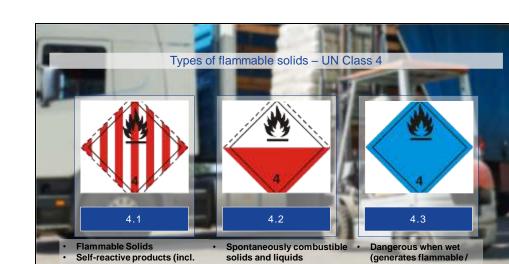


Aims & Objectives	
To review the behaviour, properties and incident management of flammable substances	
Objectives	
 Identify flammability properties of flammable solids, liquids and gases 	
Observe the characteristic behaviours of flammable substances	
Describe operational considerations surrounding flammable substances	



Slide 3



Pyrophoric Self-heating

corrosive vapours)

polymerisation materials)

Desensitised explosives

Classification 4 aren't just materials that are solid that can burn (like wood), they pose a significant risk of fire through flammability characteristics such as low ignition energies (easy to ignite), they can pose an explosive risk, can catch fire without any external influence or react violently with the air / water. This classification is not limited to solids, but also includes liquids that exhibit some of the mentioned behaviours.

4.1

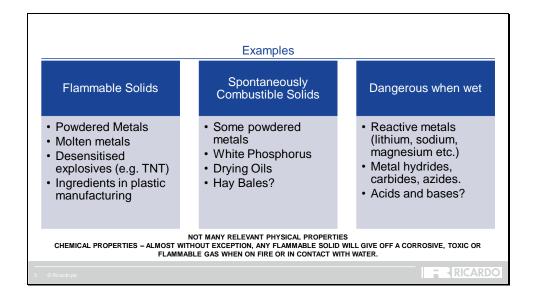
- Polymerisation is the process by which plastics are made, whereby a chemical undergoes a reaction with itself, to produce a 'polymer' – Styrene (a liquid) can react with itself to produce POLYStyrene.
- Explosive materials can fall out of UN Class 1 by being desensitised via being stored under water or dissolves in a solvent. They can however become sensitised through the removal of water (drying out) or the solvent

4.2

- Involves spontaneously combustible solids and liquids that can ignite without an external influence (these materials are sensitive to heat)
- Materials that react with the air (white phosphorus) and catch fire are classified as pyrophoric (Greek for "fire-carrier").

4.3

• Materials are dangerous when wet, often water reactive materials that generate either flammable, toxic or corrosive gases or a combination of the three.

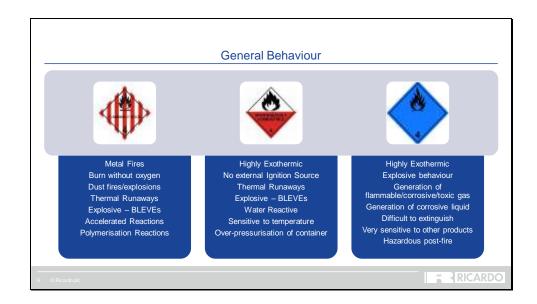


4.1

- Powdered solids have immense surface area and area very small, meaning they pose a high inhalation risk as well as a fire and explosion risk
 - Combustible dust
 - Powdered metals
- Metals exhibit few physical properties, however their chemical properties will be of primary concern
- Metals burn at very high temperatures, with bright light (often with a colour think fire works), and they give off a white wispy smoke
- · Metals involved in fire always give a corrosive fire-water run-off
- 4.2
- Spontaneously combustible materials, can exhibit a self-heating mechanism, or be pyrophoric, meaning they react and catch fire spontaneously with the oxygen in the air.

4.3

- Water reactive materials react with water to produce a flammable, toxic or corrosive gas (or any combination of those three hazards)
 - Reactive metals like lithium and sodium produce Hydrogen (Flammable)
 - Metal phosphides (pesticide Aluminium Phosphide) produces Phosphine (Flammable and toxic)
- Corrosive substances like strong concentrated acids can be water 'reactive' and generate a lot of heat that is directly proportional to the quantity of corrosive and water.



