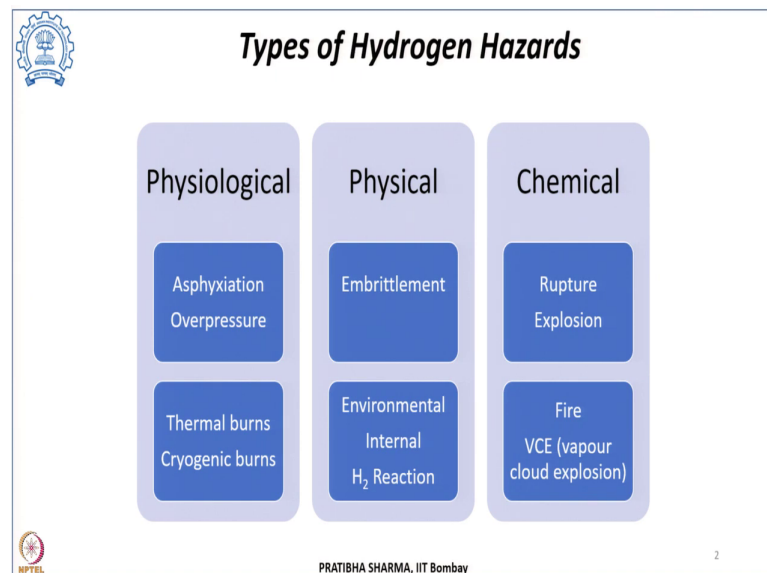


Hydrogen Energy: Production, Storage, Transportation and Safety
Prof. Pratibha Sharma
Department of Energy Science and Engineering
Indian Institute of Technology, Bombay

Lecture - 66
Classification of Hydrogen related Hazards

In the previous class we have seen the different characteristics and properties of Hydrogen which are important to know before we look at the hydrogen safety related aspects. In this lecture we will see the different Hazards associated with hydrogen, broadly we can categorize the type of hazards into 3 categories.

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Like the Physiological Hazards, Physical Hazards and Chemical Hazards. Now, among the physiological hazards if a person is present at either a hydrogen leak or at a hydrogen fire or explosion site, then because of the flammable mixture of air and oxygen resulting into ignition and then leading to fire explosions or maybe leakages maybe that could cause a severe injuries to the person.

Now, other than the direct injuries it is also possible that hydrogen leak can displace oxygen if it is in a confined space and that displacement of oxygen if it reduces below 19.5 percent by volume in that case that can lead to asphyxiation. At the same time the blast waves which comes because of explosions, blast waves which are result of

explosion and can be due to over pressurizations and the time of exposure, duration of it is exposure can result into several different types of injuries or organ failures.


Thermal burns which are because of the heat released the immediate heat radiation from a fire which is because of a hydrogen accident that can lead to injuries to the person damage to the property and many other losses.

Now these thermal burns that depends upon several parameters like how long the exposure has been to the to that thermal burn what was the burning rate, what was the environmental temperature and pressure conditions, what was the burning surface area and there are several parameters that can lead to damage because of the thermal burns.

There can be cryogenic burns when the skin comes in contact with cold fluids or cryogenic fluids that can lead to cryogenic burns frost bite or even hypothermia. There could be a physical hazards which is primarily because of embrittlement. Now we have already seen embrittlement, that embrittlement it is the change in the mechanical properties that can lead to failure, rupture or leakage from the different materials

Now, there are different types of embrittlement we will see that in more detail or there could be chemical hazards which can be because of chemical reactions taking place with the material or when it is oxidation or combustion of hydrogen air mixture that can lead to fire or it could be even rupture of the tank because of different chemical reactions or vapour cloud explosion. So, all these we will see in little more details.

