Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 65
Properties of Hydrogen Associated with Accidents

Welcome to this last section of this course which is on Hydrogen Safety, this particular section is divided into three parts. In the part one we will look at the important characteristics and properties of hydrogen which are important to be known for hydrogen safety perspective. In the second part we are going to look at the possible hazards accidents that can occur across the entire hydrogen energy value chain, including production, storage, transport, utilization.

And in the part, three we will look at the various international standards regulations and codes which are in existence for safe usage of hydrogen. Now, hydrogen has been used as a chemical feedstock and as an industrial gas for more than a century. An industry has an excellent safety record for using it in the controlled industrial premises. However, there has been a very limited historical evidence of its use and its access of risk assessment for the general public.

For a very long time the perspective of general public was related to certain incidents like the Hindenburg disaster in 1937 or hydrogen bomb or the challenger space shuttle accident explosion that was in 1986. However, over a period of time the perspective has changed experts know that the there has been a tremendous dramatic technological advancement that has occurred.

And with the confidence that has been gained in the industrial usage of hydrogen for such a long period the perspective is changing. Now, as the use of hydrogen will increase as an energy carrier, the layman the lay persons will be using hydrogen. And as such having an adequate safety measures and precautions becomes very essential.

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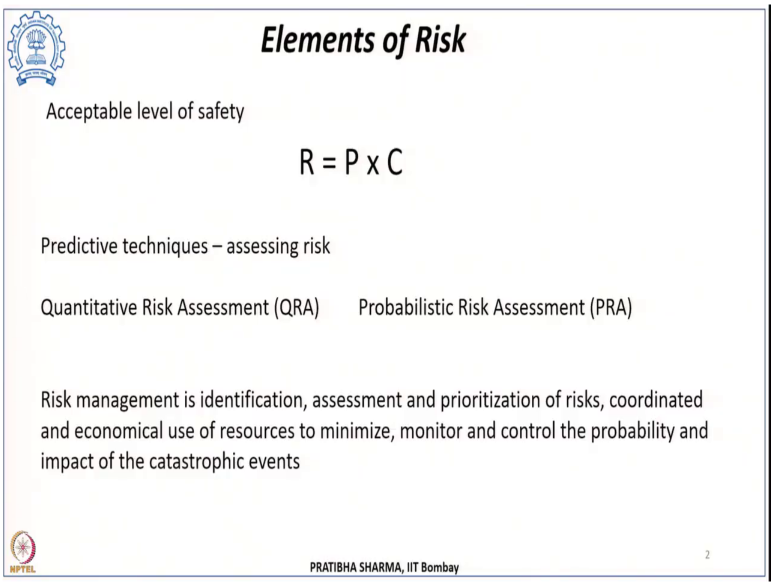

Now, when it comes to hydrogen safety what will be the acceptable level of safety that we can determine by calculating the risk which is in terms of the probability and cost. Now, to find out this risk to calculate this risk, we should know the probability of occurrence of an accident or hazard and the cost or the consequences associated with it that could be loss in terms of property unfortunately in terms of lives as well.

However, in case of hydrogen there is very limited knowledge about the probability of occurrence as well as the consequences associated with it. So, as such there are different techniques which can be used for assessing the risk associated with hydrogen use in the different energy systems.

Now, these techniques are the predictive techniques, there are several methods which can be used for finding the risk in the hydrogen energy systems, like the Quantitative Risk Assessment (QRA) commonly known as Probabilistic Risk Assessment. However, these techniques these are used for large scale systems complex systems; however, they can still be applied to small simple systems as well, but these are costly.

So, as such there are different software's which has been developed, there are different programs using which we can do a detailed study of the possible hazards, their consequences the risk associated with the use of hydrogen. When it comes to risk management it is identification, assessment and prioritizing the risk, what could be the possible risk, a detailed study, and which risk could be more devastating that we need to find out.

And thereafter, a coordinated and economical use of resources is required to minimize, monitor, and control both the probability of occurrence, the frequency of occurrence of such accidents and the impact the consequences of such catastrophic events.

