



Flammable Substances

Aims & Objectives

- To review the behaviour, properties and incident management of flammable substances

Objectives

- Identify flammability properties of flammable solids, liquids and gases
- Observe the characteristic behaviours of flammable substances
- Describe operational considerations surrounding flammable substances

Flammable Solids

Types of flammable solids – UN Class 4



4.1

- Flammable Solids
- Self-reactive products (incl. polymerisation materials)
- Desensitised explosives



4.2

- Spontaneously combustible solids and liquids
- Pyrophoric
- Self-heating



4.3

- Dangerous when wet (generates flammable / corrosive vapours)

Examples

Flammable Solids

- Powdered Metals
- Molten metals
- Desensitised explosives (e.g. TNT)
- Ingredients in plastic manufacturing

Spontaneously Combustible Solids

- Some powdered metals
- White Phosphorus
- Drying Oils
- Hay Bales?

Dangerous when wet

- Reactive metals (lithium, sodium, magnesium etc.)
- Metal hydrides, carbides, azides.
- Acids and bases?

**NOT MANY RELEVANT PHYSICAL PROPERTIES
CHEMICAL PROPERTIES – ALMOST WITHOUT EXCEPTION, ANY FLAMMABLE SOLID WILL GIVE OFF A CORROSIVE, TOXIC OR FLAMMABLE GAS WHEN ON FIRE OR IN CONTACT WITH WATER.**

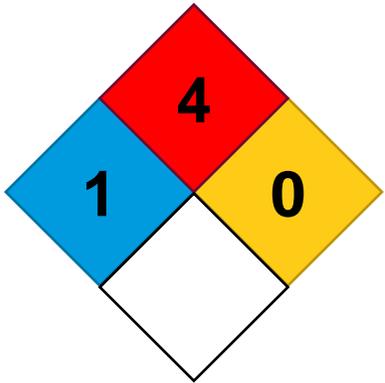
Transportation – Hazchem/ADR/NFPA

Nitrocellulose - Wetted

Magnesium Ethoxide

1Z	
2555	
Specialist Advice	NCEC

1Y	
3205	
Specialist Advice	NCEC



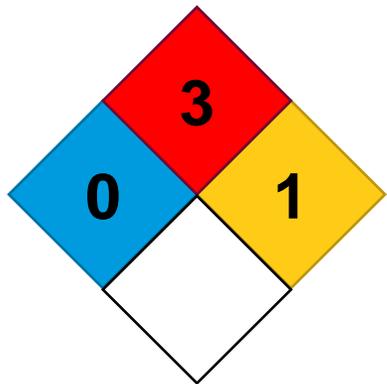
-
2555

40
3205

Transportation – Hazchem/ADR/NFPA

Aluminium - Coated

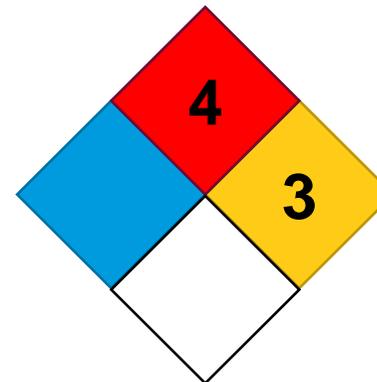
4Y	
1309	
Specialist Advice	NCEC



40
1309

Butyl Lithium - Solid

4W	
3393	
Specialist Advice	NCEC

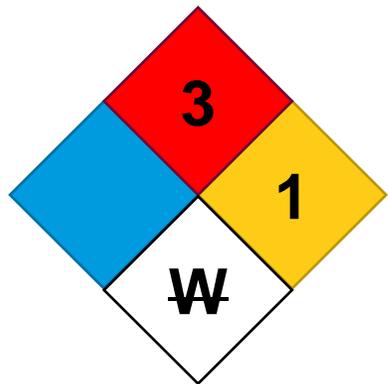


X432
3393

Transportation – Hazchem/ADR/NFPA

Calcium Carbide

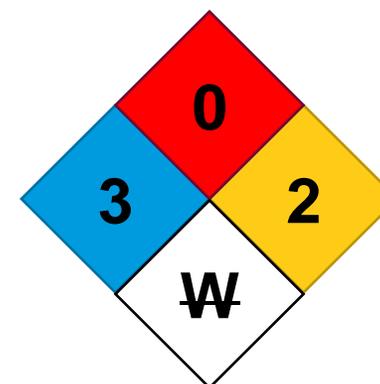
4W	
1402	
Specialist Advice	NCEC



X423
1402

Titanium Tetrachloride

4WE	
1838	
Specialist Advice	NCEC



X668
1838

General Behaviour



Metal Fires
Burn without oxygen
Dust fires/explosions
Thermal Runaways
Explosive – BLEVEs
Accelerated Reactions
Polymerisation Reactions



Highly Exothermic
No external Ignition Source
Thermal Runaways
Explosive – BLEVEs
Water Reactive
Sensitive to temperature
Over-pressurisation of container



Highly Exothermic
Explosive behaviour
Generation of flammable/corrosive/toxic gas
Generation of corrosive liquid
Difficult to extinguish
Very sensitive to other products
Hazardous post-fire

Videos

Flammable Liquids

Identification

- No sub-divisions
- Both UN number & ADR Hazard Identification Number contain a 3



33

1203

Physical & Chemical Properties

PHYSICAL PROPERTIES:

- SOLUBILITY
- VAPOUR PRESSURE
- RELATIVE DENSITY
- RELATIVE VAPOUR DENSITY
- LogP_{ow}
- MELTING POINT
- BOILING POINT

CHEMICAL PROPERTIES:

- FLASH POINT
- FLAMMABLE LIMITS
- AUTOIGNITION
- IONISATION ENERGY?
- CORROSIVE?