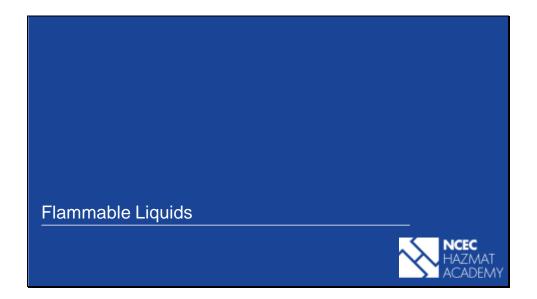
- 4.1
- Inherent risk of dust explosion / fires with 4.1 materials
 - Anticipate a large footprint and spread from a dust ignition or explosion due to more combustible dust becoming involved as the flame-front gets larger.
- Burning metals are very reactive and due to their high burn temperature can react even with inert substances like CO₂ and even sand.
- Scrap metal waste fires are difficult to quench, they react violently with application of water and can burn for a very long time
- Besides from fire risk (or inhalation hazard from powdered materials), they pose little contact risk with skin
 - They will irritate eyes and respiratory tract though (just think any solid particulates in eyes or respiratory tract), and ingestion is not a good thing
 - Decontaminate casualties with water treat for inhalation and / or burns (little risk upon skin contact)
 - Responder decon. = RRR and dry-peel safe-undress.

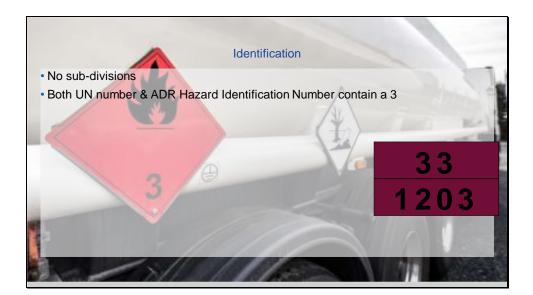
4.2

- Can be a solid, or liquid (do not encounter gaseous 4.2 materials)
- May not require an ignition source
- Materials tend to be found in small quantities as an initiator small quantities still pose a great risk for further sire spread or accelerated fire spread
- Remember that baled hay or even wood chips (due to biological action) can produce a self-heating mechanism that could start a fire

4.3

- Water can be okay to use for decontamination or as a control tactic, be aware of any potential reaction, generation of gases (and run-off) and ensure that the water in use will over-come those things
 - Quantity will be a key consideration here
- Where possible all efforts should be made to keep unaffected material into coming into contact with water.





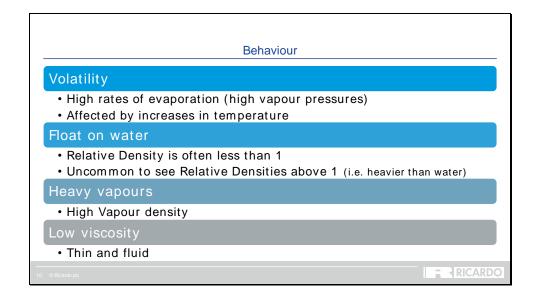
No subdivisions for UN Class 3, however, please take note of the following:

- GHS (Globally Harmonised System) labelling of chemicals includes what is called Hazard Classification for the flammable hazard:
 - Classification 1 = Extremely Flammable
 - Classification 2 = Highly Flammable
 - Classification 3 = Flammable
- Within ADR, there are things called packing groups (PG), rated for severity of hazard from PG I III. With "I" being the most severe and "III" being the least. This directly coincides with the Hazard Classification found within GHS
 - This Classification and Packing Groups is not limited to the flammable hazard, but applies to all chemicals where it is appropriate, corrosives is another good example.
- ADR Hazard Identification Number (HIN) will show duplicates of hazard class number to distinguish severity of hazard

Physical & Chemical Properties				
PHYSICAL PROPERTIES:	CHEMICAL PROPERTIES:			
SOLUBILITY	 FLASH POINT 			
VAPOUR PRESSURE	FLAMMABLE LIMITS			
RELATIVE DENSITY	 AUTOIGNITION 			
RELATIVE VAPOUR DENSITY				
• LogP _{OW}				
MELTING POINT				
BOILING POINT				

Liquids have significant more properties than solids or gases

The properties highlighted here apply to all flammable liquids and can be considerably complex. An advantage of all these properties inclusion, is, a lot of the time, this data is available, so once you are comfortable with the shown properties you can quickly establish ow the material will behave.



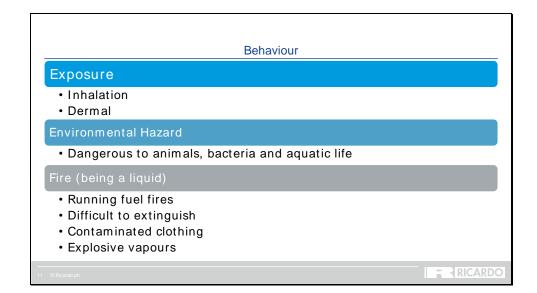
All points listed here are key

Volatility

- Remember volatility can be assessed via a substance's vapour pressure = the higher the vapour pressure the more volatile something will be (compare to water that has a V.P of 2.34 Kpa – any higher than this means that it is evaporating more quickly than water)
- A high evaporation maybe used to our advantage, the material will not be persistent and may dissipate easily and quickly. This of course needs to be monitored and is ideally suited to outside environments
- · Greater wind speed increases evaporation