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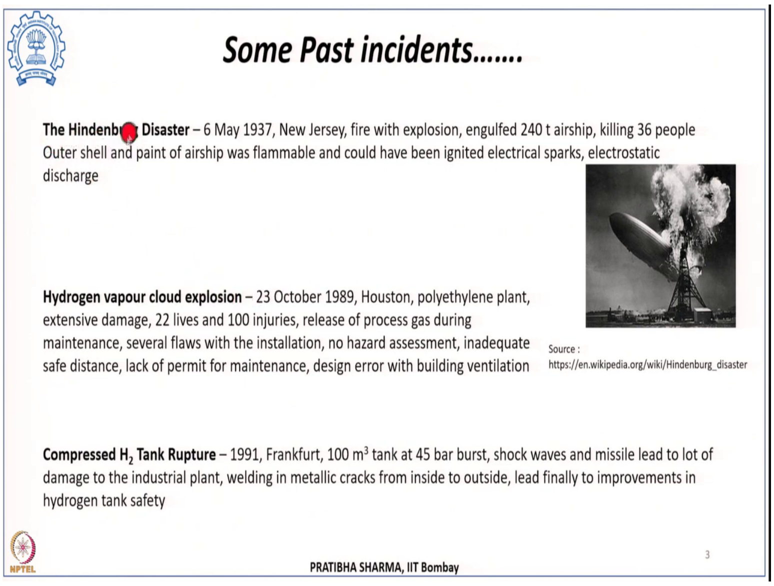

Just to give a brief background there have been some past incidents like the well-known, Hindenburg Disaster that occurred in New Jersey on the 6th of May 1937. Wherein hydrogen was used to provide buoyancy to the giant airship, Hindenburg. And that had a fire from the tail end and it exploded and this engulfed this fire engulfed the 240 tons of airship and that had loss of life 36 people they lost their life.

So, at that time it was considered that the accident occurred because of hydrogen; however, there after several studies were carried out on to understand this disaster. And it was found that the outer shell of the aircraft that as well as the paint that was there on the air ship that was flammable. And on that day the conditions were such that there were electrostatic charges which were developed.

So, that electrical sparks they initiated ignition in the airship and that led to the well-known Hindenburg disaster. Another incident that occurred in Houston that was on 23rd October 1989 was the hydrogen vapor cloud explosion. And that occurred in a very large polyethylene plant which resulted into extensive damage of the plant. Taking away 22 lives, there were 100 injuries and there the release of processed gas during maintenance was found to be the reason for that accident.

On an investigation it was found that there were several flaws with the installation in the plant, there was no hazard assessment that was carried out, there was inadequate safe distance between the control room and the reactor. There was lack of even permit for the maintenance that was being carried out, there were design errors with the building ventilation and all these together led to the catastrophic event.

One more incident to quote here was in 1991 in Frankfurt where a compressed hydrogen tank which was holding 45 bar pressure hydrogen with a volume of 100-meter cube it burst. And that explosion was such that the shock waves and missiles that originated from the compressed hydrogen tank that led to a lot of damage to the industrial plant. The reason that was found was at the welding points there were metallic cracks that were propagating from inside the tank to outside.

And these welding point became the stress centers where in hydrogen we know that it is the smallest molecule it diffuses fast it penetrates through these cracks joints welds. So, it further increased that crack size and finally, it led to the failure of the tank or rupture of the tank. However, with that incident in the country there was a lot of measures that were taken and that led to improving the standards and safety protocols; finally, led to the improvement in the hydrogen tank safety features.

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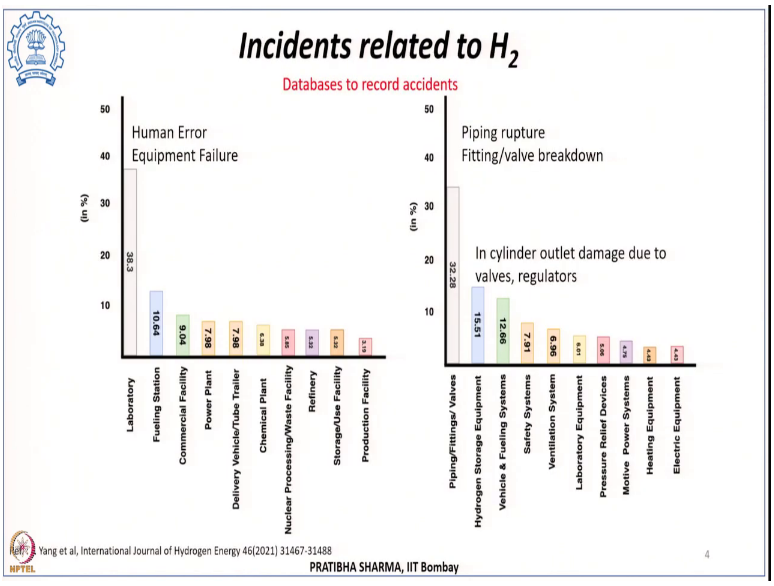

Now, there are if we look at these accidents that have happened in the past, there are several databases available to record these accidents. Like, US DOE they have record of such accidents and there have been several studies that have been carried out. So, from a reference if we see that studies they have done and they have found that out of the total accidents that have occurred incidents related to hydrogen a significant portion has been in the laboratories.