Behaviour

Volatile

- High rates of evaporation (high vapour pressures)
- Affected by increases in temperature

Float on water

- Relative Density is often less than 1
- Uncommon to see Relative Densities above 1 (i.e. heavier than water)

Heavy vapours

- High Vapour density

Low viscosity

- Thin and fluid

Behaviour

Exposure

- Inhalation
- Dermal

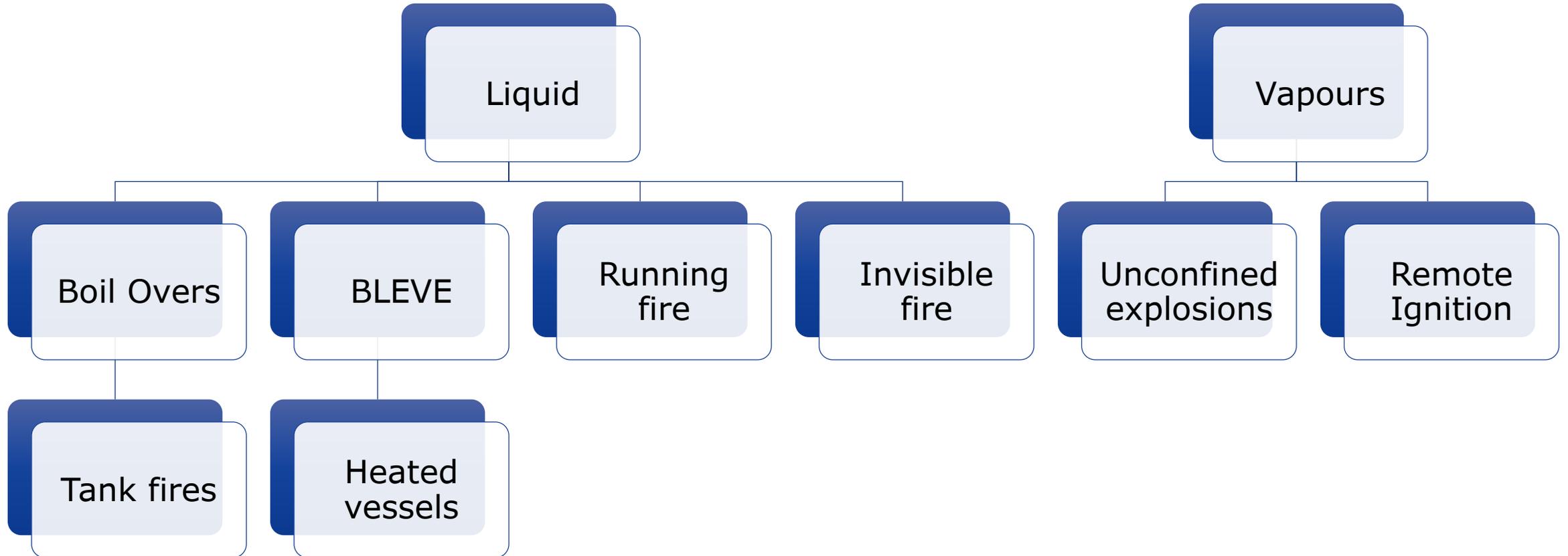
Environmental Hazard

- Dangerous to animals, bacteria and aquatic life

Fire (being a liquid)

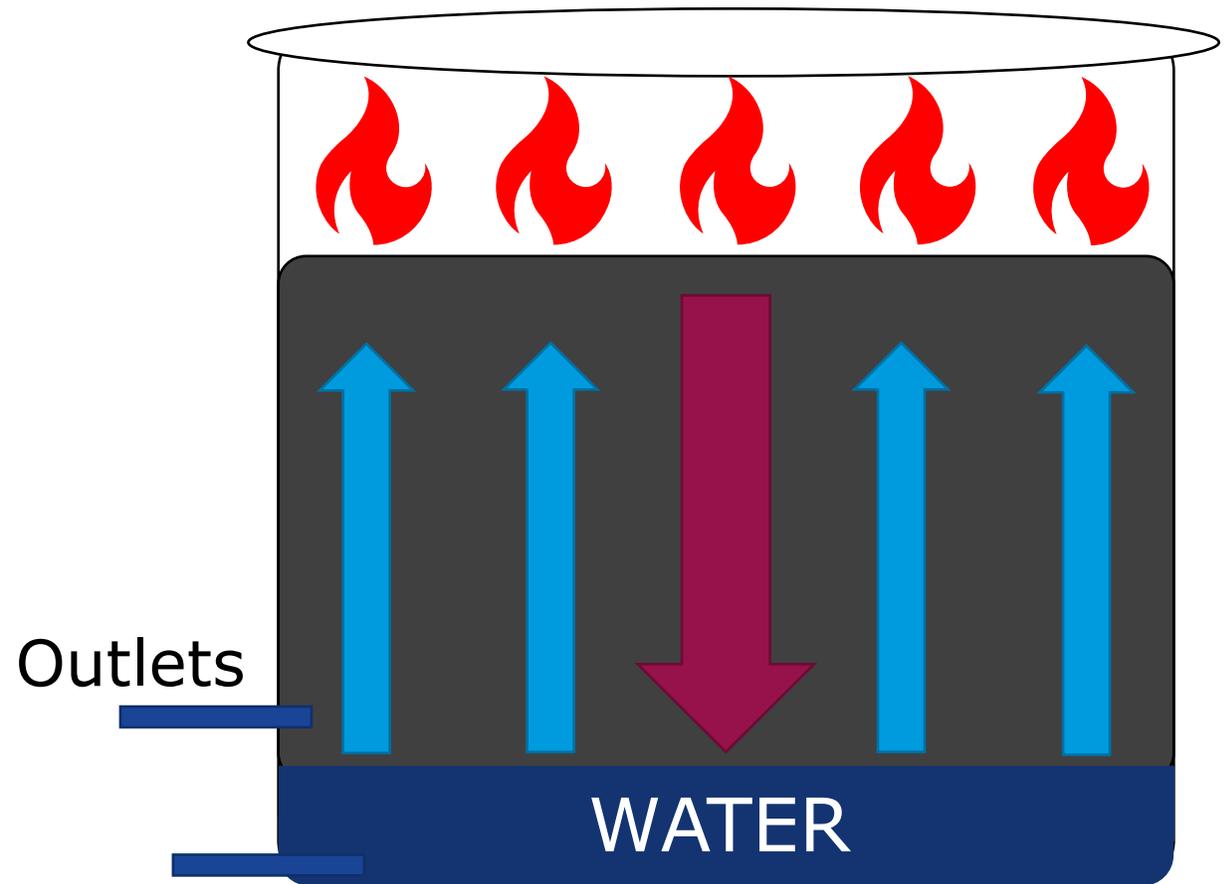
- Running fuel fires
- Difficult to extinguish
- Contaminated clothing
- Explosive vapours