Heavy Vapours

 Only 14 gases are lighter than the air (Hydrogen, Ammonia are a few examples), all other vapours are heavier than the air, meaning collection in low-lying areas and important to consider gas monitoring techniques and consideration to location of ignition sources

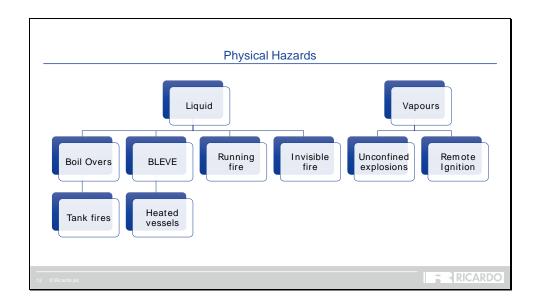


Exposure

- With volatility comes vapour, this can pose an inhalation by exposure risk, consider quantity of source, location to liquid source, vapour pressure of source, ambient temperature, inside / outside locations, wind direction, wind speed and subsequent hazards like corrosivity – some liquids can be flammable AND corrosive AND / OR Toxic too.
- Our skin is really good at keeping water out (and in!), however oils and organic hydrocarbon substances can pass through the skin very easily and can be difficult to wash off.

Being a Liquid

- It goes without saying that running fuel fires is a big problem, most liquid flams, will float on water, consider lots of water at an incident, or standing water, as this will increase the mobility of a fuel by providing the fuel with a nice unobstructed pathway to travel
- Consider remote ignition and generate that picture in your head as to where vapours might be, or going. As most flammable vapour will have a flammable range, at some point from the source there will be a flammable vapour / air mixture.
- Below are general considerations as to distance away from the source a flammable mixture maybe found (from closest to furthest):
 - Outside, on a windy day mixture will be close to source
 - Outside on a still day with no discernable wind vapours will be more concentrated further away from the source
 - Inside with a high-flow ventilation profile in comparison to outside, flammable vapour / air mixture can exist a lot further away from source
 - Inside with no ventilation
 - Temperature affects spread outside (cold temperatures = close to source, higher temperatures = further from the source
 - Compartmentation affects inside conditions more compartmental boundaries limits spread of vapour, however the size of the compartment will indicate explosive mixtures, not just flammable mixtures.



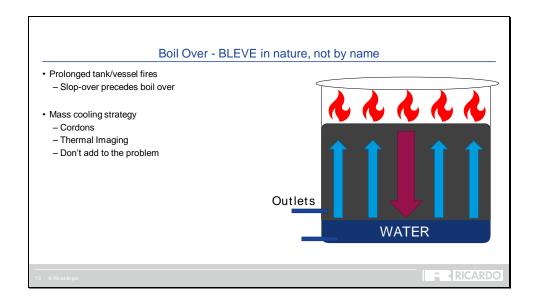
Key points to consider in addition to the points on the slide

BLEVE

 A Boiling Liquid Expanding Vapour Explosion is just that "Boiling Liquid...", so this can happen not just with liquified gases, but also flammable liquids too. In comparison though, a drum of petrol will require a lot more heating and is not under the same starting pressures as the same a mount of Liquified Propane, but the mechanism is still the same. Sustained heating, leading to increased pressure, then either loss of product through a pressure relief device or the liquid surpasses it's critical temperature, as which point the heat destabilises the structure of the vessel and with combined heating, increasing pressure, vessels can fail.

Invisible Fires

 As the name suggests, invisible fires pose significant risk. Alcohols are a prime example for invisible fires (as well as hydrogen fires), use of thermal imaging is a must! Other techniques like fine water spray or particulate s spray (throwing dirt or sand), will highlight the burning flames. Be mindful of radiant heat release and inhalation of flames (for unprotected persons)

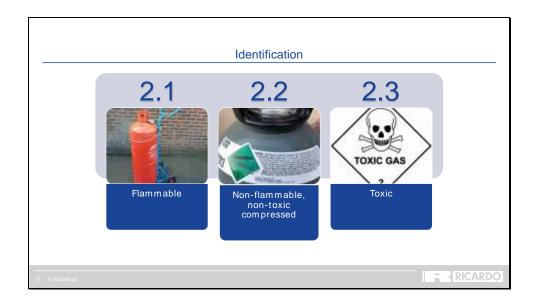


A Boil-over in all intents and purposes, is a glorified chip-pan fire (eruption). It is really only applicable to large scale oil or fuel storage tanks and relies on the presence of water. Normally large fuel or oil storage tanks have a small ingress of water from rain etc. and it is the water that erupts through the fuel if it gets to it's boiling point. The mechanism is as follows:

- A fire breaks out
- The heat from the fire propagates down through the fuel
- The fuel may undergo a slop-over, that precedes a full boil over as pockets of steam rises through the fuel causing the fuel layer on top of the water to 'pulse'
- When the heat at the bottom of the storage tank is sufficient the water will boil and erupt through the fuel, heating and expanding further as it goes up, resulting in a huge fire ball.





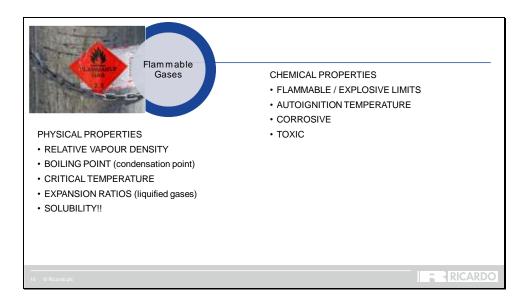


There are three sub-classifications for the dangerous goods class 2;

- Flammable gas,
- Non-flammable/non-toxic compressed gas
- Toxic gas.

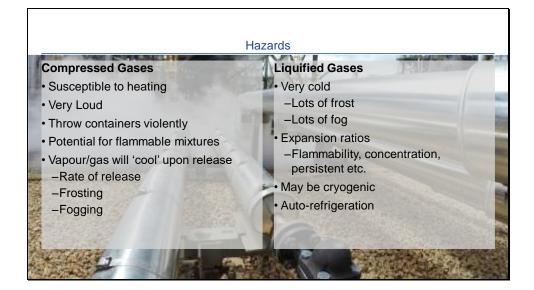
Due to the presence of multiple hazard groups, a gas that is flammable (2.1), may also be corrosive and will display multiple hazard warning diamonds. A toxic gas, assigned to classification 2.3, may also be flammable, but could also be oxidising, corrosive etc.

<u>NB</u> Common hazard combinations include FLAMMABLE:TOXIC:CORROSIVE or TOXIC:CORROSIVE:OXIDISING. You can't get a flammable / oxidising substance, these are mutually exclusive



With all the properties of substances that you are getting acquainted with, the ones listed on the slide are crucial to controlling and understanding gaseous behaviour, with a sumary of the physical attributes below:

- Relative vapour density = where will the gas go/be? (only 14 gases are lighter than the air, the rest are heavier)
- Boiling Point = liquified gases will cool the surrounding area down ton their boiling point upon release from a pressurized vessel, which may be as low as cryogenic temperatures (e.g. LPG cools to -40degC, liquid ammonia cools to -33 degC, liquid nitrogen cools to -196degC
- Critical Temperature = this is the temperature threshold where vapours turn into true gases. This is important, as only vapours can be pressurized into liquids, if a liquified gas gets beyond its critical temperature, it will cause the cylinder or containment vessel to fail, as no amount of pressure will keep that liquid a liquid, it will vaporize and expand.
- Expansion ratio = understanding the expansion ratio helps with assessing risk levels from liquified gases. Remember to convert into total vapour produced from starting quantity of liquid to assess ho much of the gas you will have (only works in volumes, litres of liquid ammonia => litres of ammonia vapour, doesn't work with mass (e.g. kilograms into litres)
- Solubility = as a control tactic, the use of water is very useful in dispersing gas into the air or scrubbing it down from the air into a solution of liquid on the ground. Assessing solubility will be informative to give an estimation as to how much vapour will be scrubbed from the air with the use of water jets (take into consideration application rates of water too in litres per minute)



This classification covers substances such as compressed gases, liquified gases, aerosols, chemicals under pressure, dissolved gases and absorbed gases. The two main forms for storing gases that I will discuss will be compressed and liquified gases:

Compressed

- A sudden release of compressed gas is very loud! Compressed gases generally have a high rate of release, if the cylinder is relatively small it will release its contents quite quickly and may even throw its container around violently
- In addition, the resulting gas coming out will also be very cold. Frosting may occur on pipework, pressure regulators or reducers. And the cooling is amplified by the rate of release, the quicker the release of the gas the more cooling will take place.
- Compressed gases under pressure are very susceptible to any rise in temperature. These are directly proportional, meaning if one goes up, so too does the other, and of course vice-versa, when one comes down, so too does the other.
 - In comparison to liquified gases, the liquid inside the cylinder acts like a heat sink and absorbs energy (to a point when pressure starts to increase), to there is a slight delay in heat build up in a liquified gas cylinder
- The resulting volume of released gas can be estimated by multiplying the hydraulic volume (volume in litres as if the cylinder we filled with water – think 9L BA cylinder), with the pressure in bar. So a 9L BA cylinder operating at 300bar has 2700L of compressed air inside it. This little calculation can be used to assess risk factors, especially for potentially flammable air mixtures or the toxicity of a toxic gas.