Then the fuelling stations and then comes the commercial facilities; there after power plant, tube trailer, or delivery system, and the chemical plant, or the nuclear process fuel processing, refineries, storage, and the production facility. So, an appreciable number of such incidents have occurred in laboratories and the major reason that was found associated with these incidents in the laboratory was human error and the equipment failure.

Among the equipment failures the major challenges or the major reasons of such equipment failure were associated with the piping, fitting, and walls, their rupture. So, the piping they ruptured or the fitting and walls they break down. 15.5 percent of such incidents they were associated with the hydrogen storage equipment. And these failures were result of the damage of the outlet of the cylinders; so, that was at the points of walls or regulators.

So, whatever were the peripheral equipment's attached to the cylinders, there was damage to those and that resulted into the failure of the hydrogen storage equipments.

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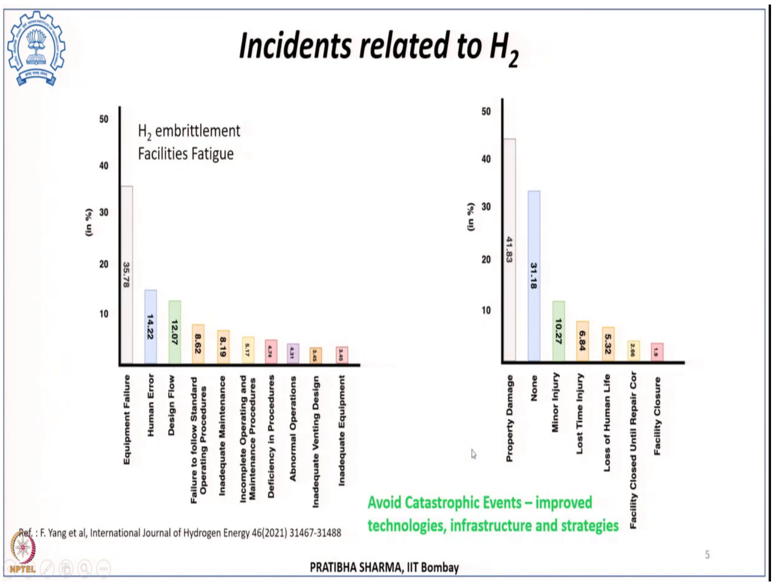

Among the major accidents as mentioned, the equipment failure and human error, the design flaws these were the three leading reasons for such incidents. And among the equipment failure hydrogen embrittlement and the facilities fatigue were the major dominating cause of these equipment failures. That led to several losses in terms of property loss, injuries to certain extent loss of human life. However, in many cases there was no loss, there was an incident and explosion, but still there was no loss that occurred at the point of accident.

Now, it becomes very much essential to avoid these unforeseen circumstances to avoid happening of such catastrophic events. And there are several projects which are undertaken globally to study this risk associated, what could be the origin of these incidents and how these can be avoided. With that there have been improved technologies infrastructure and strategies in place that we will learn in the hydrogen safety section.

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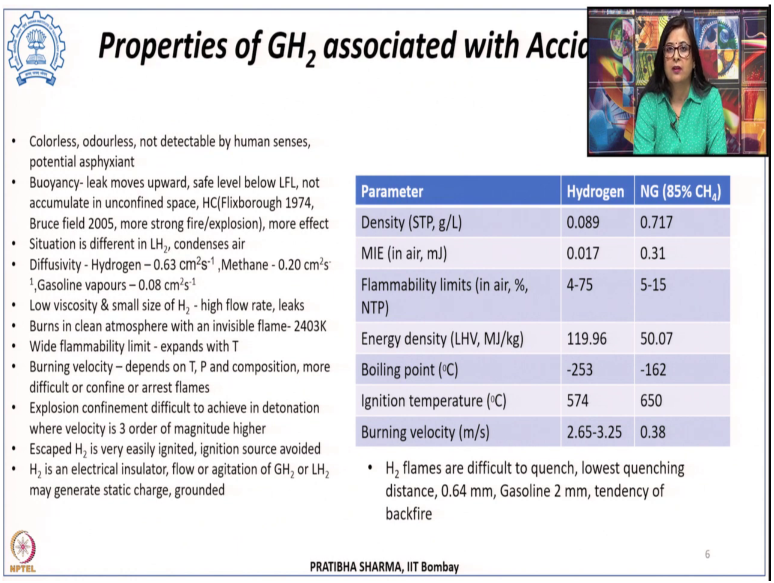