Physical Hazards



Boil Over - BLEVE in nature, not by name

- Prolonged tank/vessel fires
 - Slop-over precedes boil over
- Mass cooling strategy
 - Cordons
 - Thermal Imaging
 - Don't add to the problem



Videos

Gases



Flammable Gases

PHYSICAL PROPERTIES

- RELATIVE VAPOUR DENSITY
- BOILING POINT (condensation point)
- CRITICAL TEMPERATURE
- EXPANSION RATIOS (liquified gases)
- SOLUBILITY!!

CHEMICAL PROPERTIES

- FLAMMABLE / EXPLOSIVE LIMITS
- AUTOIGNITION TEMPERATURE
- CORROSIVE
- TOXIC

Identification

2.1



Flammable

2.2



Non-flammable,
non-toxic
compressed

2.3



Toxic

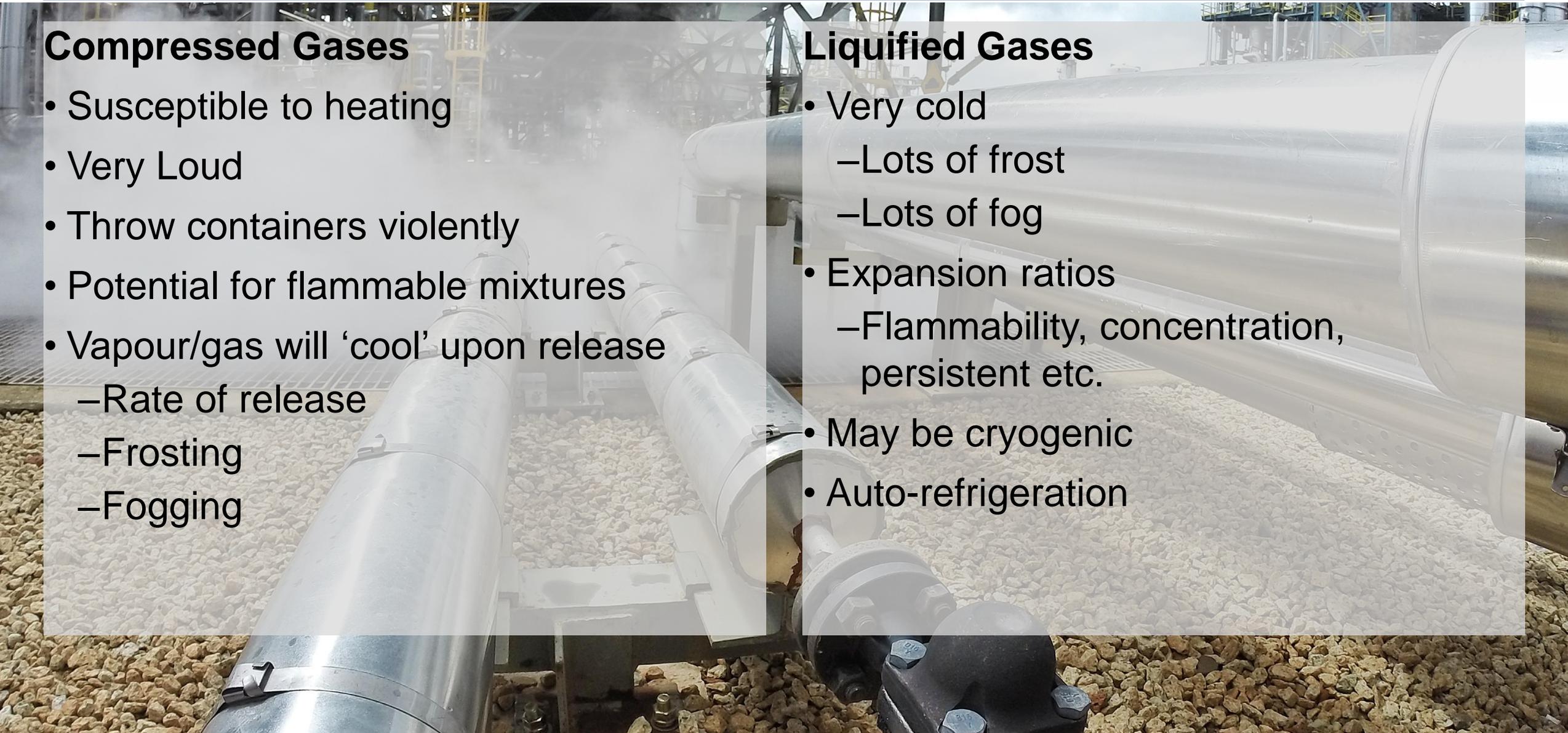
Hazards

Compressed Gases

- Susceptible to heating
- Very Loud
- Throw containers violently
- Potential for flammable mixtures
- Vapour/gas will 'cool' upon release
 - Rate of release
 - Frosting
 - Fogging

Liquified Gases

- Very cold
 - Lots of frost
 - Lots of fog
- Expansion ratios
 - Flammability, concentration, persistent etc.
- May be cryogenic
- Auto-refrigeration



