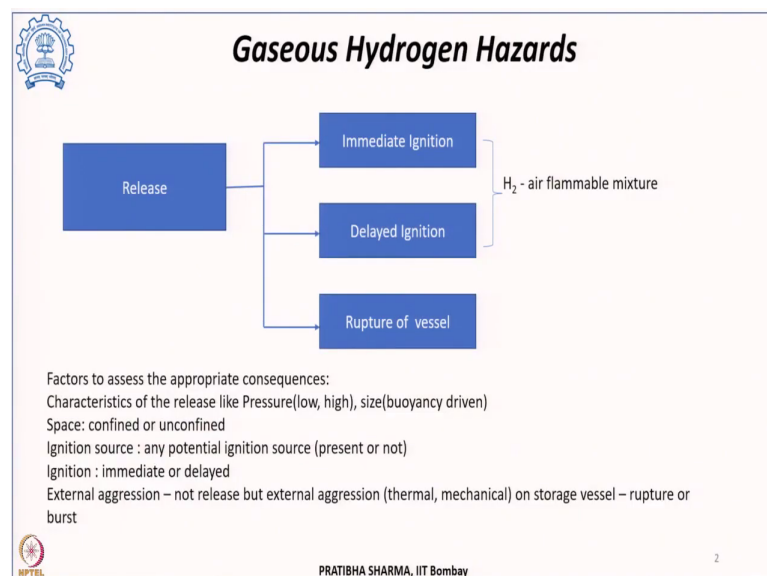


Hydrogen Energy: Production, Storage, Transportation and Safety
Prof. Pratibha Sharma
Department of Energy Science and Engineering
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Lecture - 67
Compressed and Liquid Hydrogen Related Hazards

In the previous class we have seen how we can categorize or classify the different hydrogen hazards. In this class we will see the different types of hazards which could be associated with the gaseous hydrogen or liquid hydrogen release. We will also see the different standards, codes, and regulations associated with hydrogen safety.

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Now, if there is a hydrogen release if let us say it is a gaseous hydrogen release then that can result into several hazards. Now, the release of gaseous hydrogen can be followed by an immediate ignition or it could be followed by a delayed ignition. This will happen when the hydrogen and air forms a flammable mixture, at the same time there is a source of ignition present which ignites this flammable mixture.

Now, they will have different consequences, this is when the ignition of the gaseous hydrogen release takes place. However, there could be another possibility that if there is no source of ignition, the rupture of vessel could result without any ignition. Now, there are different factors which will tell what will be the level of catastrophe, what will be the

consequences and impacts on the nearby neighborhood or the property as well as the lives because of such accidents.


And that depends on parameters like what was the release pressure was that very high or was that very low or what was the size of that release. Now, that size of the release will determine whether it will be buoyancy driven; if the release size is small, hydrogen has a very high buoyancy and diffusivity it will travel very fast upward.

However, if size of release is very large at the same time the release takes place very fast, in that case it may not have sufficient time to diffuse and it may not be that much buoyancy driven; so, as to diffuse it fast and make it diluted with the air. Another important parameter that will describe what will be the consequence will be related to whether that release was in a confined space or whether it was in an unconfined space.

And they will have different challenges, whether there was an ignition source present or not that again will lead to different hazards. If there was an ignition source present was the ignition immediate or was that delayed. Other than the ignition source if there was a rupture of the vessel that has been aggravated because of certain external aggression that could be some nearby fire which has resulted into a domino effect.


And rupture of the vessel or whether it is a mechanical impact that has resulted into the rupture or burst of the vessel. So, all these parameters will decide on to what will be the consequences of the gaseous hydrogen release.

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GH₂ Release in Unconfined Space

- release with immediate ignition- A jet fire/flash fire - flame length and associated radiative heat fluxes, thermal effects
- release with delayed ignition - If the ignition of a release is delayed, a flammable cloud will be formed before the ignition, ignition will induce a deflagration (UVCE: Unconfined Vapour Cloud Explosion) with overpressure effects impacting potential surrounding people and installations, level of congestion (e.g. presence of obstacles) of the site will be an escalating factor
- Deflagration to detonation transition (DDT) is possible in confined and/or obstructed situations



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If let us say the gaseous hydrogen release occurred in an unconfined space. In that case depending upon whether that ignition occurred immediately after the release of gaseous hydrogen or it took place after certain time giving a certain delay or certain time gap, we will have different consequences. Now, when it is unconfined space, we know that hydrogen having a high buoyancy, high diffusivity it will diffuse very fast it will get diluted; now, according to that the consequences will vary.

