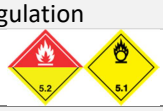
Response Considerations: Reactive Substances

Related hazards pictograms (direct and indirect hazard)

flammable / explosive:		**oxidising / peroxidising:**	
GHS	GHS	GHS	UN Regulation
			
physical hazards not otherwise classified (refer to Safety Data Sheet)			
GHS			
			

Example of relevant case studies:

Reactivity	Main Risks & Hazards - Related case studies	Example of substances
With oxygen (air)	Ignition, explosion. ***Ocean Liberty, 1947***, port of Brest, France; ammonium nitrate (3,160 tonnes) + oil (300 tonnes). Cause of spill: fire and subsequent explosion.	Some alkali metals (e.g. potassium, sodium, calcium), some metal hydrides (e.g. hydrides of sodium, h. of calcium), with phosphorus, some oxidants (e.g. acetaldehyde; diethyl etherIsopropyl ether), pyrophorics liquids (tributylphosphine, trimethyl aluminum)
With water (hydrolysis, hydration, oxidation; consider also possible reaction with moisture of the air)	Explosion or formation of hazardous products (corrosive, toxic or flammable). ***The Adamandas, 2003***, Réunion Island deoxidises iron of ore balls (21,000 tonnes) and diesel (470 tonnes). Risk of prudacion of Hydrogen gas. Cause of spill: structural damage	Some alkaline metals, sodium or potassium phosphide, alkali metal cyanide salts, aluminum chloride, calcium carbide, cyanide salts
Polymerization	Highly exothermic reaction (with violent explosion in some cases) of self-reaction of a monomer; ***Stolt Groenland, 2019***, Ulsan, South Korea; Styrene monomer (5,200 tonnes). Cause of spill: explosion, fire due to over-pressurisation and ignition of styrene.	Acrylonitrile; cyclopentadiene, hydrocyanic acid; methacrylic acid; methyl acrylate; vinyl acetate
With other substances	Fire, explosion or release of toxic vapours depend on amounts, and surrounding conditions); ***Burgenstein, 1977***, port of Bremerhaven; Sodium peroxide and other hazardous product including cyanide. Cause of spill: structural damage to a drum of Sodium peroxide.	Some incompatible gorups: flammables and toxics flammables and oxidizers acids and bases oxidizers and reducers See Chemical Reactivity Worksheets, e.g. *The Chemical Reactivity Worksheet (CRW) - NOAA*)
Self-reactive substances	***Self-reactive substance*** *means a thermally unstable liquid or solid substance liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). This definition excludes substances or mixtures classified under the GHS as explosive, organic peroxides or as oxidising (GHS, 2019).*	

	Explosive reactions	
Light induced **Mechanical shock** **Inherent unstable**	***M/V Sinbad, 1979***, 20 nautical miles west of Ijmuiden, Netherlands, offshore of Amsterdam; Chlorine (51 steel cylinders/51 tonnes). Lost of deck cargo at depht of 30 m. Cause of spill: structural damage (adverse weather) Can detonate under certain conditions of pressure and temperature.	Hydrogen and chlorine Acetylides, oxides, organic nitrates and many peroxide Acetylene

Alert and notification in case of a potential leak:

Depending on the location of the accident, MRCC, site emergency services and public emergency services must be alerted. Ships (crew) and population downwind (vapour cloud) and downstream (spill) have also to be warned in order to prevent complications arising.

Applicability and main risks:

Reactive substances include a wide range of potential consequences and highly rely upon their chemical nature. See above table. For more information and description of reactivity substances, See Chapt. 3 on hazardous substances.

Also note:
- In case of self-reactive substances fire /spillage, non-water-reactive but flammable substances, polymerising substances.

→ **Response consideration flammable-explosive substances**

- In case of fire/spillage chemicals which form toxic or corrosive products by reaction with other materials or other spillage.

→ **Response consideration: toxic substances**

→ **Response consideration: corrosive substances**

Applicability[1]	Risks for human/responders	Risks for environment	Risks for amenities
Leakage of reactive substances that cause ignition / explosion	- Direct injuries due to fire or explosion or highly exothermic reaction (violent explosion) - Oxidising substances could ignite combustible material or destroy material (e.g. responder equipment) - Anoxia, asphyxia, especially in confined space	- No major expected chronic impact - Possible indirect impact (e.g. fire residues)	- Direct and indirect damages (or destructions) to vessels, buildings, other maritime infrastructures (in some scenarios, even at a considerable distance from the accident).