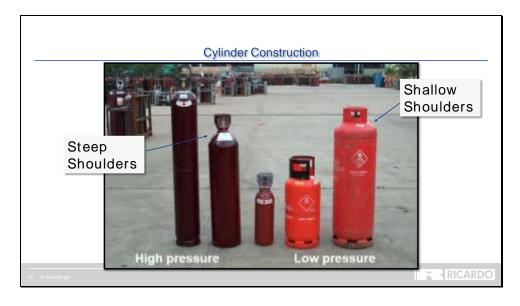
Liquefied:

- Liquified gases will again be very cold upon release, with temperatures settling to the gas' boiling point
- · Expansion ratios must now be taken into account
- Cryogenic gases are liquified gases that have boiling points below -150degC

Slide	18
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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	
18 © Ricardo pic			

Herein contains some examples of expansion ratios of some materials. The vapours of such materials occupy hundreds of times the space than their liquid form does. Controlling or at least having an awareness of the evaporation rates and factors such as impinging heat sources or contact with warm surfaces such as the ground or water can increase the rate of evaporation. Sudden expansion may occur if critical temperatures are reached, whereby the pressure of a container or the atmosphere is not sufficient to keep the material as a liquid and it will rapidly vaporise.



High Pressure

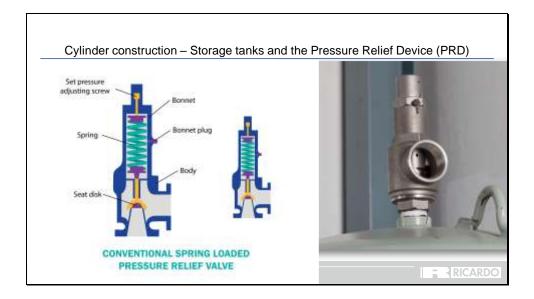
- Cylinders and tanks are made from several materials, extruded aluminium, welded steel, drawn steel and composite
- Higher pressure vessels tend to be made from aluminium out of a single piece or from composite materials.
- These cylinders and tanks tend to be more rounded in shape with steep shoulders or ends.

Low Pressure

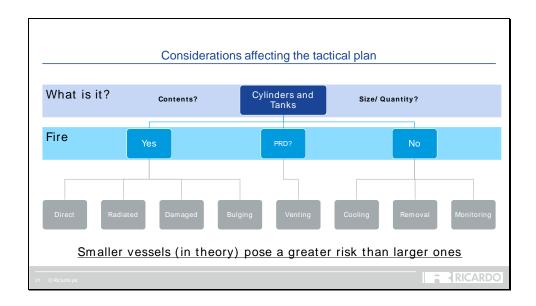
- Lower pressure vessels are made from the cheaper alternative, steel.
- They will have welding seams with quite shallow shoulders or ends. Welsing weakens the cylinder or tank body, making it inappropriate for high pressures.
- Lower pressure is still a high pressure (1.5-30bar), but not as high as truly high pressure cylinders – like automotive Hydrogen storage cylinders operating at 750bar

These structural indicators are for reference only, in circumstances such as fire damage or age for example where no formal identification can take place. Some cylinders will have stamped markings or identification numbers into the vessel wall for similar reasons. It is advised not to take this single piece of information as confirmation, several information sources must be triangulated included scientific advice and a responsible person or site specialist.

It is good to have an awareness of material types because material properties will differ in situations such as fire exposure. Aluminium melts above 650°C, steel loses 50% of its tensile strength above 550°C and the binder in composite cylinders will breakdown and melt at elevated temperatures. Understanding the effect of heat becomes applicable to operational tactics such as cooling or understanding the limitations of continued heating of a pressure vessel, which in some circumstances, PPE such as a decent pair running shoes is ideal.

