The phenol was loaded into a **cistern** which suddenly **ruptured**. A total of 400 tonnes of phenol leaked down on the quay and into the water. The fire department was alerted and by the time they arrived a large gas cloud was visible above the quay. The company personnel whom were fully equipped with chemical resistant clothing had already started the recovering of the phenol on the quay. Much of the phenol, especially that in the water, had soon **solidified** in the cool weather. Phenol solidifies at +40°C and the temperature outside was around 0°C. This meant that the evaporation soon stopped and therefore no cooling of the phenol had to be done. However, a **safety zone** of 50 m was set up and the incoming vessels were redirected. Recovering of the phenol started and could be done quite easily as the phenol had solidified. Later on, measurements in the water showed indications of phenol and divers searching the area found large stacks of solidified phenol on the bottom. These could easily be recovered by a simple dredging equipment. Measurements taken after the incident showed no signs of biological damage to the marine fauna.

Cause of Accident: A cistern ruptured, probably due to overpressure.

Comments on Response: The response was done very efficiently. This was much due to valuable information from a similar accident that had happened in Denmark. No injuries were reported and no damage was done to the environment, which marks the whole operation as a success.

Source of Information: 1) Article (in Swedish) from the news magazine of the Swedish Fire Protection Association. 2) Report from the Swedish Fire Department in Gothenburg.

(Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Poona**Maritime Chemical Accident**

1971, July 15

Port of Gothenburg, Sweden

Sodium chlorate (Class 5) in drums; solid powerful oxidizer that decomposes by heat to free oxygen and may cause fire and explosion in contact with combustibles

Summary: The Danish dry cargo vessel **Poona** of 8000 dwt was loading steel structures in the port of Gothenburg. The hold contained a cargo of, among other things, 36 tons of **sodium chlorate** in 100 kg drums and 600 tons of **rape oil** in 200 l drums. All drums of both substances were stowed on pallets in the same holds. Three heavy structures were going to be hoisted by a crane into the hold, one by one. The first structure started to swing and thereby punctured a drum of rape oil so that the content of 100 l ran out. When the last structure was handled, it struck a drum of sodium chlorate with the result that a part of its content came out and mixed with the rape oil. The structure then slid on the floor creating sparks that ignited the mixture. The sodium chlorate was decomposed by the heat to free oxygen, which started a violent fire in the hold. After one or two minutes, flames flared up out of the hold and after another few minutes three severe explosions occurred in rapid succession. They were so violent that hatch covers were thrown away onto the quay and some of them several hundred metres away. The fire fighting operation became very difficult and dangerous due to the ferocity of the fire and also due to the fact that the ship also contained **carbides**. The latter chemical prevented the use of water as fire extinguishing agent. The fire fighting went on for 4 days and had to be performed both from the quay and from the sea side. The work on final extinction of the fire continued for 10 days. Three persons were killed and six injured during the accident.

Cause of Accident: See above. It is highly inappropriate and reprehensible to stow oxidizers and combustibles in the same hold.

Comments on Response: This fire fighting operation was very complicated and perhaps the most difficult one ever happened in Gothenburg.

Source of Information: Brief article (in Swedish) in the news magazine of the Swedish Fire Protection Association.
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Propionic acid**Maritime Chemical Accident**

1975, January Shores of the Swedish West Coast, about 100 km north of Gothenburg

Propionic acid (Class 8) in drums; corrosive liquid that emits irritating and harmful vapours; VP 1.3 kPa (20EC), TLV 10 ppm (USA)

Summary: On several occasions around January 8-10, 1975, approximately 30 drums of **propionic acid** were found on different positions on shores of the Swedish West Coast about 100 km north of Gothenburg. Propionic acid is an organic acid used for fabrication of many different products like preservatives, flavours and perfume bases. Before salvage, the drums were carefully examined by the Coast Guard for any ruptures and leaks. The drums were then very cautiously salvaged from the shores and lifted on board Coast Guard cutters. It was not possible to judge how long time the drums had been moved by the sea and exposed to marine water. However, the drums were very rusty and were lacking labels, placards and inscriptions. After sampling and subsequent chemical analysis in a laboratory, the content was identified as propionic acid. The drums were taken to a temporary store until further transport to a disposal plant.

Cause of Accident: Probably lost deck cargo.

Comments on Response: Besides ordinary working-clothes, the response personnel wore only gloves and rubber boots as safety protection garments when salvaging the drums. Being aware of the nature of the chemical (corrosive liquid and fumes), the personnel should have worn full body protection. After salvage from the shore, the drums should immediately have been placed in **overpacks**. The incident was only recorded very briefly in a log-book. A full detailed report should have been written, with an evaluation of the response operation and notes on the response failures.

Source of Information: Swedish Coast Guard log-book notes and short articles in a local newspaper.

(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Puerto Rican**Maritime Chemical Accident**

1984, October 31

Off the coast west of San Francisco, California, USA

Caustic soda solution 50% (Class 8) in a cargo tank; corrosive solution that reacts with many metals, e.g. zinc generating hydrogen gas, which is flammable and explosive.

Summary: The U.S.-registered chemical tankship **Puerto Rican** was preparing to disembark a pilot about 8 miles west of the Golden Gate Bridge when an explosion occurred in the vicinity of the vessel's center void space No. 6. The main deck over the void and adjacent wing tanks was lifted up, blown forward and landed inverted over center cargo tank. An intense fire erupted and burned out of control for several hours. At the time of the explosion, the pilot, a third mate and an able seaman were standing on the port side of the main deck. As a result of the explosion, the three men were thrown over the side. The pilot and the third man were seriously injured, but were recovered alive from the water. The able seaman was not found. The remaining 26 people onboard abandoned the ship safely. A few hours after the explosion, the vessel was towed farther offshore in an effort to avoid polluting the coastline if the vessel sank. Several days later the vessel broke in two while in heavy seas, and the stern section sank. The bow section remained afloat and was later towed in to a shipyard.

Cause of Accident: The proximate cause of this casualty was the failure to repair a hole through the stainless steel cladding on the bulkhead separating 5 central port (5CP) and 6 center void (6CV). About 400-500 m³ of caustic soda solution leaked through the hole from 5 CP into 6CV, creating a liquid level height of about two feet. The caustic soda reacted with the zinc-rich epoxy coating on the bulkheads, tank supports and deck of 6CV, consuming the zinc and liberating hydrogen gas. Approximately 200 m³ of alkyl benzene in 5CP also leaked into 6CV through the hole. This created a flammable mixture which was ignited shortly before the explosion which inverted the main deck section. The most probable ignition source was a spark within 6CV, either from metal-to-metal contact or an electrostatic discharge.

Comments on Response: Contributing to the cause of this casualty was the failure of the captain to use all reasonable means to account for the caustic soda discrepancy from 5CP. Three weeks before the accident **Puerto Rican** completed loading a 50 percent caustic soda solution, at a terminal in Louisiana. Two weeks later after discharging caustic soda from three tanks in San Pedro, California, a discrepancy was noted in the amount left tank number 5CP, indicating there could be leakage. The captain of the **Puerto Rican** determined that the discrepancy was due to a recording error. Nevertheless, all double bottom and void spaces around 5CP were sounded, with the exception of 6CV. This space was supposed to be sealed and inerted with nitrogen gas. The adjacent cargo tanks were also checked for leakage of caustic soda from 5CP. No evidence of leakage was found. The captain decided to inspect tank No. 5CP later after the tank had been emptied of cargo and cleaned. Although the presence of caustic soda in space No. 6CV also could have been detected by activating the eductor system, but the crew was not aware that the eductor system existed.

Source of Information: Reports by US Coast Guard Marine Board of Investigation and US National Transportation Safety Board.
(Abstracted by Björn Loostrom, Swedish Coast Guard H.Q.)