Let us say if the release is immediately followed by ignition from an ignition source. Now, this ignition source can be a spark, it could be a hot surface, or it could be an electrical short circuit, or a nearby fire, even static discharge or person smoking can result into ignition. Now, if the ignition is immediate in that case it will burn like a jet fire or flash fire.

Now, by jet fire we mean that the hydrogen which is being released did not have sufficient time to mix with the oxidizer. And as such it comes in as it comes in contact with the ignition source burning up of that takes place and that since the outer surface has mixed with the oxidizer that burns. However, the inner region is still concentrated with fuel and does not have sufficient oxidizer; so, that appears as if that is a jet fire that occurs.

Now, that will depend and that will decide on what will be the flame length, what will be the associated radiative heat fluxes and catastrophe will be decided by what will be the

thermal effects or the consequences of this immediate ignition. So, it is a sort of fireball that will take place it will take a shape of fireball and accordingly the thermal effects will be experienced by the persons nearby or by the structure, building, enclosures which were in this type of catastrophe happens.

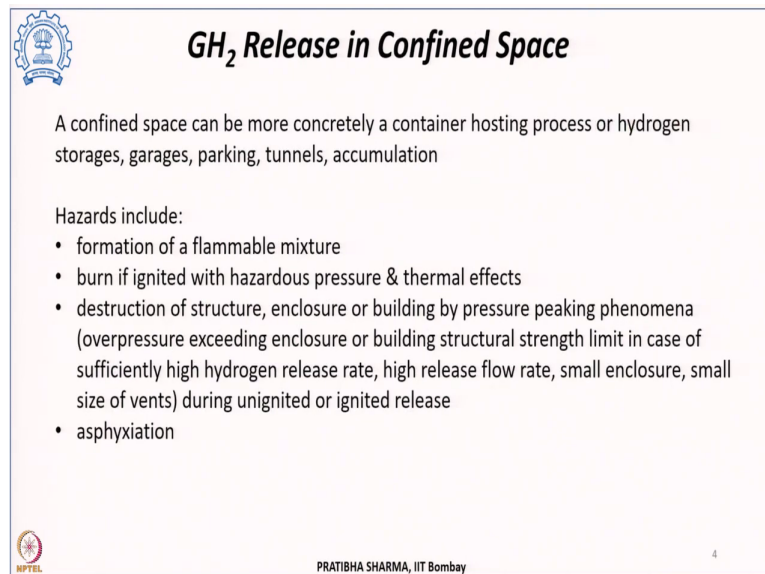
Another possibility could be that after the release the ignition took certain time; so, it is a delayed ignition. Now, if this ignition occurred after a certain time the hydrogen which was released it got sufficient time to mix up with the air in the atmosphere diluting the or the oxidizer it if it is still in the flammable limit that is 4 percent to 75 percent by volume in that case it will burn on total.

So, that will be a sort of cloud which will burn after the ignition, it will take place like a flash fire because it has completely it has combined or it has formed a uniform mixture with the oxidizer. Now, this can result into deflagration this will induce a deflagration and if it is if the release it would have been a liquid hydrogen, then it could even result into unconfined vapor cloud explosion.

Now, because of this deflagration there will be over pressure effects and that will affect the peoples in the nearby environment, the different installations, and also depending upon whether the nearby facilities they have a congestion. There is a there are several facilities close by or whether there are certain obstacles being present on the site the corresponding consequences will be different.

And that could presence of obstacles or congestion can lead to different catastrophic events and that can even accelerate or escalate the hazards. And that like it could even result from deflagration that has occurred because of the release and with delayed ignition that can even turn into detonation that is more hazardous than the deflagration. If there are certain obstacles present or if it would have happened in the confined space.

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GH_2 Release in Confined Space

A confined space can be more concretely a container hosting process or hydrogen storages, garages, parking, tunnels, accumulation

Hazards include:

- formation of a flammable mixture
- burn if ignited with hazardous pressure & thermal effects
- destruction of structure, enclosure or building by pressure peaking phenomena (overpressure exceeding enclosure or building structural strength limit in case of sufficiently high hydrogen release rate, high release flow rate, small enclosure, small size of vents) during unignited or ignited release
- asphyxiation

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Now, if the gaseous hydrogen release occurs in a confined space, like if it is in case of a parking space, or in a tunnel, or in a garage, or that is from a hydrogen storage vessel in that case there could be different type of catastrophic incident that can happen. Now, since it is a confined space there will be an accumulation of hydrogen that will occur, that accumulation will depend upon whether there is a ventilation or not in that confined space.