Now, before we go into what could be the possible accident scenario, we should understand and revise some of the important characteristics and properties of hydrogen. The hydrogen we know that it is a colourless, odourless, tasteless, gas and it is not detectable by human senses. So, if there is any hydrogen leakage, we cannot find out that leak by human senses.

However, this is a potential asphyxiant; that means, if hydrogen is released in a confined environment, it displaces oxygen. And if that oxygen level reduces below a certain level below 20 percent it can lead to health hazard. Like, if the level is between 15 to 19 percent there will be a reduction in the human activity, if it is 12 to 15 percent in that case the respiration will increase, pulse rate will increase. If it is between 10 to 12 percent then giddiness, if it is between 8 to 10 percent then unconsciousness, and if it is less than 8 percent then it can be life threatening as well.

Another important property of hydrogen is its buoyancy, hydrogen has the highest buoyancy on earth, it is 14 times lighter than air. If there is any leak it moves upwards and that is the biggest safety asset of hydrogen. If there is a leak it has a tendency it has an ability to flow away from the accident site; as such, the hydrogen leak that will very fastly diffuse it will combine with the air in the environment. And the concentration of hydrogen will reduce below the lower flammability limit making it much more safe.

So, the important characteristic that it does not get accumulated in unconfined space is the biggest asset which is associated with hydrogen. This is against the heavier hydrocarbon, where in case of heavier hydrocarbon they form a huge combustible cloud and that could lead to even dangerous accidents then compared to hydrogen. The examples of such accidents in past have been in Flicks Burg 1974 and in Bruce field 2005, where there was such hydrocarbon cloud explosion fire followed by explosion and that has led to a lot of loss.

It has been found that the buoyancy has more effect compared to the in the dispersion of hydrogen compared to its diffusivity. Diffusivity also plays an important role as well, because the diffusivity of hydrogen is if we compare with methane, it is about 3 times higher for hydrogen. And it is an order of magnitude higher than that of gasoline vapor; so, as such hydrogen diffuses very fast and it becomes safe in case of leakage.

This is a challenge when it comes to storage of hydrogen because it diffuses fast. Now, these are some of the properties where we have compared hydrogen with the closest one being the natural gas. So, the density we can see there is an order of magnitude difference and the other parameters. Now, hydrogen we know that it has a low viscosity together with its small size of hydrogen molecule, it becomes very easy for hydrogen to achieve very high flow rates.

In case of any leak which occurs at the pipings, fittings, seals or walls and that leak results into very fast escape of hydrogen. Another important characteristic of hydrogen is that it burns in clean environment with an invisible flame. In a clean environment we mean that if there is no other material around which could burn, if the other material burns then there will be volatiles that will be released and then we can see the hydrogen flame. However, if it is a clean environment the hydrogen burns with a flame which is invisible.

And as such that could be more dangerous in the sense that the average adiabatic flame temperature for hydrogen it is very high. It is like 2403 kelvin and as such it can cause very severe burns as well as very severe incidents as well. Now, if we see the flammability limit of hydrogen in air, at normal temperature and pressure it ranges in between 4 percent to 75 percent as against that for natural gas which is 5 to 15 percent.

So, we can see here that the flammability limit for hydrogen is very wide and that makes it like the leaner mixtures of hydrogen with air or oxidizer can form a combustible mixture. At the same time the concentrated mixture 75 percent of hydrogen in the in air that can also form a combustible mixture and provided if there is any ignition source can lead to fire.

Now, these flammability limits that can further expand; so, this is at NTP Normal Temperature Pressure, the lower flammability limit is 4 percent. However, if we see that at 100 degree centigrade, then this is 3 percent; so, this also changes and this expands depending upon temperature, pressure. Burning velocity of hydrogen is 2.65 to 3.25 meters per second, as against the natural gas which is 0.38 meters per second. So, we can see that it is an order of magnitude higher for hydrogen.