René 16**Maritime Chemical Accident**

1976, January 16

Port of Landskrona, Sweden

Ammonia (Class 2, 8) in tank container; liquefied compressed gas, corrosive, produces poisonous vapour cloud, TLV 25 ppm (USA), IDLH 300 ppm (USA)

Summary: In the evening of January 16, 1976, the Belgian tanker **René 16** was unloading ammonia in the port of Landskrona in Sweden. The ammonia was pumped through a **rubber hose** into a tank on the quay. After a few hours the hose suddenly **ruptured** with a loud bang. Ammonia started to spurting onto the quay and continued to squirt after the personnel on the quay had closed the valve on the quay side and shut off the compressor. The fire brigade was alerted and arrived within ten minutes. The ammonia had by then produced a **large cloud** that covered the vessel. The firemen sprayed the cloud with water washing it down on board the ship in order to clear the sight. They managed to close the valve on the ship's side and the ammonia stopped leaking. It had by that time leaked out about 180 tonnes of ammonia onto the quay and a cloud of ammonia had moved by the wind towards a shipyard nearby. Fortunately there was no one there and the cloud dispersed after about an hour. On the quay however two members of the crew were found dead. They had been captured by the cloud resulting in oedema of their lungs. It was later found out that the hose used was intended for propane and butane and not ammonia, which is **corrosive**. The inside of the hose had been partially destroyed by the ammonia and this was the direct cause of the rupture.

Cause of Accident: An incorrect choice of hose.

Comments on Response: This accident was all due to the misuse of equipment. It shows the danger of using the wrong equipment and stresses the awareness of a chemical's properties when handling the chemical.

Source of Information: Ammonia Loading Line Rupture, Report from Supra, 1976, Sweden.

(Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Rio Neuquen**Maritime Chemical Accident**

1984, July 27

Port of Houston, Texas, USA

Aluminium phosphide (Class 6) contained in aluminium flasks. The substance is a toxic biocide and is used as a fumigant to control insects. It is acutely toxic when ingested and reacts with water or atmospheric moisture to emit **phosphine**, TLV 0.3 ppm (USA), IDLH 200 ppm (USA). The latter is a highly toxic and reactive gas. Phosphine is also extremely flammable and is often contaminated by small amounts of **diphosphine** that is likely to autoignite in air and cause explosion, even at ambient temperature.

Summary: During unloading the Argentine container ship **Rio Neuquen**, a 20 foot shipping container with **aluminium phosphide** exploded. One longshoreman was killed by a flying container door and other men were exposed to **phosphine gas**. A response team found a bulged shipping container in the hold with much of the contents unaffected by the explosion. The aluminium phosphide was packed in cardboard boxes, each containing 14 aluminium flasks. Labels identified the product as **Gastoxin** which is a fumigant (disinfectant) with aluminium phosphide as the active ingredient. **The ship's master and crew, who persisted in refusing to leave the ship, had finally to be removed forcibly by the OSC.** The hazardous atmosphere aboard the ship was continuously monitored by means of **Draeger tubes** and a **HNU photoionization unit**. The flasks were transferred to 230-litre **overpacks**. Powdered lime was added as packing buffer and desiccant material. Lids were left loose on the drums to avoid accumulation of gas and reduce the risk of explosion. After careful reviewing of several different disposal options, **ocean dumping** was decided. 7000 flasks were handled on the deck of a supply vessel by personnel wearing full protective equipment. Each flask was manually punctured several times with the horn of a fire axe before releasing the flask overboard. This was done to make the flasks sink in a positive manner.

Cause of Accident: Leaking flasks containing aluminium phosphide (manufacturing malfunction?).

Comments on Response: The early information about the identity of the cargo was incorrect and had to be checked carefully. The handling of the monitoring instruments (gas indicators) was unprofessional and improper. The use of lime as packing agent was unwise. It gave tremendous dust problems and did not serve the intended purpose. There were two days delay until a final decision was taken to remove the obstinate master from the ship. After thorough evaluation, ocean dumping was shown to be a safe and satisfactory option that could be recommended for aluminium phosphide and related types of chemicals.

Source of Information: Proceedings of the 1986 Hazardous Material Spills Conference, p. 19-24.
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.).

Santa Clara**Maritime Chemical Accident**

1991, January 4

30 n.m. off the coast of Cape May, New Jersey, USA

Arsenic trioxide (Class 6) in drums; a biocide which is very poisonous by ingestion and possibly by skin absorption, a known carcinogen

Magnesium phosphide (Class 4) in drums. The substance is a toxic biocide and is used as a fumigant to control insects. It is acutely toxic when ingested and reacts with water or atmospheric moisture to emit **phosphine**, TLV 0.3 ppm (USA), IDLH 200 ppm (USA). The latter is a highly toxic and reactive gas. Phosphine is also extremely flammable and is often contaminated by small amounts of **diphosphane** that is likely to auto-ignite in air and cause explosion, even at ambient temperature.

Summary: In adverse weather the Panamanian container ship **Santa Clara I** lost 21 intermodal containers overboard some 30 nautical miles off the coast of Cape May, New Jersey. Four of these containers were loaded with arsenic trioxide. In addition, two damaged containers holding this highly toxic chemical remained on the vessel. A total sum of 414 drums each of 374 pounds arsenic trioxide were lost overboard in 125 feet of water. The search of the drums took place with participation of vessels and aircraft from the U.S. Coast guard, assisted by Navy helicopters. Some of the vessels were equipped with side-scan sonars and sophisticated navigational equipment. A special constructed salvage barge with two large ROV:s (Remotely Operated Vehicles) was used by the salvage team who managed to salvage 320 of the 414 drums of arsenic trioxide from the ocean floor. When **Santa Clara** arrived in the port of Baltimore on the day after the accident, a 40-foot container, with drums of arsenic trioxide, was dangling precariously off the port side of the vessel. In addition, a large number of blue 55-gallon drums with arsenic trioxide were strewn about the deck. It took little more than one day to clean up the arsenic trioxide from the deck. Information provided by the **Santa Clara** dangerous cargo manifest indicated that the arsenic trioxide was the only hazardous cargo on board and the vessel could depart Baltimore. In the next port (Charleston), a grey powder was found covering the floor of the number one hold. More than 400 kilograms of **magnesium phosphide** was spilled in the hold. The hold was closed and sealed to keep out any moisture. The ship was evacuated except for an emergency team of 10 crew members and was taken to a more isolated anchorage where she was decontaminated by personnel of the National Strike Force.

Cause of Accident: Improper securing of cargo in combination with foolish sailing in extremely rough weather conditions with winds of over 50 knots and seas up to 28 feet.

Comments on Response: There are several aspects of this incident which makes it unique. The first concerned the extremely hazardous nature of the cargo carried on board Santa Clara. A single dose of arsenic trioxide no larger than the size of an aspirin tablet is lethal to humans. The main deck and several cargo hatches of the vessel were literally awash with the substance when it arrived at the pier in Baltimore. Below deck in the 1 cargo hold, toxic magnesium phosphide had spilled, when exposed to water, produces phosphine gas, which is extremely toxic, flammable and explosive. These conditions made it very difficult to clean-up and decontaminate the vessel. For instance, the decontamination team had to wait to the right weather forecast before they could open the cargo hold. A second concern was the casual manner in which these hazardous cargoes

were treated. The vessel's owner and crew failed to record the drums of magnesium phosphide on the cargo manifest. A crewman scooped up some of the spilled powder in his hands, smelled it, and though he felt sick, never reported it to the ship's medical officer. The crew freely wandered about the deck contaminated with arsenic trioxide, despite the fact that they were warned of the danger. The final and, perhaps the most serious aspect of the Santa Clara incident, was an unwillingness by the owner of the vessel to step forward and call attention to the gravity of the problem. In Baltimore, a cargo surveyor hired by the ship's owner examined the condition of the cargo. He witnessed extensive cargo damage and spillage below decks, but no report was filed to the Coast Guard. Therefore, the vessel could leave Baltimore in an extremely hazardous condition, placing its crew and ultimately put the port of Charleston and its citizens at great risk. The Coast Guard recommended criminal action against Santa Clara's owner.