Now, what will happen if there is a gaseous hydrogen release is, it will mix with air present in the environment and it may form a flammable mixture. Because it is a confined space and it is not the dispersion is not occurring from that confined space; however, the conditions will differ whether there is ventilation or not. Now, once it has formed a flammable mixture it can burn if there is an ignition source.

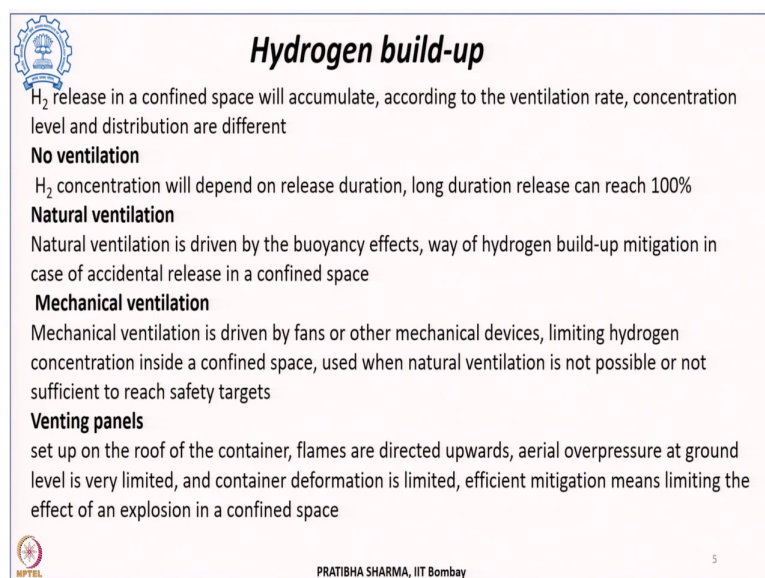
If it burns then it can result into different thermal effects as well as there will be a pressure rise which can lead to destruction of the building or enclosure or the structure. And the process that that causes this type of destructions is the pressure peaking phenomena. Now, this pressure peaking phenomena is when the rate of release of hydrogen is very high in a confined space in such a way that the over pressure which is enforced by the hydrogen.

And that exceeds the strength of that building enclosure or structure in that case there will be either ignited or unignited release depending upon whether there is an ignition

source or not. However, this pressure peaking phenomena is a complicated phenomena and it depends upon what is the hydrogen release rate, whether that is what is the size of that enclosure, what is the size of that vent; so, it depends upon many factors.

Now, let us say if there is a release of gaseous hydrogen in a confined space, but there is no ignition source present nearby. In that case it will displace air or it will reduce the oxygen concentration and can cause asphyxiation for the persons present in that enclosure or confined space.

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Hydrogen build-up


H₂ release in a confined space will accumulate, according to the ventilation rate, concentration level and distribution are different

No ventilation
H₂ concentration will depend on release duration, long duration release can reach 100%

Natural ventilation
Natural ventilation is driven by the buoyancy effects, way of hydrogen build-up mitigation in case of accidental release in a confined space

Mechanical ventilation
Mechanical ventilation is driven by fans or other mechanical devices, limiting hydrogen concentration inside a confined space, used when natural ventilation is not possible or not sufficient to reach safety targets

Venting panels
set up on the roof of the container, flames are directed upwards, aerial overpressure at ground level is very limited, and container deformation is limited, efficient mitigation means limiting the effect of an explosion in a confined space

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Now, as mentioned that if hydrogen release takes place in a confined space, it will start accumulating and that will build up hydrogen concentration in that confined space. Now, depending upon what is the ventilation rate the concentration level of hydrogen as well as its distribution in that confined space may vary. Let us say if there is no ventilation, in that case hydrogen will keep on building and depending upon for how long it has been released before being shut off it can even reach to a concentration level of 100 percent.


If there is natural ventilation present because of buoyancy effect it will be driven out. So, natural ventilation if present then it is a way to mitigate such hydrogen buildup related catastrophe. And in that way it can mitigate the accidental release in case of a confined space. Now, at places where there is no ventilation possible or if it is not sufficient to reach the safety targets it is possible to have mechanical ventilation.

Wherein, we can have fans or certain mechanical devices; so, as to vent off; so, as to remove that hydrogen released and that will again help in limiting the hydrogen concentration in that confined space. Another way could be venting panels; now, these venting panels these are usually present on to the roof of the container or the building or enclosure. And these are such that if let us say because of the hydrogen buildup in that chamber container enclosure and there is an ignition source then it can lead to an explosion.