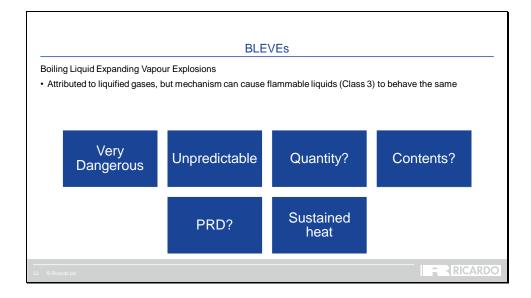


- Pressure Relief Devices relieve excess pressure often as a result of heating
- Extremely common type is this spring-loaded Pressure Relief Valve (PRV).
- PRVs can operate a number of times as and when the pressure needs to be reduced. Release of a flammable substances often leads to a flamethrower type release into the air.
- New PRVs fitted to vehicles (including Hydrogen powered vehicles), must be at the back of the vehicle, at a 45degree angle facing downwards, towards the road – the HSE are currently undertaking research in to burn patterns for this application and it should be indicative as to whether the cylinder has vented and should form part of the 360 scene assessment in the future.

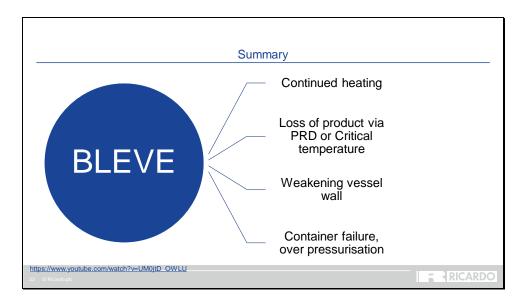


Assessing risks with gases and pressurised vessels

- Confirm whether cylinders are present at an incident and whether or not they are or have been involved in fire – It is essential to identify the risk of explosions as soon as possible.
- The type, size and what the material in the cylinder is, is important, is the cylinder compressed? Liquified? Flammable, toxic etc.
- How much of the material is present?
- Does the cylinder or tank have a pressure relief device, if so, has it activated and is it working correctly?
- If a cylinder is not affected currently by fire and shows no signs of damage or increased temperature then removal is the best option, unless they can't be moved then they may require cooling and monitoring with thermal imaging
- If cylinders or tanks are involved in fire, there are two main strategies to address this scenario; a strong offensive strategy, or a strong defensive strategy. Needless to say, a defensive strategy may mean taking large steps in the opposite direction.







Our next section focusses on the most feared and loathed hazard resulting from a sudden release of gas is the risk of explosion, and rightly so. According to our gas laws and taking into account critical temperatures and expansion ratios, any sealed vessel can explode regardless of what its contents is. Even a tank of water can explode when heated.

As we have discussed the effect of temperature on compressed and liquified gas storage, compressed gas is more susceptible to pressure increase from heating, however, liquified gases have the potential to have a greater immediate area of impact.

IF the contents is flammable we can have a boiling liquid expanding vapour explosion or BLEVE, causing huge amounts of damage and releasing a tremendous amount of heat.

In short, a summary can be made on key factors leading to a BLEVE. Continued heating will increase the pressure of a sealed vessel. If a pressure relief device is fitted, product will be lost to the atmosphere reducing the liquid contents. For a time the liquid inside a vessel acts as an intermediary buffer against the impingement of heat, as continued PRD operation reduces liquid contents, the ability of the liquid to resist increase in temperature decreases. As the heat begins to build further the vessel wall will weaken and hot spots or bulging will occur. This will ultimately lead to the failure of the container with the immense over pressurisation and release all that stored energy. Operationally, an offensive measure will result in some form of temperature management. Either direct cooling onto the affected container or cylinder, or adjacent vessels at risk of heating.

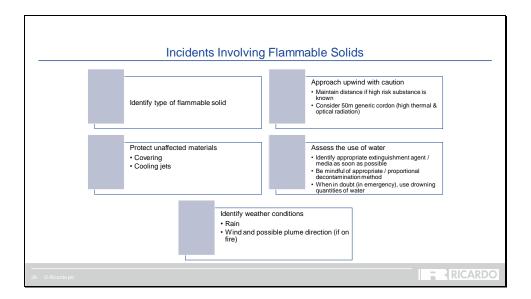
Cryogenics			
Remember liquified gases cool to their boiling points upon release	Contents/DG	Boiling Point	
Boiling points below -150°C	Ammonia LPG	-33 ⁰ C ≈ -40°C	
Persistant upon release	Methane (Natural gas) Oxygen	-161ºC -183ºC	
Persistent upon release	Argon Nitrogen	-185.9°C -196°C	
Freeze object very quickly	Hydrogen	-253°C	
	2 Colorest		