Source of Information: Proceedings of the Marine Safety Council, Jan-Feb 1993, Vol. 50, No. 1
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Sindbad**Maritime Chemical Accident**

1979, December 10

North Sea, 20 n.m. west of IJmuiden, Holland

Chlorine (Class 2) in steel cylinders; corrosive and highly toxic gas
TLV 0.5 ppm (USA), IDLH 30 ppm (USA); **marine pollutant**

Summary: In adverse weather, the Iraqi ship **Sindbad** lost her deck cargo on her way from Hamburg to Rotterdam at a depth of 25-30 metres. Among the cargo, there were 51 steel cylinders (size 0.9x2 m), each filled with 1000 kg liquefied **chlorine** (Bp. 34°C) that gives pressure of 340 kPa at a bottom water temperature of 5°C. A search started in two 1x18 km areas by two ships equipped with **side-scan sonars**. In January 1980, 5 cylinders were located. They were attached to steel lines by divers, and recovered. After these finds, the state-organised search had to be suspended, but a premium was offered to fishermen for each cylinder brought ashore. During the following four years, 7 cylinders were found and **trawled by fishermen**. The last cylinders found in this period were very corroded and thereby showed that the cylinders constituted a great hazard to fishermen and other seafarers. The Dutch authorities elaborated a special response strategy for the situation. In 1984 a new extensive search started with side-scan sonars. Registered bottom echoes were closer inspected by a **remotely operated vehicle** (ROV) Duplus II. Some of the found cylinders were moored to a safer place on the seafloor. Divers then placed 6 kg of the explosive Donarit S under each cylinder, which then was blasted under control. The chlorine content of each cylinder raised to the surface and developed, in one hour, a cloud 300 m wide, 3000 m long and 300 m high. It was made better visible by **releasing ammonia** from a ship upwind. The reaction between ammonia and chlorine formed a clearly visible white cloud of ammonium chloride. No ecological damage was detected from chlorine. Single seabirds were occasionally observed flying into the gas cloud and falling immediately like stones to the water surface. The total cost for the Dutch authorities was around \$ 1 million.

Cause of Accident: Lost deck cargo in adverse weather.

Comments on Response: It was a long delay, of almost 5 years until 1984, before the final response operation started. The reason for this is unclear and might be questioned. The strategy with controlled blasting of the cylinders was elaborated after careful studies of different alternatives. It proved to be a successful method as performed in this operation with careful supervision of the spreading of the gas clouds. It was an ingenious method to highlight the chlorine cloud with ammonia.

Source of Information: Proceedings of the 1986 Hazardous Material Spills Conference, p. 25-36, and personal communication.
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Stanislaw Dubois Maritime Chemical Accident

1981, April 2

North Sea, off the Dutch island of Texel

Calcium carbide (Class 4) in drums; solid that produces the highly flammable gas **acetylene** on contact with water or moisture

Summary: In Gdynia/Gdansk, the Polish general cargo ship **Stanislaw Dubois** loaded 857 tons of **calcium carbide** in drums and 955 tons of **caustic soda** (solid sodium hydroxide) in bags. Then proceeding to Hamburg she loaded 5.4 tons of a flammable **organic peroxide** and 5.6 tons of an **explosive**. With this dangerous goods as well as other cargo she left for South East Asia, via Antwerp. On her way in the North Sea, she collided with the Sudanese ship **Omdurman** off the Dutch island of Texel. Stanislaw Dubois was struck in her port side creating a hole of 7 x 7 m, one meter above the bilge keel. The holds no. 2 and 3 became immediately flooded. The bulwark, hatch covers, main deck and mast house were also damaged. Tugs arrived and towed the ship towards Rotterdam with the intention to be repaired. The flooded hold contained 500 tons of calcium carbide and 400 tons of **cellulose**. The latter cargo had swollen up by the water. Thereby, it had pressed on the cargo of calcium carbide, which was contained in **drums with removable heads**. This caused drum heads to open and water could penetrate to the calcium carbide. As there was a risk of explosion, the ship was not allowed to enter neither any Dutch port, nor any other port in the EEC countries. On the other hand, the vessel's draught increased by the water flooding to 45 feet, which made it impossible to enter any port in Europe. After 7 days of negotiations, Dutch authorities ordered Stanislaw Dubois to be **sunk**. Salvage vessels kept her afloat through continuous pumping and lightered all her fuel oil. Finally, the Dutch Navy frigate Callenburgh escorted Stanislaw Dubois to a position 90 n.m. NW of the island of Texel. There she was **sunk (scuttled)** at a depth of 72 m on April 9, 1981.

Cause of Accident: Flooding of holds through a hole in the port side, which was created by a collision. The water penetrated to a cargo of calcium carbide, which caused an imminent risk of explosion. The water flooding of the ship, caused her draught to increase to such an extent that it was impossible for her to enter any port for repair.

Comments on Response: The drastic response option to sink the ship, was perhaps the only alternative in view of the low possibility to enter any harbour for repair.

Source of Information: Brief report prepared in 1991 by the Polish Ocean Lines, Gdynia, Poland.
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Styrene Barge**Maritime Chemical Accident**

1992, January 26

Wax Lake Spillway, Louisiana, USA

Styrene (Class 3) in cargo tanks; flammable liquid, produces irritating vapour, may polymerize if contaminated or subjected to heat

TLV 20 ppm (USA), IDLH 700 ppm (USA); **marine pollutant**

Summary: On January 26, 1992, two barges **collided** on the Intracoastal waterway close to Wax Lake in Louisiana. One of the barges was in tow by the tug De Lasalle and the other by the tug Scaup. The barge towed by De Lasalle carried a cargo tank with 340,000 litres of styrene. The collision caused a breach in the tank and **styrene** started **leaking**. The barge was released from the tug and dropped below the water level, causing more styrene to leak out. The styrene spread very quickly and within minutes it had begun moving downcurrent. The waterway was closed a few kilometers from the spill and booms were deployed to stop the spreading of styrene. As styrene is a clear and colourless liquid it was only the strong odour that showed where it was spreading. Later however it was found out that the styrene was easily monitored with the help of **forward-looking infrared imager** (FLIR). The styrene reached the soil on the south embankment and contaminated it. Some of it also polymerized and formed clumps with silt and other solids, causing it to sink. Later on this sunken polymer was washed ashore by waves. It was first attempted to pick up the styrene with the help of a belt skimmer with an oleophilic belt. However, the belt was dissolved by the styrene and it was found out that in order to use the belt it was necessary to first put peat moss on the styrene. The main part was therefore done with **mechanical pickup** by vacuum trucks mounted on barges. The operations lasted for almost a month and were finished by the end of February.

Cause of Accident: A collision between two barges, each in tow by a tug.

Comments on Response: The response towards this incident was late and not effective enough. It took three days to establish an area monitoring plan and by this time much of the spill had already sunk into the shoreline. The use of oleophilic belts on the belt skimmer is of course something that should have been foreseen. The use of FLIR to detect the styrene proved to be an excellent tool.

Source of Information: Report from the National Oceanic and Atmospheric Administration, USA.

(Abstracted July 2002 by Edvard Molitor, Swedish Coast Guard H.Q.)