However, if the over pressure which is created because of this ignition or explosion, if that over pressure can be removed or can be reduced in such a way that when the flames are directed upwards that aerial over pressure at ground level is limited and that pressure could be reduced by these venting panels such that the container deformation could be limited.

Now, this is again a very efficient mitigation method which could limit the after effects of an explosion in a confined space. Now, another possibility could be the loss of containment or loss of confinement where in a pressurized vessel either ruptures or bursts. Now, this is actually a physical explosion wherein if let us say there is no ignition source present, it explodes because of the over pressurization. There could be several reasons for this bursting or rupture of the pressure vessels and that results into over pressure wave.

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Burst of a pressurized vessel

Burst (LOC) of a pressurized vessel is a physical explosion, with rapid expansion, generating overpressure wave in addition to fragments

Burst can occur at :

- normal operating pressure (working pressure), due to: degradation with time of the pressurized volume (e.g. corrosion, fatigue, embrittlement), mechanical impact(s) on the pressurized volume
- bursting pressure (rupture pressure), due to : overfilling, inadequate pressure relief, like internal explosion or reaction, fire aggression



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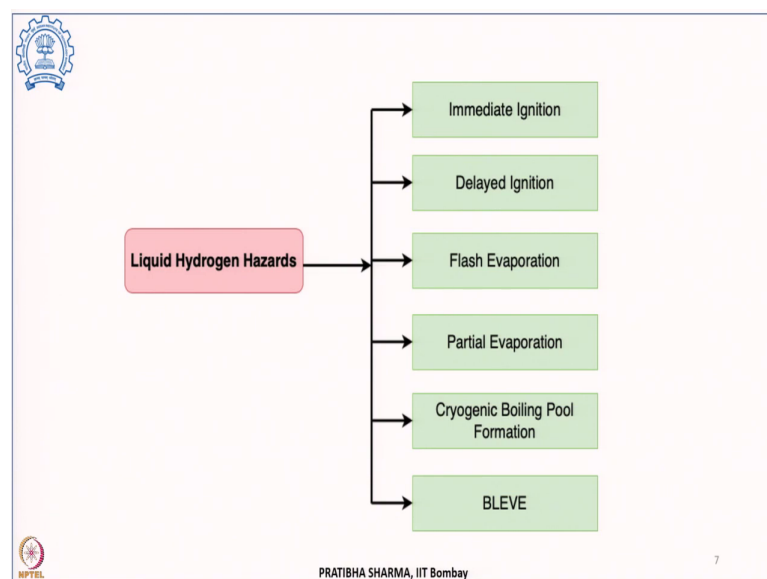
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So, there will be the one will be like release of hydrogen because of the burst or rupture of the pressure vessel at the same time there will be debris, projectiles, or missiles, or fragments of that pressure vessels which will spill out in all directions. Now, this burst or rupture of the tank can occur either at normal pressure, operating pressure that is the working pressure of that tank.

And that the reason could be either the tank has degraded the tank material has degraded with time because of either corrosion attack or fatigue or because of the embrittlement. Or there could be certain external mechanical impact on to the pressurized vessel which has resulted into bursting or rupture of the tank.

It could also be possible that the rupture occurs at a certain bursting pressure and this can arise because of either filling, over filling of the tank. If there is a pressure relief valve that is not working or there is an inadequate pressure relief or it could be because of certain internal explosion, or reaction. Or maybe it could be because of fire regression from outside all that can lead to or a temperature rise because of certain nearby thermal effects, Temperature rise, because of a nearby fire which can further cause an expansion into the gas inside the tank and resulting into bursting or rupture of the pressurized vessel.