- The commonly accepted criteria for cryogenic materials is to be below -150°C.
- -150°C is incredibly cold and will cause frost burns very quickly and most certainly damage equipment and PPE.
- Tychem TK material used for gas tight chemical protective clothing is only rated to -40°C.
- Thermal imaging cameras often 'bottom-out' cold temperatures between -20 and -30degC – no further information beyond this
- Most permanent gases like nitrogen, oxygen and argon are all cryogenic, with boiling points of -196, -183 and -185.9°C respectively.
- Biggest question for scientific advice, is how long (or how persistent) will pooled liquefied gas be? It is a million-dollar question, relies heavily on what the surface type is that is underneath the pool, wind speed, air and ground temperature, boiling point of gas, humidity in the air, and the list goes on. Suffice to say, high water content surfaces like concrete will cause pooled liquified gas to evaporate more quickly.
 - Liquified gases can undergo auto-refrigeration and keep themselves cold, increasing persistence
- Water can be used as a control tactic to encourage evaporation and help dispersal, but generally, with large quantities this is not advised, but an option nonetheless

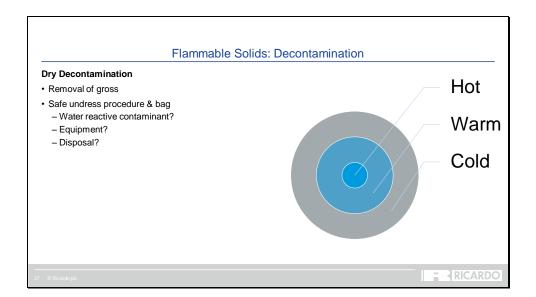
Some gases are also difficult to liquify and maintain as a liquidin small vessels, such as LNG and liquid hydrogen, it is not uncommon to see these two alternative fuels in compressed cylinders.



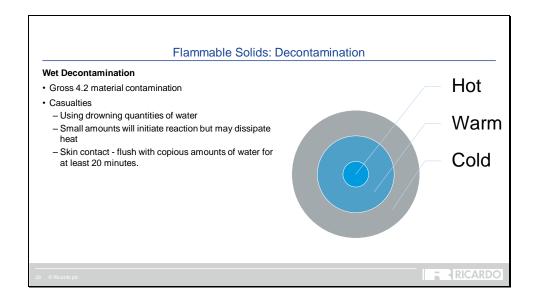




- Approaching an incident involving UN Class 4 will largely depend on identifying the material present, you can get away with the base hazard such as flammable liquid oxidizer or flammable gas, largely without knowing what it is, bu UN Class 4 covers such a wide breadth of materials, it is crucial to find out what you are dealing with.
- Like with any hazmats, knowing quantity is crucial
- Maintain safe approach at all times consider toxic products of combustion or gases produced by other reactions.
- Protect unaffected materials
- · Consider control and management of temperature and ignition sources
- Fire-water runoff will always be corrosive
- Use minimal quantities of water, unless you absolutely have to large amounts.



- Assess contamination location and quantity of contamination. Is it confined to boots and gloves only etc.
- Remove big pieces first if not on fire, this is safe to do so
- Employ RRR tactics and safe-undress
- Re-assess any irritation or skin exposure underneath PPE
 - Wash affected area if needed
- Consider washing PPE and equipment at the scene prior to disposal or bagging. This will prevent any contamination finding its way off-site.



- If gross contamination of 4.2 is confirmed (unlikely case, but possible), then copious amounts of water will be required
- Whenever casualties are involved, it will undoubtably be wet decontamination that is required
 - If substance is water reactive, expect a pop, whizz or a bang, but DON'T let that stop crews from applying water, if will be necessary to keep going at that point to negate the effects of any reaction.

Slide 29

_	Incidents Involving Flammable Liquids			
	~	Approach up wind		
	٠	Be mindful of ignition sources		
		Vapour management		
		Prevent contamination		
	2	Suppress/monitor vapours (if applicable)		
	*	Keep things cool		
	*	Environmental Protection	Damming & Booming (surface area)	
	9	Hazards of absorbing		
 29				

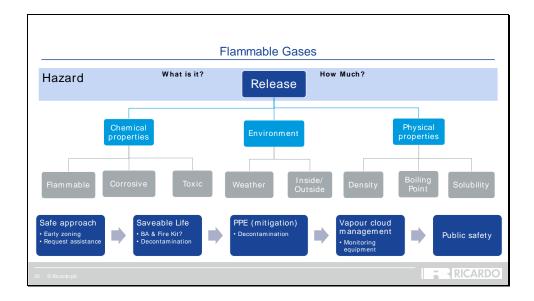
Incidents involving flammable liquids have two major considerations, the liquid component and the vapour component