Sunken Barge

Maritime Chemical Accident

1988, November 22

Herculaneum, Upper Mississippi River, Missouri, USA

Sulphuric acid (Class 8) in cargo tanks; oily liquid which reacts violently with water creating heat and mist, corrosive when mixed with water, TLV 1 mg/m³ (USA), IDLH 15 mg/m³ (USA)

Summary: On November 22, 1988, a barge sank in the Mississippi river loaded with 1400 tonnes of **93% sulphuric acid**. The barge laid under 3 m of water and there were no signs or readings that showed any leak from the cargo. Many different authorities were notified and the situation was evaluated by a team of specialists. The greatest threat at first was a major rupture in the tank. This was not unlikely as water could have entered the tanks and this would dilute the sulphuric acid which would then make it much more corrosive. Therefore it was necessary to remove the acid from the tanks. Three alternatives were discussed. The first option would be to transfer the acid from the sunken barge. This option was abandoned because of the difficulties to transfer the acid safely without endangering the personnel. The second option was refloating the barge with the cargo aboard. This would be safer, but the weight of the barge posed a threat as the barge might break if lifted incorrectly. Therefore the third alternative was chosen: **acid discharge** into the river. The environmental impact of a discharge of the acid into the river was evaluated thoroughly. A close monitoring of the pH in the river was considered as being sufficient protection against pollution of the area. Safety regulations for all personnel were set up and emergency back-ups were prepared. The operation started one week after the accident. An air-lift tube was lowered into the barge and compressed air was delivered by an air compressor. By letting the air bubble upwards through the acid inside the tube the acid was drawn from the tank and slowly discharged into the water. The rate of the discharge was easily controlled by altering the rate of introduced air in the system. After discharging a sufficient amount of acid the **barge could be lifted** and the remaining acid recovered. The whole operation took several months but proved to be successful.

Cause of Accident: Not available.

Comments on Response: The choice to discharge the acid proved to be safe. The impact on the environment was kept to a minimum and the method can therefore be described as successful. The operation was handled in an efficient and professional way.

Source of Information: Cargo removal and salvage of the tank barge ACO-501, Report from the US Coast Guard.
(Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Testbank

Maritime Chemical Accident

1980, July 22

Mississippi River Gulf Outlet, Louisiana, USA

Pentachlorophenol (Class 6) in paper bags; very toxic solid biocide; **severe marine pollutant**

Hydrogen bromide (Class 2) in steel barrels; corrosive and very toxic gas; TLV 3 ppm (USA), IDLH 50 ppm (USA)

Summary: The outbound West German container ship **Testbank** collided with the inbound Panamanian bulk carrier **Sea Daniel**. Four containers on **Testbank** were knocked overboard into the 11 m deep river. The contents of greatest concern in the lost containers were 16 tons of **pentachlorophenol** (PCP) in 23 kg paper bags and 3 steel barrels (first reported 16) of **hydrogen bromide** (reported as hydrobromic acid). Shortly after the collision, a white haze of hydrogen bromide enveloped **Testbank**. The crew secured the ship's ventilation system and took shelter below decks. The white haze was carried by the winds into a village where the sheriff evacuated 75 residents from their homes. A **safety zone** was established, closing the channel to all non-emergency traffic. A federal OSC from the US Coast Guard was commissioned and a strike team was alerted shortly after the accident. An extensive search started for the sunk chemicals in the low-visibility, muddy river water at first by means of a recording fathometer, magnetometer and a sidescan sonar. Not until after 8 days, the search was successful by a **colour video fishfinder** ("Chromascope"). Three barrels with hydrogen bromide were first very carefully salvaged and sealed in **overpacks**. The PCP containers were found damaged and the PCP scattered on the seabed. A **grid** of 24x33 m was established by long piles driven into the bottom and rising above the water surface. During 10 days approximately 90% of the PCP was recovered by an **air lift dredge**, guided by the pile grid. The dredged mud-water mixture was cleaned in a **flocculation** treatment barge and an **active carbon** filtration system. It was finally tested in a clean water barge before being returned to the environment. Totally 1100 tons of dewatered solid waste residue was packaged in fibre drums for transportation to disposal sites.

Cause of Accident: Improper actions by the steersman on board **Sea Daniel** were primarily responsible for the collision.

Comments on Response: The Chromascope was found to be an outstanding bottom search tool. Its images provided accurate and comprehensive information about variations in bottom density. The air lift dredge appeared to be effective for recovery of spilled granular materials. The safety zone caused enormous financial losses for the maritime community but was ideal for controlling access to the area. Without this zone, positive control of the traffic through the spill area would have been impossible.

Source of Information: Proceedings of the 1982 Hazardous Material Spills Conference, p. 68-76.

(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Val Rosandra**Maritime Chemical Accident**

1990, April 28

Port of Brindisi, Italy

Propylene (Class 2) in gas tanks; liquefied compressed gas, flammable

Summary: On the night of April 28 1990 the gas carrier **Val Rosandra** was discharging a cargo of propylene in the port of Brindisi in south-eastern Italy. A **fire** started between the compressor room and the No 3 cargo tank. The crew was unable to settle the fire and alerted authorities. For safety reasons the ship was towed out 10 km off the coast. Fire crews continued to douse the vessel with water from a safety distance of 300 m. The salvage attempts continued for three weeks before it was decided to change the course of action. On May 15 Val Rosandra was towed to a position about 50 km off the coast where a **safety zone** of 12 mile radius and 6 km height was set up. The four intact cargo tanks were ruptured with **explosives** to allow the remaining 1800 tonnes of propylene to burn off. Later on also the bunker fuel was burnt off with the help of explosives. On June 11 a final round of explosives were used to sink the ship. Measurements taken after the incident have shown no evidence of pollution in the area.

Cause of Accident: A fire between the compressor room and the No 3 tank.

Comments on Response: The incident of the Val Rosandra started out as only a small fire. The fact that the ships crew and fire extinguishing systems did not settle this fire is of course discussible. However, the following operation was a success as no harm was done to the environment and no personnel were injured. The decision to let the propylene **burn out** and then sink the ship proved to be correct and the operation was handled in a professional way.

Source of Information: 1) The fire of gas carrier Val Rosandra. Report from REM-PEC by G. Tosco. 2) "Hard nuts to crack", Hazardous Cargo Bulletin, September 1990. (Abstracted July 2001 by Edvard Molitor, Swedish Coast Guard HQ)

Viggo Hinrichsen **Maritime Chemical Accident**

1973, September 29

Baltic Sea, 1 n.m. north of Oland, Sweden

Chromium trioxide (Class 5) in drums; corrosive and dangerous solid; powerful oxidizer that decomposes by heat to free oxygen and may cause fire and explosion in contact with combustibles; **Sodium dichromate** (Unclassified) in drums; both substances form corrosive **chromic acid** in water

Summary: The West German dry cargo ship **Viggo Hinrichsen** encountered machinery failure during stormy weather on her way from Rotterdam to Rönnskär in northern Sweden. The ship was towed towards land but listed during the tow and sank at the depth of 17 m, with a cargo of 234 tons of **chromium trioxide** in 1100 drums and 180 tons of **sodium dichromate** in 700 drums. All drums had removable heads. The cargo was stowed in the holds, except for 27 drums stowed on deck. Bottom water samples, taken the day after, showed that chromium compounds had started to leak out and dissolve in the water. When informed of the leakage, responsible Swedish authorities jointly decided that the ship should be salvaged. The concentration of chromic acid was less than 1 g/l in the water close to the vessel and a few mg/l 100 m downstream. Three days after the accident, the place was treated with 11 tons of **ferrosulphate** that was poured onto the wreck from sacks that were cut open at the water surface. Ferrosulphate is a **reducing agent** that converts the chromic acid to a form which is less dangerous for the environment. During the towage, before the ship sank, 10 drum fell overboard. Eight of these drums were located by **sonar equipment** carried on a naval submarine salvage ship. Some of the drums were found damaged and empty. Six days after the accident two big **pontoon cranes** heaved the ship up to the surface and towed her hanging in the cranes to a port where the cargo was taken care of. The total loss of chromium compounds to the environment was estimated to 1-2 tons. The environmental damage was slight - some dead fish and jellyfish. The total cost of the operation was USD 3 millions in today's money value.