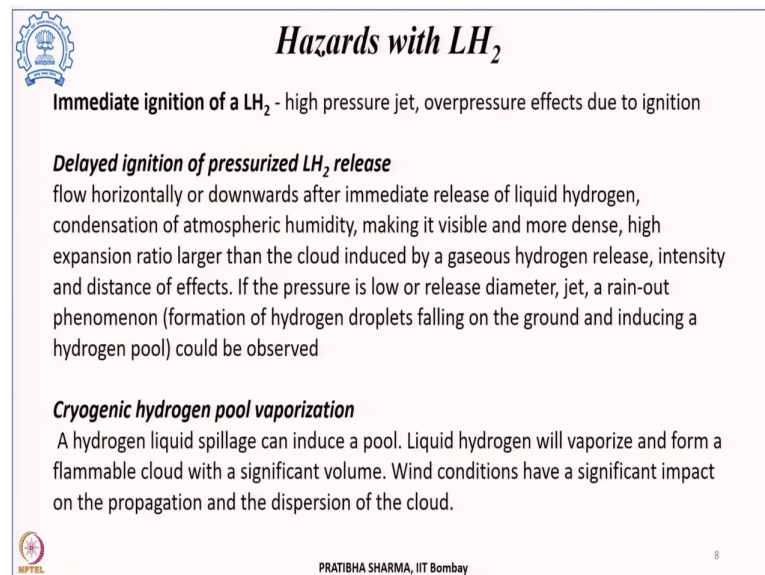
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Now, this was with gaseous hydrogen; now, if there is liquid hydrogen in that case there can again it can lead to different types of hazards. Same as we have seen in the gaseous

hydrogen, if there is a liquid hydrogen spill and it can undergo either an immediate ignition. If there is an ignition source present or there could be a delayed ignition or it could be flash evaporation, partial evaporation, cryogenic boiling pool formation, or BLEVE.

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Hazards with LH_2

Immediate ignition of a LH_2 - high pressure jet, overpressure effects due to ignition

Delayed ignition of pressurized LH_2 release
flow horizontally or downwards after immediate release of liquid hydrogen, condensation of atmospheric humidity, making it visible and more dense, high expansion ratio larger than the cloud induced by a gaseous hydrogen release, intensity and distance of effects. If the pressure is low or release diameter, jet, a rain-out phenomenon (formation of hydrogen droplets falling on the ground and inducing a hydrogen pool) could be observed

Cryogenic hydrogen pool vaporization
A hydrogen liquid spillage can induce a pool. Liquid hydrogen will vaporize and form a flammable cloud with a significant volume. Wind conditions have a significant impact on the propagation and the dispersion of the cloud.

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Now, the hazards associated with liquid hydrogen release or spill could be either with an followed by an immediate ignition that is the consequences are same as we have seen in case of gaseous hydrogen release. There will be a high-pressure jet that will be formed and then over pressure effects will be there due to ignition. Or it is possible that it could be a delayed ignition of pressurized liquid hydrogen release. Now, in case of delayed ignition of pressurized liquid hydrogen release, what will happen is it will form a cloud.

Now, since we know that we have also seen the expansion ratio between the liquid hydrogen and the gaseous hydrogen. When liquid hydrogen is released in that case it will form a cloud and that cloud because of high density of liquid hydrogen compared to air it will move either parallel to the ground horizontally or it will move downwards after immediate release of this liquid hydrogen.

What will happen is with time because of the low temperature, the atmospheric air, the humidity in the air, and the contents of the air they will condense. And then there will be liquid or solid particles in that cloud and that cloud will start becoming more dense and visible because of the atmospheric humidity. At the same time since expansion ratio is


higher there will be also different effects like depending upon what is the intensity, what is the distance there will be different catastrophic effects which will be observed.

Now, if the pressure of release is low or if the release diameter is small, then there can be other phenomena's. It could be a jet or a rain out phenomena, it could be either or it could be both of them that could be observed wherein hydrogen droplets they fall onto the ground inducing a hydrogen pool. Another possibility could be cryogenic hydrogen pool vaporization.

Now, as the liquid hydrogen, it spills it can form a pool it can induce a pool. Now, this liquid hydrogen that will also vaporize because of the temperature difference liquid hydrogen is at 20 K and atmospheric conditions, temperatures are at the room temperature. Now, this will form a flammable cloud and the expansion ratio is higher; so, that will have a significant volume.

Now, the top layers will be like sort of boiling films and it will because of the lower temperature it will freeze the ground. So, depending upon what are the conditions environmental conditions, there will be propagation as well as dispersion of the cloud. So, wind conditions will have a high impact on to the propagation or the dispersion of this cloud.

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Hazards with LH₂

UVCE - cold reactive H₂/air cloud formed, ignited then flame could interact with the obstacles (vaporizer, pipe rack, vegetation) possibly leading to flame acceleration and even to a deflagration to detonation transition in the worst case scenario

BLEVE
liquid which is stored at a temperature above its saturation temperature at atmospheric pressure, some of the liquid will flash to vapour resulting in the generation of overpressure, ignition of the released contents produces a large fireball which can determine the hazard range

LH₂ vessels have pressure relief valves, failure/blockage of this system could lead to a BLEVE, or fire attack could raise pressures and lead to a BLEVE with a fireball due to inadequate venting of pressure



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Other possibilities could be unconfined vapor cloud explosion where the cold reactive hydrogen air cloud formed. And that could ignite if there is a ignition source present that could even interact with the obstacles present like the vaporizer, pipe rack, vegetation present, leading to flame acceleration. And even there could be in the worst case scenario, this deflagration can convert into detonation also.