Hazards – Liquified gases (liquids... but dialled up to 11)

- Liquified gases will expand upon vaporisation
- Evaporation/Boiling

Material	Expansion Ratio	Boiling Point
Water	1700:1	100°C
Nitrogen	700:1	-196°C
LPG	270:1	-40°C
Ammonia	800:1	-33°C
Methane	600:1	-161°C

Cylinder Construction



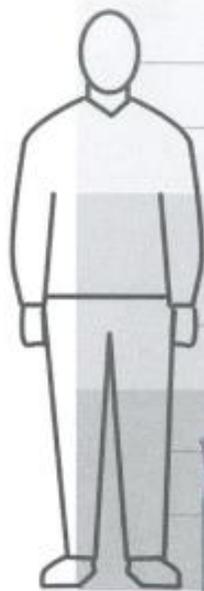
Steep
Shoulders

Shallow
Shoulders

High pressure

Low pressure

Cylinders that have dip tubes show a vertical white line



1800mm
1600mm
1400mm
1200mm
1000mm
800mm
600mm
400mm
200mm

Small Drinks Dispense cylinders

10 litre mixed gas and CO₂ cylinders 6.35kg and smaller

Identification points:

- Valve guard colours
- Refer to valve guard colour charts

High pressure/CO₂ cylinders

All high pressure industrial gas cylinders (large and small) and industrial gas CO₂ cylinders (large and small)

Any Drinks Dispense CO₂ 12.7kg or greater

All Helihi cylinders

Acetylene or Propane cylinders

Any large or small acetylene or propane cylinders

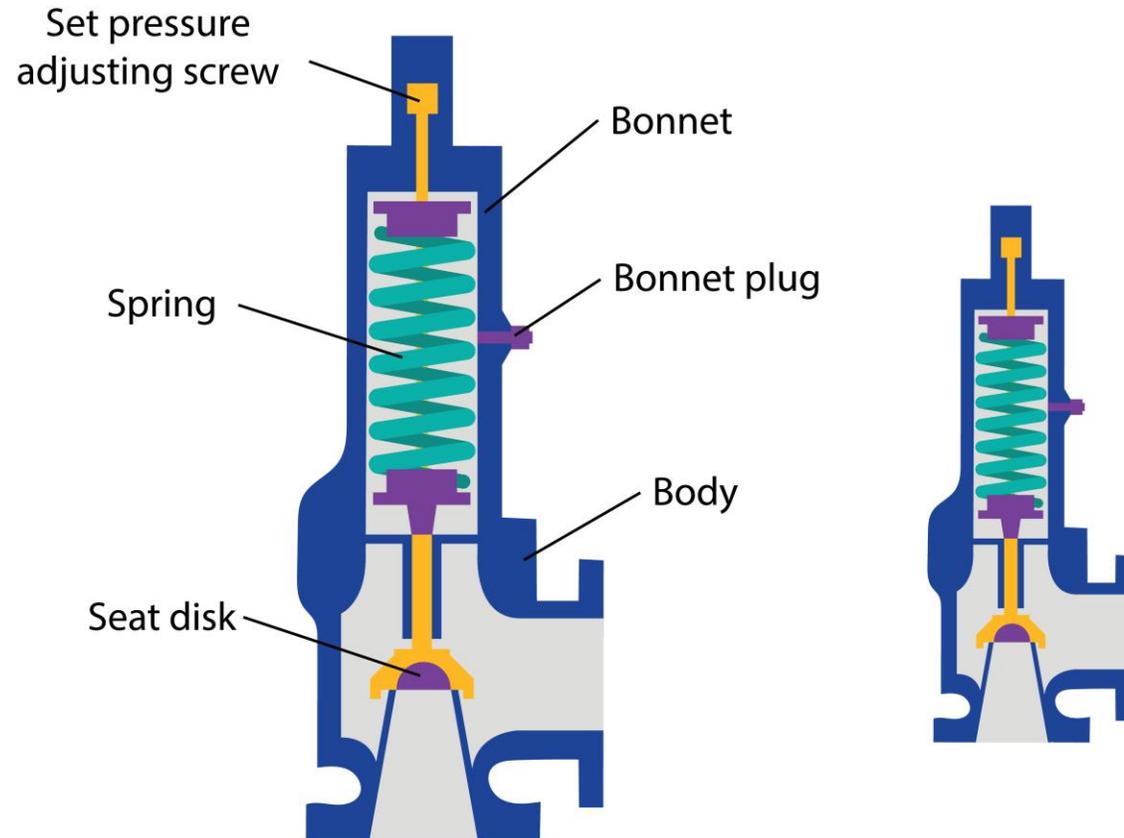
Large Aluminium cylinders

Identification points:

- Light green, turquoise or orange band around neck
- Any mixture containing a ppm, vpm or ppb component
- No rust on cylinder

Small Aluminium cylinders

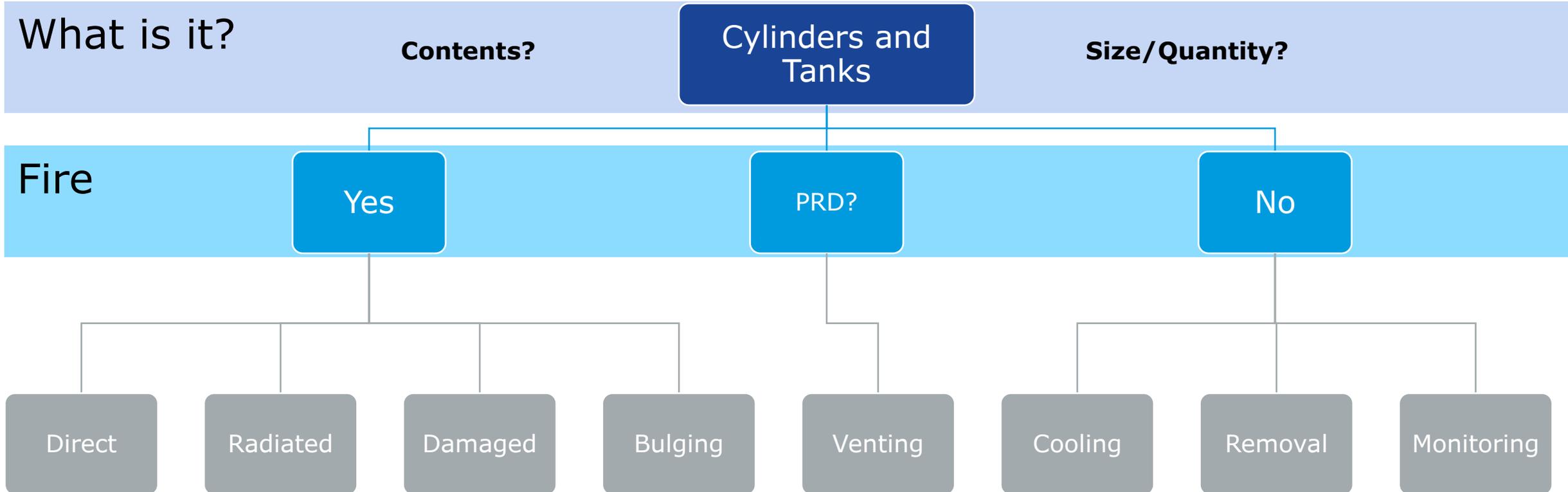
Cylinder construction – Storage tanks and the Pressure Relief Device (PRD)



**CONVENTIONAL SPRING LOADED
PRESSURE RELIEF VALVE**



Considerations affecting the tactical plan



Smaller vessels (in theory) pose a greater risk than larger ones

BLEVEs

Boiling Liquid Expanding Vapour Explosions

- Attributed to liquified gases, but mechanism can cause flammable liquids (Class 3) to behave the same

Very
Dangerous

Unpredictable

Quantity?

Contents?

PRD?

Sustained
heat

Summary



Continued heating

Loss of product via
PRD or Critical
temperature

Weakening vessel
wall

Container failure,
over pressurisation

Videos

ERG – BLEVE guidance

100,000 L

Diameter	0.3 m
Length	1.52m
Propane mass	56,000 kg
Min time to failure for severe torch	9 min
Approx. time to empty for engulfing fire	85min
Fireball Radius	104m
Emergency Reponse Distance	967m
Min Evacuation Distance	1541.5m
Preferred Evacuation Distance	2070m
Cooling Water Flow Rate	9,640l/min

WARNING:

The data given are approximate and should only be used with extreme caution. These times can vary from situation to situation. LPG tanks have been known to BLEVE within minutes. Therefore, never risk life based on these times.

Cryogenics

Boiling points below -150°C

Persistent upon release

Freeze object very quickly

Refrigeration units required for transportation

Contents/DG	Boiling Point
Ammonia	-33°C
LPG	$\approx -40^{\circ}\text{C}$
Methane (Natural gas)	-161°C
Oxygen	-183°C
Argon	-185.9°C
Nitrogen	-196°C
Hydrogen	-253°C



Operational Response

- Guidance and Considerations

Incidents Involving Flammable Solids

Identify type of flammable solid

Approach upwind with caution

- Maintain distance if high risk substance is known
- Consider 50m generic cordon (high thermal & optical radiation)

Protect unaffected materials

- Covering
- Cooling jets

Assess the use of water

- Identify appropriate extinguishment agent / media as soon as possible
- Be mindful of appropriate / proportional decontamination method
- When in doubt (in emergency), use drenching quantities of water