Cause of Accident: Machinery failure during storm on undermanned ship (only 2 crew on board!). Cargo listed during tow and the ship sank.

Comments on Response: The accident showed that better information is needed about what chemicals are transported in the Baltic Sea. Better general preparedness is also needed regarding response to chemical accidents at sea, including measures like chemical analysis of chemicals spreading in the water. After the operation some scientists claimed that the ferrosulphate treatment did not do any good - but not any harm either. In 1973, the responsibility was not stated in Sweden for actions against chemical accidents at sea. By this reason, the command responsibility was unclear. However, the year after, the Swedish Coast Guard was commissioned this responsibility.

Source of Information: Brief reports (in Swedish) written by the different authorities involved in the operation.
(Abstracted by Björn Looström, Swedish Coast Guard H.Q.)

Classification of chemical spills in water and connection to related response methods

Property group definition flow chart

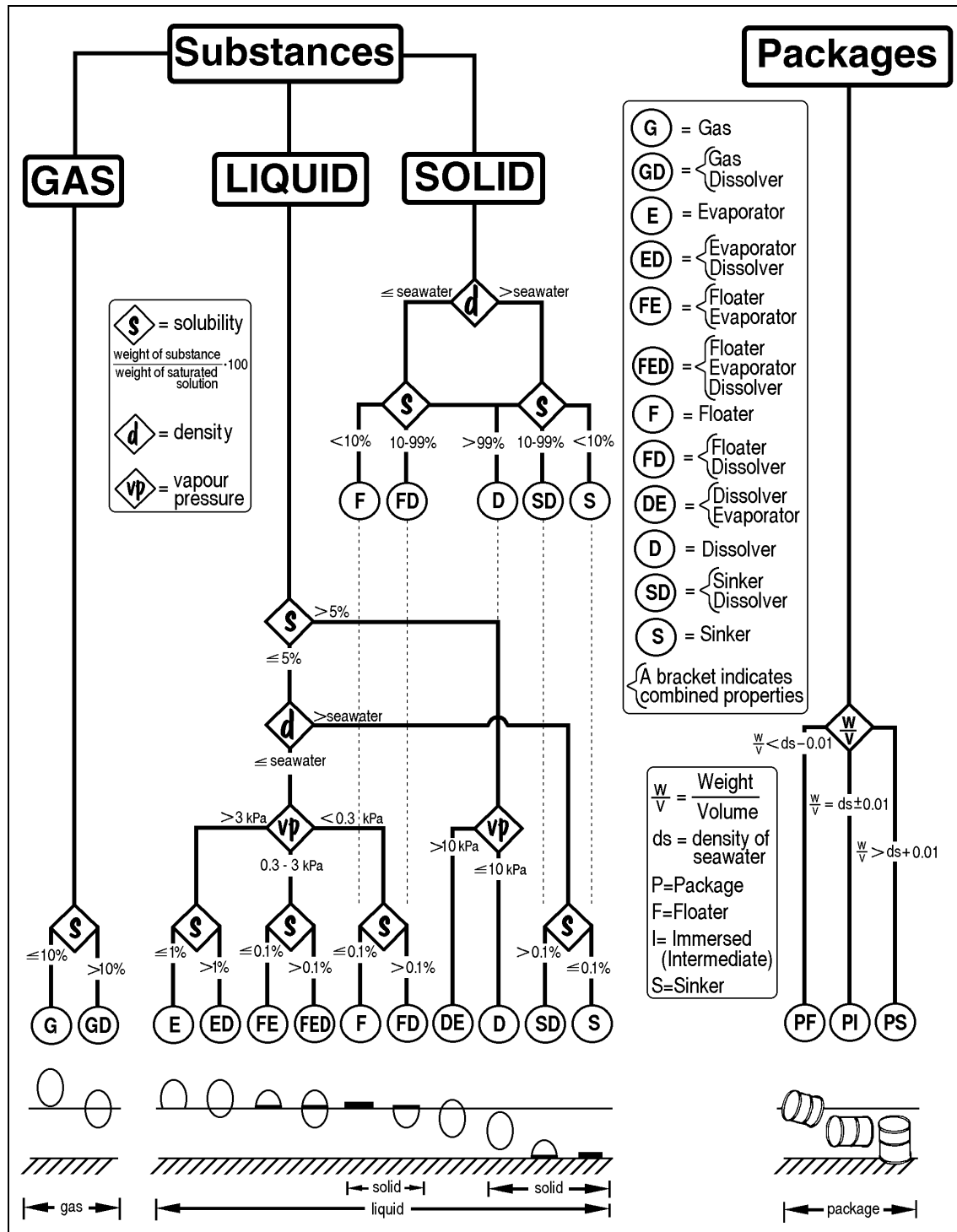


Figure a4 - 1 Flow chart of a joint European system for classification of chemical spills in water

Figure a4 - 1 shows a flow chart of a joint European system for classification of chemical spills in water ("European Classification System"). The system is based on the physical behaviours in water (solubility, density, vapour pressure) and comprises 12

Property Groups (G, GD, E, ED, etc.) for substances and 3 Groups for packages (PF, PI and PS). These groups are fully defined by Figure a4 - 1 (after a temperature is selected) and further explained by Figure a4 - 2.

Property Group Designations for spilled chemicals in water

G	gas	FE	floaters/evaporator	DE	dissolver/evaporator
GD	gas/dissolver	FED	floaters/evaporator/dissolver	D	dissolver
E	evaporator	F	floaters	SD	sinker/dissolver
ED	evaporator/dissolver	FD	floaters/dissolver	S	sinker

Figure a4 - 2

Property Group Designations for dropped packages in water

PF Package Floater	PI Package Immersed	PS Package Sinker
The package floats	The package has the same bulk density as water and is waterlogged	The package sinks
$w/v < ds - 0,01$	$w/v = ds \pm 0,01$	$w/v > ds + 0,01$
w = the package's gross weight, grams ds = water's density, grams/millilitre v = the package's gross volume, millilitres		

Figure a4 - 3

Examples of chemicals in the 12 Property Groups

	Group	Properties	Examples
Evaporate Immediately (Gases)	G	Evaporate immediately	propane, butane, vinyl chloride
	GD	evaporate immediately, dissolve	ammonia
Evaporate Rapidly	E	float, evaporate rapidly	benzene, hexane cyclohexane
	ED	evaporate rapidly, dissolve	methyl-t-butyl ether vinyl acetate
Float	FE	float, evaporate	heptane, turpentine toluene, xylene
	FED	float, evaporate, dissolve	butyl acetate isobutanol ethyl acrylate
	F	float	Phthalates, vegetable oils, animal oils dipentene, isodecanol
	FD	float, dissolve	butanol butyl acrylate
Dissolve	DE	dissolve rapidly, evaporate	Acetone, monoethylamine propylene oxide
	D	dissolve rapidly	some acids and bases, some alcohols, glycols, some amines, methyl ethyl ketone
Sink	SD	sink, dissolve	dichloromethane 1,2-dichloroethane
	S	sink	butyl benzyl phthalate, chlorobenzene creosote, coal tar, tetraethyl lead, tetramethyl lead

Figure a4 - 4

Body protection levels

When response activities are conducted where atmospheric contamination is known or suspected to exist, personal protective equipment must be worn.

Personal protective equipment is designed to prevent/reduce skin and eye contact as well as inhalation or ingestion of the chemical substance.