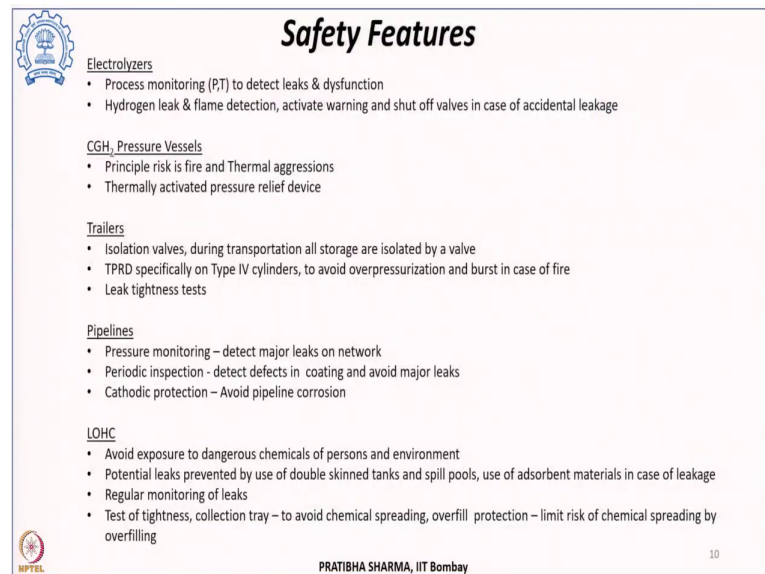
Another possibility could BLEVE, Boiling Liquid Expanding Vapor Cloud Explosion. Now, if the liquid which is stored at temperature which are above the saturation temperature and atmospheric pressure. In case of rupture of this tank because of the several reasons we have seen in the last class, this will be a physical explosion until it comes in contact with an ignition source.

Now, because of this explosion the sum of the liquid there could be possibilities could be like it could be flash evaporation, it could be partial evaporation forming a pool, it will condense the surrounding air, forming a visible cloud. And that will result into even over pressure, if there is an ignition source can even ignite, forming either depending upon whether it is an immediate ignition, or it is a delayed ignition it could be a fireball or flash fire.

Now, the liquid hydrogen vessels usually they are equipped with pressure relief valves. However, at times because of the failure or blockage of this pressure relief valves such type of incidents can happen. Or even there could be a fire attack from a nearby side that could increase the pressure inside the liquid hydrogen vessel and that could lead to BLEVE.

And with a fire ball being formed and this could be due to inadequate venting of the pressure in the liquid hydrogen vessel.

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Safety Features

Electrolyzers

- Process monitoring (PT) to detect leaks & dysfunction
- Hydrogen leak & flame detection, activate warning and shut off valves in case of accidental leakage

CGH, Pressure Vessels

- Principle risk is fire and Thermal aggressions
- Thermally activated pressure relief device

Trailers

- Isolation valves, during transportation all storage are isolated by a valve
- TPRD specifically on Type IV cylinders, to avoid overpressurization and burst in case of fire
- Leak tightness tests

Pipelines

- Pressure monitoring – detect major leaks on network
- Periodic inspection - detect defects in coating and avoid major leaks
- Cathodic protection – Avoid pipeline corrosion

LOHC

- Avoid exposure to dangerous chemicals of persons and environment
- Potential leaks prevented by use of double skinned tanks and spill pools, use of adsorbent materials in case of leakage
- Regular monitoring of leaks
- Test of tightness, collection tray – to avoid chemical spreading, overflow protection – limit risk of chemical spreading by overfilling

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Now, we know that usually these equipments these devices which wherein hydrogens are hydrogen is stored or it is being utilized these are all well equipped with the different safety features. So, as to avoid these, unprecedented situations or these hazards or catastrophic accidents. For example, electrolyzers, they have different process monitoring devices to monitor the pressure, temperature; so, as to detect leaks and any sort of dysfunction in the electrolyzer.

There could be hydrogen leak and flame detections possible. So, flame detection by means of UVIR or there could be hydrogen leak detectors which are there which will activate warning signals and these will shut off the different valves in case of any accident leakage. In compressed gaseous hydrogen pressure vessels, the principle-risk that comes from is the fire and thermal aggressions.