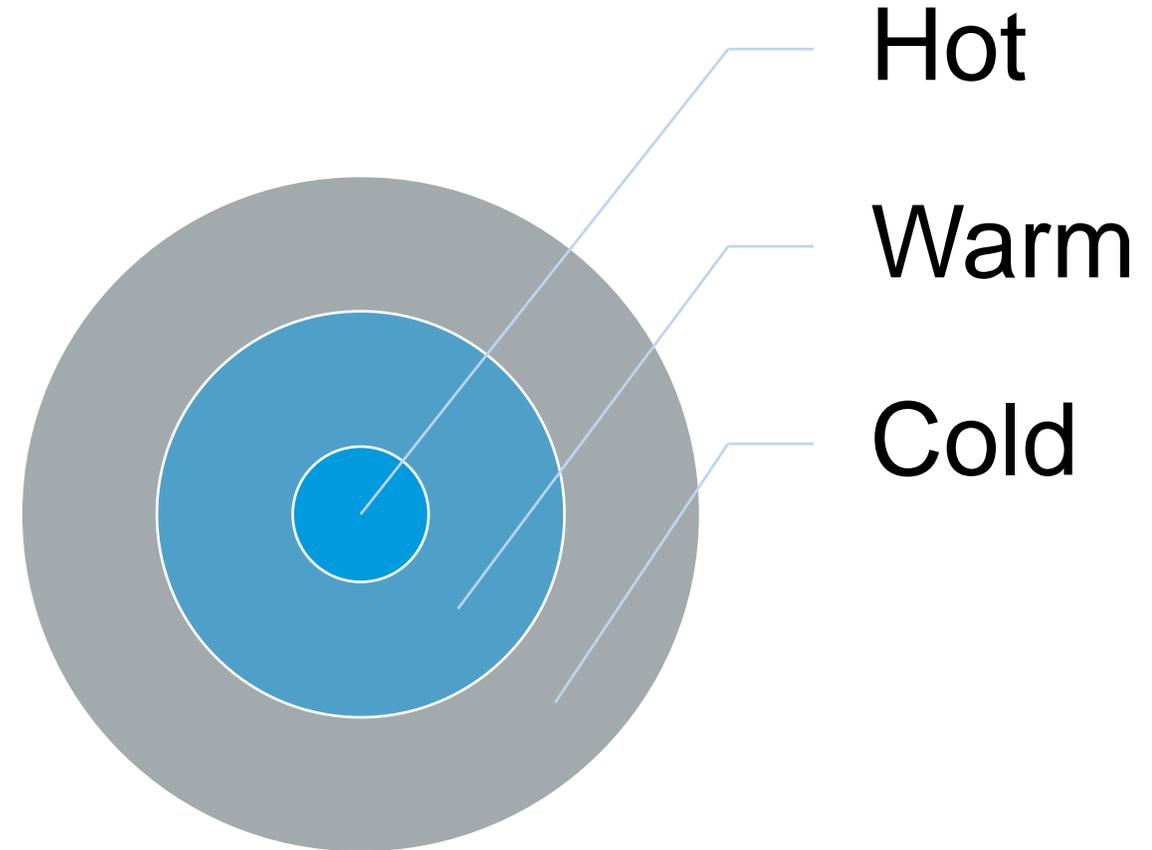
Identify weather conditions

- Rain
- Wind and possible plume direction (if on fire)

Flammable Solids: Decontamination

Dry Decontamination

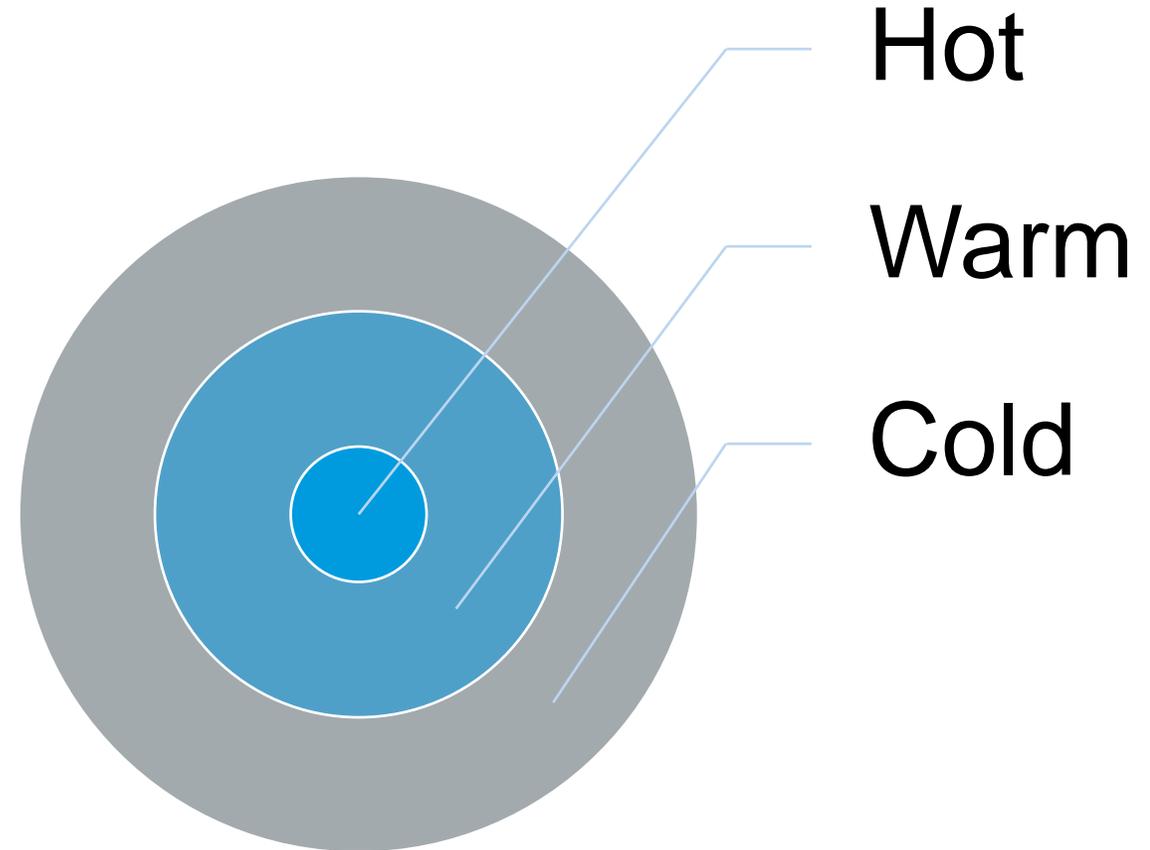
- Removal of gross
- Safe undress procedure & bag
 - Water reactive contaminant?
 - Equipment?
 - Disposal?