This burning velocity it depends upon temperature, pressure, composition and it gets very difficult to arrest to quench to confine a flame which comes from hydrogen. It is explosion it is very difficult to confine, if it is detonation because the velocity involved in the detonation is 3 orders of magnitude higher. And the pressures involved the speed involved in detonations these are much higher than in deflagration. Now, what are these terms that we will see in the next class.

The escaped hydrogen is very easily ignited if there is any ignition source. Now, this ignition source can be a strong ignition source or a very weak ignition source, but the minimum ignition energy of hydrogen in air we can see it is very small. So, for hydrogen it is 0.017 milli joule, as against natural gas which is 0.31 milli joule; that means, it can be ignited very easily if there is any ignition source.

Now, this ignition source can be open flame, it can be electrical short circuit, it can be a hot surface, it can be a spark, a person smoking, or even it could be a static charge that could initiate the process of ignition. So, it is required for hydrogen safety that any sort of ignition source should not be in the proximity of the place where we are using hydrogen, hydrogen as such as an electrical insulator.

However, when hydrogen flows or because of any agitation there is if there is a movement in the liquid hydrogen or gaseous hydrogen there is any agitation while we are transferring the storage vessel. In that case that itself may generate static charge and as such all these storage vessels these are grounded; so, as to avoid that static charge.

Hydrogen flames these are very difficult to quench, their quenching distance lowest quenching distance is 0.64 millimetre, as against that for gasoline which is 2 millimeter. That means hydrogen flames they travel very close to the cylinder and that makes them very difficult to quench and they also have a tendency to backfire.

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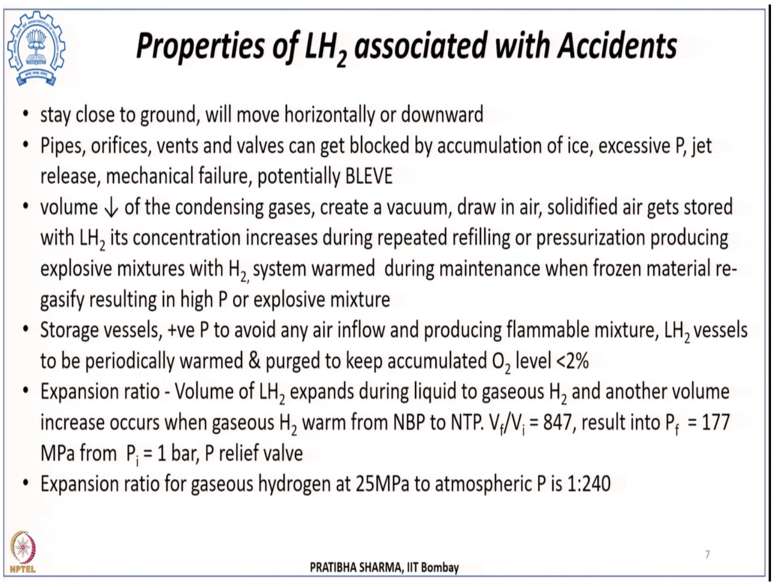

So, what we have seen earlier was the properties of gaseous hydrogen associated with the accidents. The properties of liquid hydrogen we need to consider when it comes to using liquid hydrogen transporting or storing liquid hydrogen. Now, there is a difference between the compressed hydrogen and the liquid hydrogen. The major difference is if there is a leakage or if there is a spill of liquid hydrogen, the density of liquid hydrogen at these cryogenic temperatures is very high and its density is higher than air.

So, if there is a liquid hydrogen spill, it will move close to the ground and immediately after the release it will move downward. So, it will continue to stay close to the ground and thereafter after some time it will gain heat from the environment that liquid hydrogen will start evaporating and then it will convert into gaseous hydrogen. So, it is if in that particular time there is an ignition source that can lead to fire or explosion or the BLEVE.

Another interesting thing that we need to note here is that the pipes, orifices, vents and walls. If there is air inflow into these elements then the moisture in the air that can get condensed into the liquid hydrogen and that can block these components like the pipes, orifices, vents and walls. For example, if there are there is a pipe between two walls, the air can get condensed can form ice and when it will reclassify the pressure will immensely increase and that later can lead to failure of that pipe.

So, that moisture in the air can get condensed inside these pipes and components which can later on lead to excessive pressure and release of hydrogen in the form of a jet. Resulting into mechanical failure and it could even lead to potentially boiling liquid, expanding vapor cloud explosion BLEVE. Now, when we are liquefying hydrogen or condensing any gas, we know that the volume of the gas it reduces.