Liquid

- The liquid will move with the gradient of the ground
- Can be contained
- Poses a contamination risk
- Is visible
- Can be dammed and boomed on a water course
- Maybe corrosive, so care for skin contact
- Any absorbent material like environmental pads and socks, take on the hazard of what's absorbed into them, they should then be disposed of as hazardous waste, dangerous goods class 3 flammable liquid

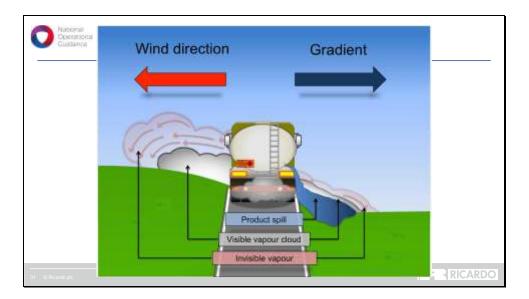
Vapour

- Could easily be ignited
- Requires monitoring
- Will be heavier than the air, low-lying
- Requires no decontamination
- Poses inhalation risk, high priority to protect unprotected persons

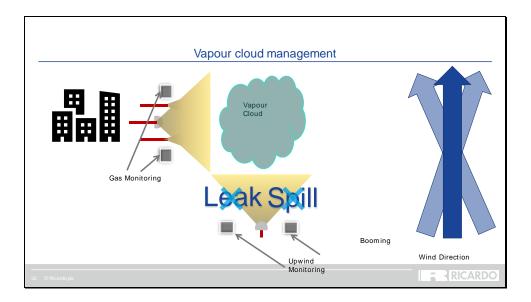


In addition to the points on the slide, incidents involving gases will include discussions around saveable life.

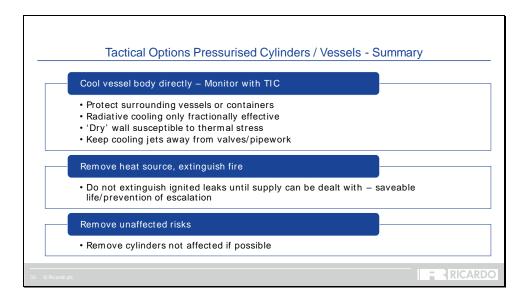
- As we know, life-saving activities are carried out in BA & fire kit, gases pose a significant risk to unprotected persons, so all things should be considered:
 - Time of incident, time of call, turn-out, mobilisation, initial attendance and 360, rescue activities
 - Toxic and corrosive gases can incapacitate persons very quickly and cause a lot o fdamage in a short space of time
 - Toxicity is always prioritised over flammability due to the concentration levels involved i.e flammability is dealt within percentage (%), toxicity is dealt within parts per million, (PPM). PPM levels are on a scale 10,000 times smaller than percentages, so toxicity levels will be reached way sooner that flammability levels e.g. Lethal concentrations of Carbon monoxide (in 10minutes) = 1,700 ppm, the LEL of CO is equivalent to 125,000ppm (12.5%)



- It is better to maintain an upwind position, even if that means being down hill to something.
 - Better to be upwind and downhill, than uphill and downwind.
- If an upwind approach cannot be afforded (or wind direction is against approach or changes mid incident), consider greater cordon distances and stopping earlier upon approach.



- Vapour clouds however can be managed using water sprays, fog branches, mists, monitors etc
- Booming should be setup to contain or manage the water application
- The water spray will help to disperse vapours or scrub them from the air and bring them to the ground, depending on solubility
 - The use of water can not only be used to reduce inner cordons (potentially), but to protect against structures and vulnerable areas that cannot be moved
- It is crucial to implement gas monitoring equipment to check for effectiveness of using water
- Avoid directing water onto a spill or in the vicinity of leaking materials.
 - Water onto a contained spill could cause flammable liquids to rise and spill over any containment measures
 - Water onto pooled liquified gas could increase evaporation of the spill causing more vapour to be formed
 - Water onto leaking liquified gas pipework could flash freeze the water, causing further damage to any orifice
 - The tactic is called 'vapour' cloud management and not spill or leak management.



- Vessels must be cooled directly onto the body, avoiding valves or directly pointing cooling jets towards venting or release areas.
- Depending on the amount of product in a tank or cylinder, there may be so called 'dry' wall areas where there isn't any product acting like a heat sink against heat impingement, causing the structure of the vessel to weaken
- Avoid extinguishing flammable gas release from a pipe or utility works for example, until the supply can be shut off, it is better to control and deal with the fire.
 - Unless a saveable life is identified or a prevention of further escalation however, water 'shields' (wide angled cones sprays) can be used upon effecting a rescue, protecting against the flames, but not necessarily extinguishing the ignited leak.