Flammable Solids: Decontamination

Wet Decontamination

- Gross 4.2 material contamination
- Casualties
 - Using drowning quantities of water
 - Small amounts will initiate reaction but may dissipate heat
 - Skin contact - flush with copious amounts of water for at least 20 minutes.



Hot

Warm

Cold

Incidents Involving Flammable Liquids

✓ Approach up wind

💧 Be mindful of ignition sources

⚠️ Vapour management

☃️ Prevent contamination

🏭 Suppress/monitor vapours (if applicable)

☢️ Keep things cool

☀️ Environmental Protection

Damming & Booming (surface area)

🧠 Hazards of absorbing

Proportionate Risk – Flammable Liquids

Surface area

- Containment/bunding
- Suppression
- Vapour cloud management

Temperature

- Cooling Jets
- Removal of products
- Management of ignition sources

Enclosed Spaces

- Ventilation
- Inert agents/gases

Invisible fire

- TIC Sweep

Contaminants

- Prevent contact
- Manage the overall risk

Flammable Gases

Hazard

What is it?

Release

How Much?

Chemical properties

Environment

Physical properties

Flammable

Corrosive

Toxic

Weather

Inside/
Outside

Density

Boiling
Point

Solubility

Safe approach

- Early zoning
- Request assistance

Saveable Life

- BA & Fire Kit?
- Decontamination

PPE (mitigation)

- Decontamination

Vapour cloud
management

- Monitoring equipment

Public safety

Tactical Options Pressurised Cylinders / Vessels - Summary

Cool vessel body directly – Monitor with TIC

- Protect surrounding vessels or containers
- Radiative cooling only fractionally effective
- ‘Dry’ wall susceptible to thermal stress
- Keep cooling jets away from valves/pipework

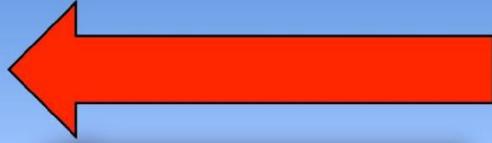
Remove heat source, extinguish fire

- Do not extinguish ignited leaks until supply can be dealt with – saveable life/prevention of escalation