Thus, these pressure vessels these are well equipped with thermally activated pressure relief devices. So, that in unprecedented situation that device that pressure relief device could release the excess pressure which is being created inside the vessel. In the compressed gaseous hydrogen trailers which carry these pressure vessels there will be isolation valves present. Now, these isolation valves are such that each tank is isolated and have us individual or independent valve these are equipped with independent valves.

So, that during transportation all these storage tanks they are isolated by a valve. Also, these trailers have thermally activated pressure relief devices and these are specially

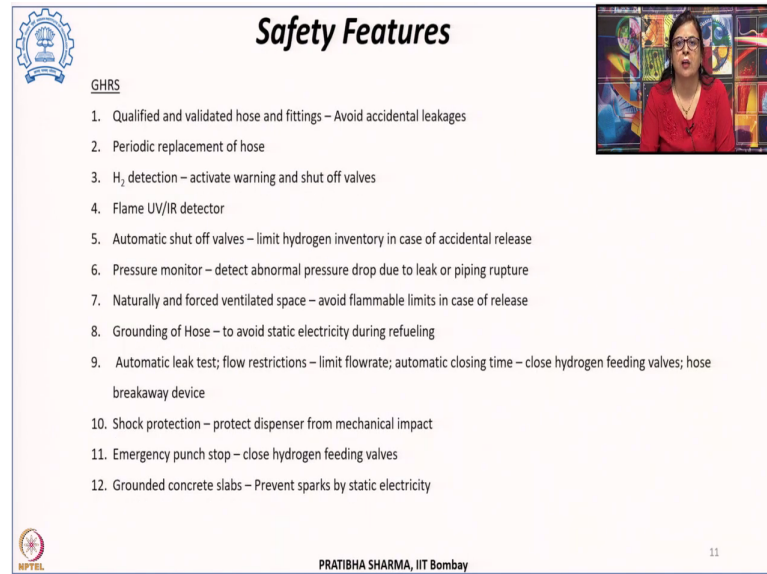
when the loaded tanks are or cylinders are type four type of tank. So, as to avoid any kind of over pressurization or burst in case of fire and these are located on to the top and pointing towards sky.

So, that if there is any release that should be that should go up very fast, then there are different leak tightness test which are performed before these trailers they start their journey. Pipelines they are well equipped with pressure monitoring devices to detect, if there is any leak into the network these the periodic inspections are carried out to detect any leak in the coating and to avoid any sort of major leaks. Even we have also studied that in pipelines cathodic protection is included; so, as to avoid any sort of pipeline corrosion.

If the storage or transport is in the form of liquid organic hydrogen carrier, then it is important to avoid the contact of toxic materials with the persons who are working there or any sort of leakage from these liquid hydrogen carrier containers. So, in order to avoid exposure to dangerous chemicals to the persons and environment, there are different safety features which are included in such containers.

Like the potential leaks are prevented by using double skinned tanks and then there are spill pools also adsorbent materials these are used if there is any leakage. At the same time regular monitoring of leak is being conducted in such tanks. Where in the test of tightness then there are collection trays; so, as to avoid spreading up of the chemical, over filling protection is being considered which limit the risk of chemical spreading by means of over filling.

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Safety Features

GHRS

1. Qualified and validated hose and fittings – Avoid accidental leakages
2. Periodic replacement of hose
3. H₂ detection – activate warning and shut off valves
4. Flame UV/IR detector
5. Automatic shut off valves – limit hydrogen inventory in case of accidental release
6. Pressure monitor – detect abnormal pressure drop due to leak or piping rupture
7. Naturally and forced ventilated space – avoid flammable limits in case of release
8. Grounding of Hose – to avoid static electricity during refueling
9. Automatic leak test; flow restrictions – limit flowrate; automatic closing time – close hydrogen feeding valves; hose breakaway device
10. Shock protection – protect dispenser from mechanical impact
11. Emergency punch stop – close hydrogen feeding valves
12. Grounded concrete slabs – Prevent sparks by static electricity