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Some Terms

Explosion – Rapid release and P rise


Deflagration – flame front moves through a flammable mixture in the form of subsonic wave with respect to the unburned mixture

Detonation – flame front coupled to a shock wave propagates through a detonable mixture in the form of a supersonic wave with respect to the unburned mixture, propagates 1000 times faster than deflagration

BLEVE – sudden release of a large mass of pressurized liquid into the atmosphere, if flammable ignites forming a nearly spherical burning cloud, **fireball**

UVCE & CVCE- confined/unconfined vapour cloud explosion

Flash fire – very dilute or very concentrated fuel mixture but in FL, flame travels in cloud at low speed and very less P increase



PRATIBHA SHARMA, IIT Bombay

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Let us first understand certain terms before we see the different types of hazards, there is a difference between fire and explosion. Explosion may not always be leading to fire or fire may not always leading to explosion.

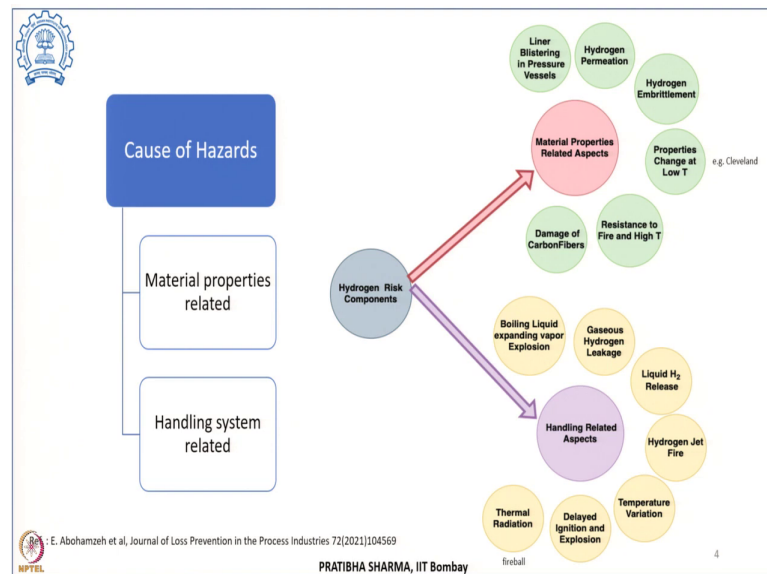
Explosion term is used when it is loss of confinement, initially that is confined if there is an unusual pressure rise and then there is a release of the fuel inside from the containment vessel then it is an explosion. Another term which is used in hydrogen related hazards is the deflagration, now this deflagration refers to the process where the flame front moves through a flammable mixture in the form of subsonic wave and that is with respect to the unburned mixture of hydrogen and the oxidant.

Another term is detonation where in the flame front it coupled with the shock wave propagates through a detonate mixture in the form of supersonic wave and that is with respect to the unburned mixture. However, detonation caused much more devastation compared to the deflagration and it propagates thousand times faster than the deflagration.

BLEVE that is boiling liquid expanding vapour explosion, this is a sort of sudden release of a large mass of pressurized liquid into the atmosphere which can lead to two incidents it can be a fireball or it could be a flash fire. Now if flammable mixture it ignites that forms a spherical burning cloud it is known as fireball, it could be in a confined space or it could be in a unconfined space.

So, it is accordingly unconfined vapour cloud explosion or it could be confined vapour cloud explosion depending upon; whether it is confined or unconfined release. It could be flash fire, in flash fire if very dilute or very concentrated fuel air mixture, but which is within the flammability limit if it ignites then in that case it forms a sort of you know flash fire and that flame travels in cloud at a low speed and at very less pressure.

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Now, let us see what are the different issues related to hydrogen hazards, like the hazardous issues could be broadly classified into 2 classes like which could be either arising because of the material property related or it could be because of hydrogen handling related. Now these can be evaluated the hazards which leads to different accidents these can be either evaluated through experimental techniques or through the computational techniques.

Experimental techniques they provide a valuable insight at the same time these are expensive and sometimes become impossible, especially when these are large scale incidents that needs to be replicated.