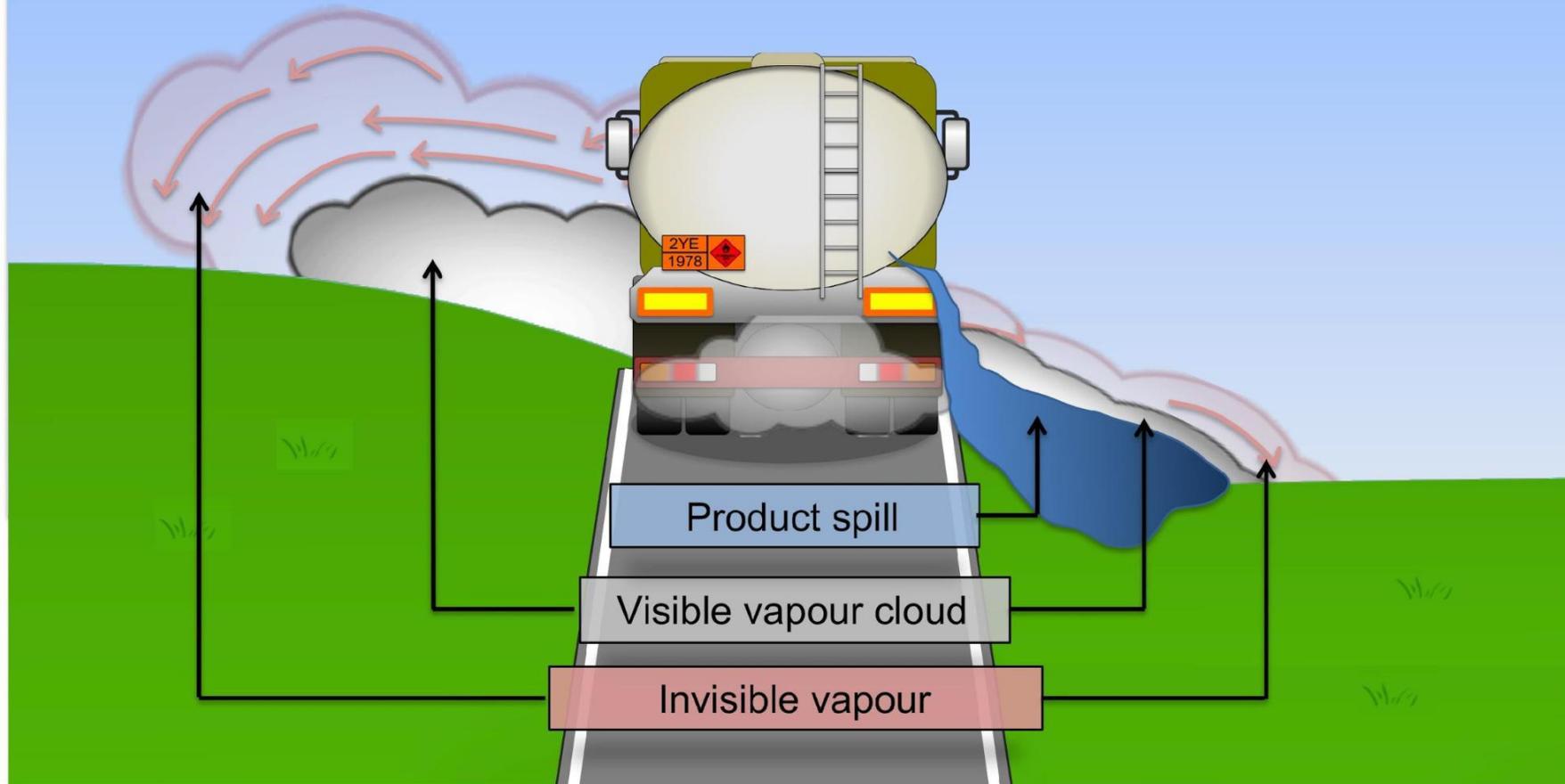
Remove unaffected risks

- Remove cylinders not affected if possible

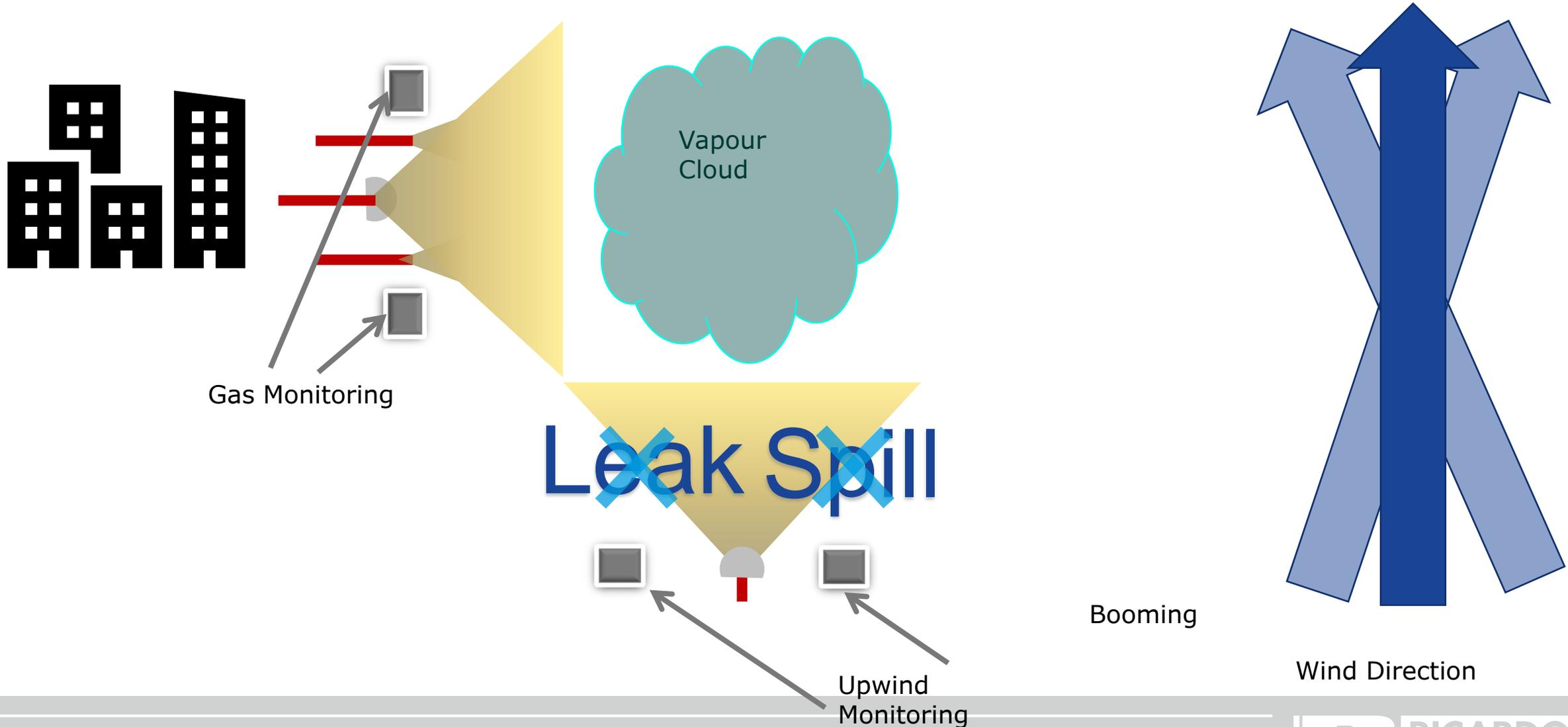
Wind direction



Gradient



Vapour cloud management



Any Questions?