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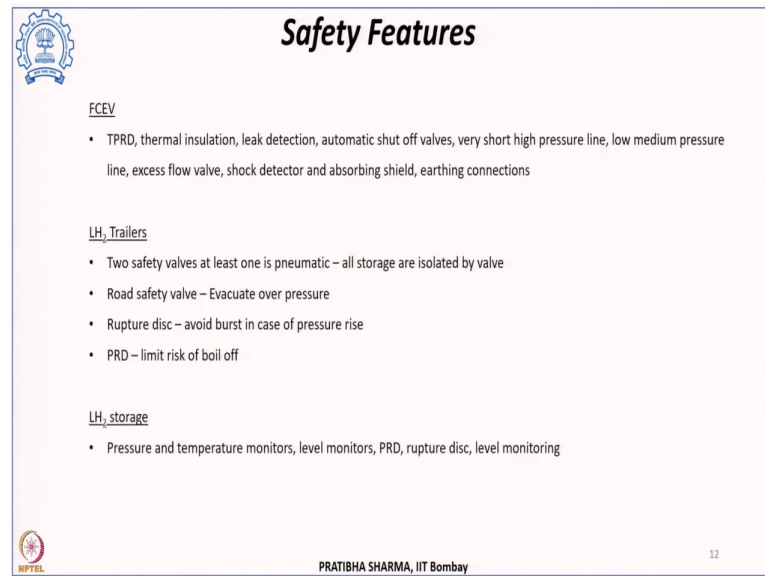
When it comes to gaseous hydrogen refueling stations, there are series of safety measures which are taken; so, as to avoid any sort of accidents. Like the hose and fittings they which are used they are qualified and validated hoses and fittings which are as per the standards; so, as to avoid any accidental leakage. At the same time these hoses and fittings these are periodically tested checked, monitored and replaced at the time require whenever required.

There are hydrogen detectors which are there at refueling stations which activate warning and then they shut off the valves. There are flame detectors which are present at the point of hydrogen refueling station, there are automatic shut off valves which limit the hydrogen inventory in case of accidental release. Pressure monitors are present; so, as to detect any abnormal pressure drop which could arise because of any sort of leak or piping rupture.

And these spaces are either naturally ventilated or forced ventilated; so, as to avoid any sort of flammable conditions when in case of a release. These hoses are grounded; so, as to avoid any sort of static electricity which could be generated during the refueling. And then automatic leak testing and flow restrictions are included automatic closing times; so, as to not only limit the flow rate, but to close the feeding valves hose breakaway devices are present.

Then there are shock protection to protect the dispenser from the mechanical impact, emergency punch stops; so, as to close the hydrogen feeding valves. Then these slabs are grounded; so, as to avoid any sort of sparks by static electricity.

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The slide is titled "Safety Features" and is presented in a white box with a black border. In the top left corner, there is a logo of a gear with a flame inside, representing a fuel cell. The text is organized into three sections: "FCEV", "LH, Trailers", and "LH, storage". Each section contains a list of safety features. At the bottom left, there is a small circular logo with the text "NPTEL" below it. At the bottom center, the text "PRATIBHA SHARMA, IIT Bombay" is displayed. At the bottom right, the number "12" is shown.

Safety Features

FCEV

- TPRD, thermal insulation, leak detection, automatic shut off valves, very short high pressure line, low medium pressure line, excess flow valve, shock detector and absorbing shield, earthing connections

LH, Trailers

- Two safety valves at least one is pneumatic – all storage are isolated by valve
- Road safety valve – Evacuate over pressure
- Rupture disc – avoid burst in case of pressure rise
- PRD – limit risk of boil off

LH, storage

- Pressure and temperature monitors, level monitors, PRD, rupture disc, level monitoring

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When it comes to fuel cell electric vehicles these are equipped with various safety devices. Like thermally activated pressure relief device, thermal insulation, there are leak detectors, automatic shut off valves. Then the high-pressure line is kept very short and a small sized, medium pressure line, excess flow valve is there, shock detectors, absorbing shield, earthing connections are provided in the fuel cell electric vehicle.

With liquid hydrogen trailers there are two safety valves provided at least one of which is pneumatic and all storage these are isolated by means of valves. Besides that, road safety valve to evacuate if there is any over pressure, there is a rupture disk which bursts, if there is a pressure rise into the trailer, and then there are pressure relief devices; so, as to limit the risk of boil off.

When liquid hydrogen storage tanks are considered, then there are different monitors present. Like, the pressure and temperature monitors, level monitors, pressure relief devices, rupture disk, and level monitoring which is being provided. So, these are the safety features which are there with the different hydrogen infrastructure.

Now, to conclude this particular part we have seen the different hazardous situation which can arise because of the gaseous and liquid hydrogen release. And at the same time, we have seen what are the safety features which are included at the point of refilling or at the point of usage and while storing of hydrogen.

Thank you.