Protective equipment to protect the body against contact with known or anticipated chemical hazards has been divided into the four categories Level A-D.

Level A

Level A protection should be worn when the highest level of respiratory, skin, eye and mucous membrane protection is needed.

Personal Protective Equipment

- Positive pressure (pressure demand), self contained breathing apparatus, or positive-pressure supplied air respirator with escape SCBA.
- Fully encapsulating chemical protective suit.
- Gloves, inner, chemical resistant.
- Gloves, outer, chemical resistant.
- Boots, chemical resistant, steel toe and shank; (depending on suit boot construction, worn over or under suit boot.)
- Underwear, cotton, long-john type.*
- Hard hat (under suit).*
- Coveralls (under suit).*
- Two-way radio communications (intrinsically safe/non-sparking).*

* *Optional*

Level B

Level B protection should be selected when the highest level of respiratory protection is needed. Personnel under Level B are easier to secure by rescue lines. Level B protection is the minimum level recommended on initial site entries until the hazards have been further identified and defined by monitoring, sampling, and other reliable methods of analysis, and equipment corresponding with those findings utilized.

Personal Protective Equipment

- Positive-pressure (pressure-demand), self-contained breathing apparatus, or positive-pressure supplied air respirator with escape SCBA. The breathing apparatus is worn outside the suit (which is the main difference from Level A).
- Chemical resistant suit.
- Gloves, outer, chemical resistant.
- Gloves, inner, chemical resistant.
- Boots, outer, chemical resistant, steel toe and shank.
- Boot-covers, chemical resistant (disposable).*
- Two-way radio communications (intrinsically safe, non-sparking).*
- Hard hat.*
- Face shield.*

** Optional*

Level C

Level C protection should be selected when the type of airborne substance is known, concentration measured, criteria for using air-purifying respirators met, and skin and eye exposure is unlikely. Periodic monitoring of the air must be performed.

Personal Protective Equipment

- Full-face mask, air-purifying respirator.
- Chemical resistant clothing (one piece coverall, hooded two piece chemical splash suit, chemical resistant hood and apron, disposable chemical resistant coveralls.)
- Gloves, outer, chemical resistant.
- Gloves, inner, chemical resistant.
- Boots, steel toe and shank, chemical resistant.

- Boot-covers, chemical resistant.*
- Cloth coveralls (inside chemical protective clothing).*
- Two-way radio communications (intrinsically safe, non-sparking).*
- Hard hat. *
- Escape mask. *
- Face shield.*

** Optional*

Level D

Level D is primarily a work uniform and is used for nuisance contamination only. It requires only coveralls and safety shoes/boots. Other PPE is based upon the situation (types of gloves, etc.). It should not be worn on any site where respiratory or skin hazards exist.

The type of environment and the overall level of protection should be reevaluated periodically as the amount of information about the site increases and as workers are required to perform different tasks.

Level upgrading or downgrading

Reasons to upgrade to a higher level (D is lowest, A is highest):

- Known or suspected presence of dermal hazards
- Occurrence or likely occurrence of gas or vapour emission
- Change in work task that will increase contact or potential contact with hazardous materials
- Request of the individual performing the task

Reasons to downgrade:

- New information indicating that the situation is less hazardous than was originally thought
- Change in site conditions that decreases the hazard
- Change in work task that will reduce contact with hazardous materials

Examples of European protective suits

Level A



Picture source: MSA

Figure A5 - 1



*Picture source: Swedish
Rescue Services Agency
(Lars Gyllendorff)*

Figure A5 - 2



Picture source: Draeger

Figure A5 - 3

Level B



Picture source: Draeger

Figure A5 - 4



Picture source: Vautex

Figure A5 - 5



*Picture source: Swedish
Rescue Services Agency
(Lars Gyllendorff)*

Figure A5 - 6

Level C



Picture source: Draeger

Figure A5 - 7

International labelling of dangerous goods

IMDG Code labels, marks and signs




























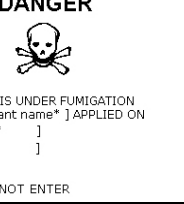
Class					
1					
2					
3					
4					
5 - 6					 Elevated temperature mark
7					
8 - 9			Fumigation warning sign *Insert details as appropriate		 DANGER THIS UNIT IS UNDER FUMIGATION WITH [fumigant name*] APPLIED ON [date*] [time*] DO NOT ENTER

Figure A6 - 1

The NFPA diamond

The US National Fire Protection Association (NFPA) has a marking system (“the NFPA fire diamond”) designed for the benefit of first responders in chemical accidents. Though often used worldwide in transportation of chemicals and dangerous goods it is not required in transportation. It is intended for use on fixed installations storage containers, storage rooms and warehouses, entrances to laboratories, and chemical processing equipment.