However, the CFD techniques are widely used as predictive tools in order to understand the influencing parameters and at the same time to know what could be the physical phenomena's that could result into hazard risk components. So, these are several tools which are being used to understand the hazards, what are the risks associated and what could be the possible consequences because of these hazards.

Now, let us look at the different risk components related to hydrogen hazards at different hydrogen facilities and at different hydrogen applications. Let us first see the materials related hazards the first and foremost is hydrogen embrittlement, now hydrogen embrittlement we know that this is the change in the mechanical properties of metals or non metals when these are exposed to hydrogen.

So, the material becomes brittle it changes its characteristics from ductile to brittle. Now this hydrogen embrittlement this is a complex phenomena and it depends upon several parameters, like it depends upon the exposure time it depends upon the purity of the metal, it depends upon the concentration of the gas, it depends upon what are the temperature and pressure conditions, it depends upon what are the surface properties of the material mechanical properties of the material, what alloy we have selected what is the grain structure micro structure of that material; so it depends upon several characteristics.

And hydrogen embrittlement is in fact it is of 3 types, so one is environmental hydrogen embrittlement wherein the embrittlement of the crack propagation starts from the outer surface, internal hydrogen embrittlement in which the cracks they start to propagate from the inner side or the inner surface and hydrogen reaction embrittlement in which the hydrogen which gets absorbed into the metal, it reacts with the metal forming metal hydride or it can react with the carbon resulting in decarbonisation of the steel and leading to failure.

So, the environmental hydrogen embrittlement and internal hydrogen embrittlement they are seen in the temperature range of 200 to 300 kelvin or they maximize in this range while the hydrogen reaction embrittlement that occurs at temperatures above the room temperature. And it has been found that hydrogen embrittlement it increases with the increasing strength of the steel, increasing exposure time, with the increase in the hydrogen pressure.

Now, there are different ways to address the challenges related to hydrogen embrittlement or to reduce the impact of hydrogen embrittlement and that could be done by either having oxide layer coating or it could be reduction in the stress concentration inside the material confinement vessel or the piping's and all and it could be having adding additives to the hydrogen, it could be proper selection of the material as well as

the grain structure. So, all these can be used as a means to reduce the hydrogen embrittlement.

Now, another material property related hazard could be hydrogen permeation. Now we know that hydrogen is a very small molecule and this can migrate through the permeable material. Now this hydrogen permeation is actually defined as the flux of hydrogen or the rate of hydrogen migrating into the permeable material in such a way that this can cause into later on hydrogen embrittlement.

Now, this permeation of hydrogen this is insignificant in case of type 1, type 2 or type 3 containers; however, in type 4 containers this is also restricted. But this hydrogen permeation it depends upon the temperature it depends upon pressure and it also depends upon edging. So, in case of type 4 vessels as the vessel edge this permeation increases.

Now, another property material property related hazard could be the change in the properties at low temperature or the cryogenic temperature. When materials they are subjected to liquid hydrogen or low temperature hydrogen like the containment vessels or pipelines, in that case there is a change in their mechanical properties.

Like at low temperatures there could be a change from ductile to brittle behaviour there could be a certain unprecedented plastic deformation that can occur or it is also possible that there could be a phase transformation resulting into a change in the elastic and mechanical properties of the material.

At the same time it is also possible at such low temperatures there could be thermal contraction of the materials and that varies from material to material. So, at such low temperatures of liquid hydrogen both the embrittlement and thermal contractions they play an important role.

Now, this thermal contraction for metals this is like less than 1 percent while for structured plastics this ranges in the range of 1 to 2.5 percent. Such an accident has related to the hydrogen embrittlement for with the low temperature, hydrogen embrittlement has occurred in Cleveland in us where in LNG vessel it got ruptured and that has spilled off its content and that the process it started as a domino effect.

So, the nearby vessel got the fires or the missiles from the nearby vessel initiated rupture of this tank and that spilled up the entire vessel and it got exploded and ignited and that caused lot of damage not only property damage, but that has resulted into 128 lives and 200 to 400 injuries.