[1] *Leakage that may lead to hazardous / violent reactions. Consult*

Leakage of reactive substances that form corrosive products	- Injuries due to direct contact with substance (dermal necrosis, inhalation, ingestion)	- Direct impact on animals and environment - Chronic impact - Possible indirect impact (e.g. extinguishing water, dissolver in water curtain)	- Chemical corroding drums or tanks, leading to a pollution - Corrosion of metals (ship's deck, crane, etc.) (limitation/interference to the legitimate use of the sea/amenities)
Leakage of reactive substances that form toxic products	- Injuries due to direct contact with substance (skin/mucosa contact, ingestion, inhalation) - Carcinogenetic issues	- Direct impact on animals and environment - Acute and chronic impact - Possible indirect impact (e.g. extinguishing water, dissolver in water curtain)	Contamination of marine environment by toxic-persistent product may lead to a closure/limitation/interference to the legitimate use of the sea

Risk Assessment

General considerations. As reactive substances may lead to many different consequences, responders have to focus on:

- assessing the risks on the basis of physic state and possible consequences of reactions:
  - risks of flammability or explosion by monitoring LEL/LFL and UEL/UFL values and evolution through time / assess the risks of polymerisation by monitoring temperature increase, inhibitor expiry date exceeded, friction or shock
    → **Response consideration flammable-explosive substances**
    → **Sheet Monitoring**
  - risks of toxicity and to humans and the environment, collecting data on the substances and considering the accidental scenario
    → **Response consideration: toxic substances**
  - risks of corrosivity
    → **Sheet Response consideration: corrosive**
- assessing associated hazards if present and evaluate the priority of response;
- analysing weather data and detector measurements;
- if possible modelling the behaviour and movement of the hazard gas/vapours/fume clouds if produced. Consider to model hazardous floater/dissolved/sinker products (consider reactions rate) and by-product if spilled in waters column;
  → **HNS Spill Modelling**
- in case of toxic, corrosive persistent reaction products: evaluate measure to protect sensitive areas (environmental, ecological, social, industrial sites) and facilities, including through preventive shutdown, determine the hazards posed by any products that may be formed in the scenarios and assess the associated hazard levels (smoke from fire, reaction with the environment, etc.);
  → **Information gathering**
- evaluate location of facilities and equipment to quick response.

Areas to consider for intervention :

→ **Response consideration flammable-explosive substances**
→ **Monitoring**
→ **Response consideration: toxic substances**

→ **Response consideration: corrosive substances**

Consider (and control) aggravating factors:

- hazardous reactions occur often releasing heat (exothermic reactions) or producing flammable gases, explosive materials, corrosives or toxics, with serious consequences for and the human health and the environment, determining risk of explosions and fire, which make intervention very difficult;
- in case of response to fire and/or spillage must consider the actions to avoid or limit the formation of dangerous products (e.g. unsafe combination of substances, mechanical shock, exposure to light, heating, contact with water / air, where applicable);
- some substances (eg. white phosphorus and other oxygen/air-reactive substances) are not dangerous as long as they are immersed in water and therefore the necessary precautions must be taken during the recovery phase on surface.
- consider thet reactive substances can be also classified for other hazard (e.g. potassium phosfide that is also toxic)

Protective measures (human health, environment & amenities)

Protective measure has to be tailored regarding the hazards put by occurred reactions for the decision making on response techniques application, PPE and portable detection selection.

→ **PPE**

→ **Portable gas detectors for first responders**

On board

- attention should be paid to avoid direct contact with the skin and protect against inhalation of vapours or mists and check atmosphere before entering in confined space; do not operate without self-contained breathing apparatus;
- evacuation must be done immediately downwind the area (gas/evaporator/fume);
- sources of ignition must be eliminated, non-sparking footwear worn and fire suppression or ventilation systems activated in order to lower LEL/LFL (for no oxygen-reactive substances);
- cloud or vapours should be prevented from entering closed area, obstacles and turbulences (gas/vapours) should be limited;
- the high risk zone must be defined: shape/mark off the exclusion zone and control access

→ **Safety Zones**

Population and amenities

- evacuation must be done immediately downwind the area (in case of hazardous vapours, gas clouds, fumes);
- possible impacted areas (targets of polluted runoff, liquids and solids spill) must be considered downstream the spill for zoning;
- some limitations may be defined on the use of the sea and amenities

Response measures

On board

- priority of intervention must be evaluated: generally, first response goes to flammable/explosive reactions;
- when possible valves must be shut off to stop leaking;

→ **Sealing and plugging**

→ **Using Water Curtain**

- in the event of fire and risks of explosion, appropriate extinguish methods and techniques on the base of substances involved and scenarios should be used (SOLAS chapter regulation II-2 10 and Ems guide, IMO 2018);
- in case of on board leak appropriate containment and recovery methods and techniques on the base of substances involved and scenarios should be used (Ems , IMO, 2018).

<u>In the environment</u>

- refers to behaviour, fate and characteristics of hazardous reaction by-products

→ **Response consideration flammable-explosive substances**
→ **Response consideration toxic substances**
→ **Response consideration corrosive substances**
→ **Safety Zones**

Behaviour:

→ **Response considerations : Gases and Evaporators**
→ **Response considerations : Floaters**
→ **Response considerations : Sinkers**
→ **Response considerations : Dissolvers**
→ **Packaged Goods Response**

Techniques:

See Chapt. 563

(HYNDAI FORTUNE)