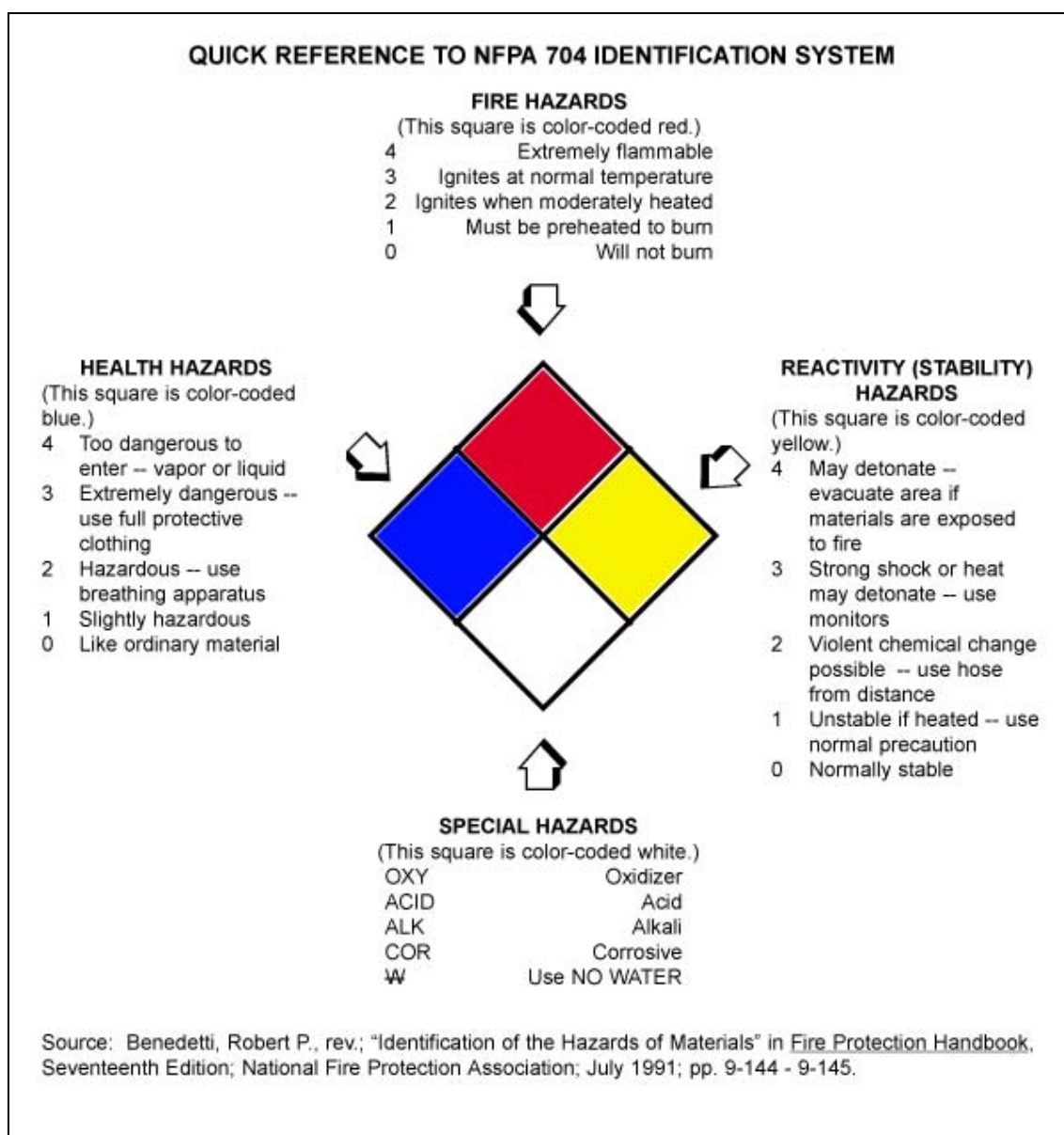


Figure A6 - 2

USFA Hazardous Materials Guide for First Responders National Fire Protection Association (NFPA) Fire Diamonds (NFPA No. 704-1991)					
Identification of Health Hazard Color Code: BLUE		Identification of Flammability Color Code: RED		Identification of Reactivity Color Code: YELLOW	
Type of Possible Injury		Susceptibility of Materials to Burning		Susceptibility to Release of Energy	
Signal		Signal		Signal	
4	Materials that on very short exposure could cause death or major residual injury.	4	Materials that will rapidly or completely vaporize at atmospheric pressure and normal ambient temperature, or that are readily dispersed in air and that will burn readily.	4	Materials that in themselves are readily capable of detonation or of explosive decomposition or reaction at normal temperatures and pressures.
3	Materials that on short exposure could cause serious temporary or residual injury.	3	Liquids and solids that can be ignited under almost all ambient temperature conditions.	3	Materials that in themselves are capable of detonation or explosive decomposition but require a strong initiating source or which must be heated under confinement before initiation or which react explosively with water.
2	Materials that on intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury.	2	Materials that must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.	2	Materials that readily undergo violent chemical change at elevated temperatures and pressures or which react violently with water or which may form explosive mixtures with water.
1	Materials that on exposure would cause irritation but only minor residual injury.	1	Materials that must be preheated before ignition can occur.	1	Materials that in themselves are normally stable, but which become unstable at elevated temperatures and pressures.
0	Materials that on exposure under fire conditions would offer no hazard beyond that of ordinary combustible material.	0	Materials that will not burn.	0	Materials that in themselves are normally stable, even under fire exposure conditions, and which are not reactive with water.

Figure A6 - 3

USFA Hazardous Materials Guide for First Responders						
First Responder Strategy Using the NFPA 704 Diamond						
		NFPA Reactivity Rating 0 - 1 (Rating 2 - 4 Defensive Only)				
NFPA Health Rating	4	Defensive operation only.	Defensive operation only.	Defensive operation only.	Defensive operation only.	
	3	Defensive operation only when materials identified and deemed safe.	Defensive operation only when materials identified and deemed safe.	Defensive operation only when materials identified and deemed safe.	Defensive operation only when materials identified and deemed safe.	
	2	Attack from safe distance in full SCBA. Decontaminate personnel/equipment thoroughly when complete.	Attack from safe distance in full SCBA. Decontaminate personnel/equipment thoroughly when complete.	Attack from safe distance in full SCBA. Decontaminate personnel/equipment thoroughly when complete.	Attack from safe distance in full SCBA. Decontaminate personnel/equipment thoroughly when complete. Consider extra attack lines.	
	1	Attack with full protective clothing and SCBA. Decontaminate when finished.	Attack with full protective clothing and SCBA. Decontaminate when finished.	Attack with full protective clothing and SCBA. Decontaminate when finished.	Attack with full protective clothing and SCBA. Decontaminate when finished. Consider extra attack lines.	
	0	Attack with full protective clothing and SCBA.	Attack with full protective clothing and SCBA.	Attack with full protective clothing and SCBA.	Attack with full protective clothing and SCBA. Decontaminate when finished. Consider extra attack lines and master stream appliances.	
		0	1	2	3	4
		NFPA Flammability Rating				
Last Updated: November 3, 1998						

Figure A6 - 4

The ADR Hazard Identification Number HIN ("The Kemler Code")

The ADR Hazard Identification Number HIN, also known as the Kemler Code, is carried on placards on tank cars and tank containers running by road under international ADR regulations. Identification numbers are shown in such a way, that the upper number is indicating the danger and the lower number identifies the substances with the UN-number given in the UN Recommendations on the Transport of Dangerous Goods.

An orange blank placard without any numbers indicates vehicle carrying dangerous load (drums, packages, etc.) or multi-load tanker.

The ADR Hazard Identification Number HIN
(The Kemler Code)

The substance's UN Number

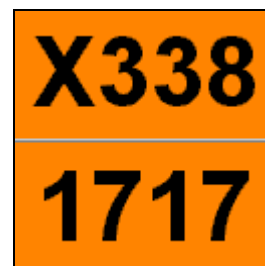


Figure A6 - 5

The first figure of the Kemler Code indicates the primary hazard:

2	gas
3	flammable liquid
4	flammable solid
5	oxidizing substance or organic peroxide
6	toxic substance
7	radioactive substance
8	corrosive substance
9	miscellaneous/environmental hazard
X	reacts dangerously with water

The second and third figure generally indicate secondary hazards:

0	the hazard is adequately described by the first figure
2	(flammable) gas may be given off
3	fire risk
4	fire risk
5	oxidizing risk
6	toxic risk
8	corrosive risk
9	risk of spontaneous, violent reaction

Doubling of a figure indicates an intensification of that particular hazard. Where the hazard associated with a substance can be adequately indicated by a single figure, this is followed by a zero.

If a hazard identification number is prefixed by letter 'X', this indicates that the substance will react dangerously with water.

The hazard identification number combinations have following meanings:

20	inert gas
22	refrigerated gas
223	refrigerated flammable gas
225	refrigerated oxidizing (fire-intensifying) gas
23	flammable gas
236	flammable gas, toxic

239	flammable gas, which can spontaneously lead to violent reaction
25	oxidizing (fire-intensifying) gas
26	toxic gas
265	toxic gas, oxidizing (fire-intensifying)
266	highly toxic gas
268	toxic gas, corrosive
286	corrosive gas, toxic
30	flammable liquid or self-heating liquid
323	flammable liquid which reacts with water emitting flammable gases
X323	flammable liquid which reacts dangerously with water emitting flammable gases
33	highly flammable liquid (flash point below 21°C)
333	pyrophoric liquid
X333	pyrophoric liquid which reacts dangerously with water
336	highly flammable liquid, toxic
338	highly flammable liquid, corrosive
X338	highly flammable liquid, corrosive, which reacts dangerously with water
339	highly flammable liquid, which can spontaneously lead to violent reaction
36	self-heating liquid, toxic
362	flammable liquid, toxic
X362	flammable liquid, toxic, which reacts dangerously with water emitting flammable gases
38	self-heating liquid, corrosive
382	flammable liquid, corrosive, which reacts with water emitting flammable gases
X382	flammable liquid, corrosive, which reacts dangerously with water emitting flammable gases
39	flammable liquid, which can spontaneously lead to violent reaction
40	flammable self-heating solid
423	solid, which reacts with water emitting flammable gases
X423	flammable solid, which reacts dangerously with water emitting flammable gases
44	flammable solid, in molten state, at elevated temperature
446	flammable solid, toxic, in molten state, at elevated temperature
46	flammable or self-heating solid, toxic
462	toxic solid, which reacts with water emitting flammable gases
48	flammable or self-heating solid, corrosive
482	corrosive solid, which reacts with water emitting flammable gases
50	oxidizing (fire-intensifying) substance
539	flammable organic peroxide
55	strongly oxidizing substance
556	strongly oxidizing substance, toxic
558	strongly oxidizing substance, corrosive
559	strongly oxidizing substance, which can spontaneously lead to violent reaction
56	oxidizing substance, toxic
568	oxidizing substance, toxic, corrosive
58	oxidizing substance, corrosive
59	oxidizing substance which can spontaneously lead to violent reaction
60	toxic or harmful substance
63	toxic or harmful substance, flammable (flash point between 21°C and 55°C)
638	toxic or harmful substance, flammable (flash point between 21°C and 55°C),