So, the impact of low temperature on to the properties that needs to be monitored and this can lead to hazards as well. Another important material property related hazard is liner blistering in pressure vessels, we have already studied type four vessels which has an overlap of carbon fiber composite and an inner polymer liner.

Now, in these type of tanks when hydrogen is filled at higher pressure certain amount of hydrogen gets absorbed into the inner polymer and if the depressurization rate is greater than the rate at which the hydrogen escapes by diffusion during depressurization; in that case there could be a delamination or blistering of the polymer liner that can take place.

Now, this blistering of liner it depends upon parameters like what was the initial filling pressure, what is the discharge rate, what is the dwell time and that could lead to failures in the type 4 tank. Another possibility could be damage to the carbon fibres we know that type 4 tanks these are highly complicated structures, these are highly complicated equipment storage vessels and they actually are meant for certain safety requirements.

In such a way that they should avoid matrix cracking fiber breakage delamination and the dome structure should be such that it should bear the over pressure and any sort of impact from the environmental condition. Now, the characteristics of the vessel the filling characteristics all that are determined by the fiber density and stacking phenomena of the carbon fibres, sometimes that carbon fiber damage can lead to catastrophic incidents.

Now these were the material property related hazards; however, handling of hydrogen related hazards can also give rise to accidents at hydrogen facilities and applications, usually these handling related hazards these are associated with loss of confinement or loss of containment, in which either a gaseous hydrogen or liquid hydrogen this is released because of the loss of confinement and that can lead to several types of hazard.

The first one let us consider is the gaseous hydrogen leakage, now we have seen in the properties of hydrogen we know that hydrogen is the smallest molecule and it is much

more prone to leakages. So, hydrogen can leak through small joints these can leak through walls piping's through vessels through different cracks that is a hydrogen leakage.

However if there is certain deformities or crack formation maybe because of the embrittlement that can lead to rapid release of gaseous hydrogen and that rapid release of gaseous hydrogen could either be followed by immediate ignition or it could be followed by a delay ignition and that will have different impacts. So, it could be gaseous hydrogen leakage that can arise and can lead to later hazards which could be in the form of either hydrogen jet fire or it could be in the form of delayed ignition leading to explosion.

So, one of the phenomena which results because of the gaseous hydrogen leak is hydrogen jet fire. If the ignition occurs immediately after the gaseous hydrogen release and that ignition can occur from any of the source it could be either an open flame, it could be an electrical short circuit, it could be an electrical equipment nearby electrical equipment some spark it could be a hot instrument a heating device present or a person smoking nearby that can lead to hydrogen jet fire.

So, immediate ignition after the hydrogen release can lead to hydrogen jet fire. Now hydrogen jet fire it is a sort of high velocity turbulent flame which arises because of combustion of hydrogen air mixture in a flammable range and in such a way that the if the release in a certain direction then it takes place with very high momentum and then it can lead to damage of property as well as it can lead to several injuries.

However if the ignition takes place which is after a certain time, so if there is a delayed ignition after the gaseous hydrogen leakage in that case explosion can occur. Now in case of delayed ignition and explosion hydrogen gets time to mix with the air and that finally leads to thereafter if there is an ignition source present it can result into explosion, it could also be a thermal radiation.

By thermal radiation here we mean if there is a high temperature or if there is flame hydrogen or a high temperature or a fire nearby that is taking place that can lead to catastrophic events.

Now, this usually is it can lead to the damage to the property to the equipment, it can lead to damage to the structure of the different hydrogen facilities, this flame fire or

thermal radiation or high temperature can lead to loss of confinement in compressed gaseous hydrogen vessel or liquid hydrogen vessel.

Now, what happens is like in compressed gaseous hydrogen vessel because of the increase in the temperature there is an expansion that can occur and finally it can lead to the rupture of the vessel. In case of liquid hydrogen tanks we know that these tanks are not made to bear very high pressures.