	corrosive
639	toxic or harmful substance, flammable (flash point between 21°C and 55°C), which can spontaneously lead to violent reaction
66	highly toxic substance
663	highly toxic substance (flash point not above 55°C)
68	toxic or harmful substance, corrosive
69	toxic or harmful substance, which can spontaneously lead to violent reaction
70	radioactive material
72	radioactive gas
723	radioactive gas, flammable
73	radioactive liquid, flammable (flash point not above 55°C)
74	radioactive solid, flammable
75	radioactive material, oxidizing
76	radioactive material, toxic
78	radioactive material, corrosive
80	corrosive or slightly corrosive substance
X80	corrosive or slightly corrosive substance, which reacts dangerously with water
83	corrosive or slightly corrosive substance, flammable (flash point between 21°C and 55°C)
X83	corrosive or slightly corrosive substance, flammable (flash point between 21°C and 55°C), , which reacts dangerously with water
839	corrosive or slightly corrosive substance, flammable (flash point between 21°C and 55°C), which can spontaneously lead to violent reaction
X839	corrosive or slightly corrosive substance, flammable (flash point between 21°C and 55°C), which can spontaneously lead to violent reaction and which reacts dangerously with water
85	corrosive or slightly corrosive substance, oxidizing (fire-intensifying)
856	corrosive or slightly corrosive substance, oxidizing (fire-intensifying) and toxic
86	corrosive or slightly corrosive substance, toxic
88	highly corrosive substance
X88	highly corrosive substance, which reacts dangerously with water
883	highly corrosive substance, flammable (flash point between 21°C and 55°C)
885	highly corrosive substance, oxidizing (fire-intensifying)
886	highly corrosive substance, toxic
X886	highly corrosive substance, toxic, which reacts dangerously with water
89	corrosive or slightly corrosive substance, which can spontaneously lead to violent reaction
90	miscellaneous dangerous substance

Conversion table for measurement units

Length			
<input type="text"/>	inches	* 2.54 =	<input type="text"/> centimetres
<input type="text"/>	feet	* 30.48 =	<input type="text"/> centimetres
<input type="text"/>	feet	* 0.3048 =	<input type="text"/> metres
<input type="text"/>	yards	* 0.9144 =	<input type="text"/> metres
<input type="text"/>	miles	* 1.609 =	<input type="text"/> kilometres
<input type="text"/>	nautical miles	* 1.852 =	<input type="text"/> kilometres
<input type="text"/>	centimetres	* 0.3937 =	<input type="text"/> inches
<input type="text"/>	centimetres	* 0.03281 =	<input type="text"/> feet
<input type="text"/>	metres	* 1.0936 =	<input type="text"/> yards
<input type="text"/>	kilometres	* 0.6214 =	<input type="text"/> miles
<input type="text"/>	kilometres	* 0.5400 =	<input type="text"/> nautical miles

Area			
<input type="text"/>	square inches	* 6.4516 =	<input type="text"/> sq cm
<input type="text"/>	square feet	* 0.0929 =	<input type="text"/> sq metres
<input type="text"/>	square yards	* 0.836 =	<input type="text"/> sq metres
<input type="text"/>	square miles	* 2.590 =	<input type="text"/> sq kilometres
<input type="text"/>	square cm	* 0.155 =	<input type="text"/> sq inches
<input type="text"/>	square metres	* 10.7639 =	<input type="text"/> square feet
<input type="text"/>	square metres	* 1.196 =	<input type="text"/> sq yards
<input type="text"/>	square km	* 0.386 =	<input type="text"/> sq miles

Volume			
<input type="text"/>	US gallons	* 3.7854 =	<input type="text"/> litres
<input type="text"/>	UK gallons	* 4.5461 =	<input type="text"/> litres
<input type="text"/>	oil barrels	* 42 =	<input type="text"/> US gallons
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<input type="text"/>	litres	* 0.2100 =	<input type="text"/> UK gallons
<input type="text"/>	US gallons	* 0.02381 =	<input type="text"/> oil barrels
<input type="text"/>	litres	* 0.0063 =	<input type="text"/> oil barrels
Mass and Weight			
<input type="text"/>	ounces	* 28.3495 =	<input type="text"/> grams
<input type="text"/>	pounds	* 0.4536 =	<input type="text"/> kilograms
<input type="text"/>	short tons	* 0.9072 =	<input type="text"/> metric tons
<input type="text"/>	long tons	* 1.016 =	<input type="text"/> metric tons
<input type="text"/>	grams	* 0.035274 =	<input type="text"/> ounces
<input type="text"/>	kilograms	* 2.2046 =	<input type="text"/> pounds
<input type="text"/>	metric tons	* 1.1023 =	<input type="text"/> short tons
<input type="text"/>	metric tons	* 0.9842 =	<input type="text"/> long tons
Temperature			
<input type="text"/>	Fahrenheit (F)	$(F - 32) * 5/9 =$	<input type="text"/> Celsius
<input type="text"/>	Celsius	$* 9/5 + 32 =$	<input type="text"/> Fahrenheit

Pressure				
	atmosphere, stand. (atm)	* 101.325 =		kilopascal (kPa)
	atmosphere, techn. (at)	* 98.0665 =		kilopascal (kPa)
	bar	* 100 =		kilopascal (kPa)
	millimeter of mercury (0 °C)	* 133.322 =		kilopascal (kPa)
	dyne/square centimeter	* 0.0001 =		kilopascal (kPa)
	foot of mercury, convent. (ftHg)	* 40.63666 =		kilopascal (kPa)
	inch of mercury (32 °F)	* 3.38638 =		kilopascal (kPa)
	inch of mercury, convent. (inHg)	* 3.386389 =		kilopascal (kPa)
	kg-force/square cm (kgf/cm2)	* 98.0665 =		kilopascal (kPa)
	kip/square inch (ksi) (kip/in2)	* 6894.757 =		kilopascal (kPa)
	psi (pound-force/sq inch) (lbf/in2)	* 6.894757 =		kilopascal (kPa)
	torr	* 0.1333224 =		kilopascal (kPa)

	kilopascal (kPa)	* 0.00987 =		atmosphere, stand. (atm)
	kilopascal (kPa)	* 0.010197 =		atmosphere, techn. (at)
	kilopascal (kPa)	* 0.01 =		bar
	kilopascal (kPa)	* 7.5006 =		millimeter of mercury (0 °C)
	kilopascal (kPa)	* 10000 =		dyne/square centimeter
	kilopascal (kPa)	* 0.024608 =		foot of mercury, convert. (ftHg)
	kilopascal (kPa)	* 0.2953006 =		inch of mercury (32 °F)
	kilopascal (kPa)	* 0.2952998 =		inch of mercury, convert. (inHg)
	kilopascal (kPa)	* 0.010197 =		kg-force/square cm (kgf/cm ²)
	kilopascal (kPa)	* 0.000145 =		kip/square inch (ksi) (kip/in ²)
	kilopascal (kPa)	* 0.1450377 =		psi (pound-force/sq inch) (lbf/in ²)
	kilopascal (kPa)	* 7.500615 =		torr

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