So, if there is a nearby high temperature which is caused by some other fire or flame nearby flame, in that case it will increase the temperature of the liquid hydrogen tank; not only changes the mechanical properties of the vessel or the tank, but it also provides the required heat for evaporation of the liquid hydrogen.

Now, the change in the both the mechanical properties of the vessel at the same time evaporation of liquid hydrogen will increase the pressure inside the vessel, finally leading to rupture of the liquid hydrogen tank.

Now this is the after effect if there is a thermal radiation now this thermal radiation could be because of a nearby incident, where in a primary incident could be a fire or a rise in temperature could have led to a secondary incident or it can lead to a series of accidents. Such that the final outcome are much more high temperature, high pressure or more devastating than the primary accident this is known as Domino effect.

It is also possible that there could be temperature variation. Now by temperature variation here we mean that when hydrogen is filled to high pressure in an on-board hydrogen storage tank, in that case when it is pressurized to fill in the tank and we want that filling process should be as fast as possible or comparable to the conventional gasoline based vehicle.

In that case when the filling process is made faster there is an increase in the temperature while compressing, at the same time when there is a release of hydrogen then there is a cooling effect which is observed.

So, that heating effect as well as cooling effect these temperature variations can lead to change in the mechanical properties of the liner material or the fiber there could be stress

concentrations in the regions between the liner and the composite and all that can in long run lead to catastrophic events or it could reduce the life of the storage tank.

It is also possible that there could be a liquid hydrogen release. Now this liquid hydrogen release can be from a containment vessel or liquid hydrogen tank in the form of a flow jet, wherein the liquid hydrogen is released it forms the pool onto the ground thereafter it the vaporization will take place it will form a cloud of liquid hydrogen and that cloud will either flow horizontally to the ground or it will flow downward.

Now, in this case what happens is there could be several phenomena that could be possible, either it could be flash evaporation wherein the vaporization of the liquid hydrogen takes place in such a way that immediate vaporization will occur that will cause a flash or there could be a partial vaporization; wherein the partial vaporization can lead to the formation of a pool of liquid hydrogen.

Now, this pool of liquid hydrogen which is formed vaporization will form a sort of boiling vapour film and when it is close to the ground it will freeze the ground. In the due course of time because the temperature of the liquid hydrogen is very low what will happen is it will condense the surrounding nitrogen oxygen humidity in the environment and that condensation will add up to the moisture content to the liquid and solid particles into the liquid hydrogen cloud making it more dense.

Now, there are two competing effects that are taking place one because of this condensation of the atmospheric humidity, moisture content, the nitrogen, oxygen the cloud will become more dense and then there will be a negative buoyancy effect. At the same time because of the phase transition there will be a there will be a increase in heat and that will have a positive Buoyancy effect.

So, there will be these two competing effects that will occur; however, that will be driven by environmental conditions like wind speed, what is the external temperature, what is the other condition environmental conditions prevailing. Other handling hydrogen handling related issues which is also associated with liquid hydrogen is boiling liquid expanding vapour explosion.

Then hydrogen rapid hydrogen release takes place from a containment vessel in such a way that the hydrogen is released at atmospheric pressure. However, it is at a

temperature higher than the boiling point. In that case the fast release of hydrogen will be taking place this is actually an explosion phenomenon that will occur because of rupture of the vessel.

Here in the internal pressure of hydrogen it increases beyond the bearing strength of the liquid hydrogen vessel and that results in 2 explosions. Now we need to remember here that this is a physical explosion that takes place rather than a chemical reaction explosion and this can be in confined space, this can be in unconfined space. So, it could be a confined vapour cloud explosion or it could be an unconfined vapour cloud explosion.

However we need to remember that vapour cloud explosions these are much more hazardous compared to jet fire or flash fire. So, these are the different possible hazards that can result from hydrogen related accidents at the point of application or different facilities.

Thank you.