Now, as the volume reduces it creates a vacuum, because of that there could be an air inflow it can draw air inside, that air will carry moisture, that air will solidify and get stored along with the liquid hydrogen. Now, during repeated filling, repeated pressurization, repeated filling, this concentration of air which gets into the liquid hydrogen will increase and at times it may produce a explosive mixture with hydrogen.

So, when the liquid hydrogen will be warmed for maintenance the frozen material that will re-gasify and that can result into a very high pressure and increased pressure and it can also lead to an explosive mixture. So, usually what is being done is, these storage vessels they are kept under a positive pressure. So, as to avoid any air inflow into the vessel, avoiding the formation of flammable mixture.

So, these liquid hydrogen vessels are from time to time these are warmed, they are purged to remove that condensed air that gets into the oxygen level that is kept below less than 2 percent by warming and purging from time to time. Now, when liquid hydrogen spill takes place, this liquid hydrogen as mentioned that will form a cloud and that will move close to the ground unlike the gaseous hydrogen which rises very fast.

Now, this liquid hydrogen spill, that liquid hydrogen itself will convert into gaseous hydrogen by taking the atmospheric heat the surrounding heat. And that leak gaseous hydrogen which will be at normal boiling point will further convert into gaseous hydrogen at normal temperature pressure condition. Thus, this conversion from liquid hydrogen to gaseous hydrogen that will result into volume increase.

So, this volume of liquid hydrogen expands during this transition phase, transition from liquid hydrogen to gaseous hydrogen at normal boiling point, and then to gaseous hydrogen at normal temperature pressure condition. So, if we see how much is the volume change? This volume change, the final volume to initial volume ratio is 847.

So, the volume increases when liquid hydrogen forms gaseous hydrogen at NTP by 847 times and that could lead to an increase in pressure to 177 MPa from an initial pressure of 0.1 MPA. So, as such to release this excessive pressure, pressure relief valve is an integral part of liquid hydrogen storage facilities or places where liquid hydrogen is being used.

Similarly, there could be expansion when gaseous hydrogen compressed gaseous hydrogen leak is developed. So, expansion ratio for gaseous hydrogen which is say stored at 25 MPa and if there is a leak to atmospheric pressure then the expansion ratio is of 240; so, it is 1 is to 240 from 25 MPa to atmospheric pressure.

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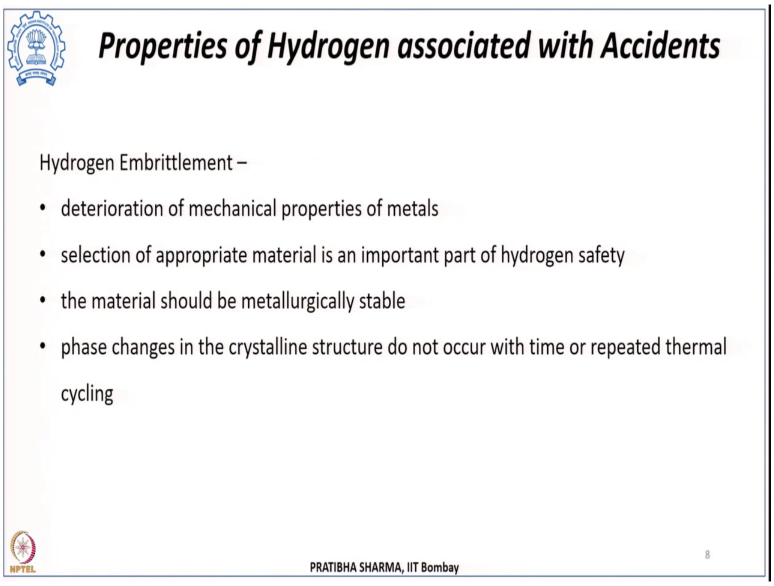

Hydrogen embrittlement we have seen earlier that this is the major challenge when it comes to selecting the materials for hydrogen storage. Whether these are different materials for confining for hydrogen storage, for pipings, fittings, tubings, walls and all the peripheral components. When these materials are subjected to hydrogen or when they come in contact with hydrogen for a longer duration at a certain temperature and pressure the properties of the material changes.

There is deterioration in the mechanical properties of metals which is observed, the metals they usually change their characteristics from ductile to brittle. And as such it is very important to select an appropriate material when it comes to hydrogen safety. So, that material which is selected should be metallurgical stable and the phase change should not occur with time with repeated thermal cycling.

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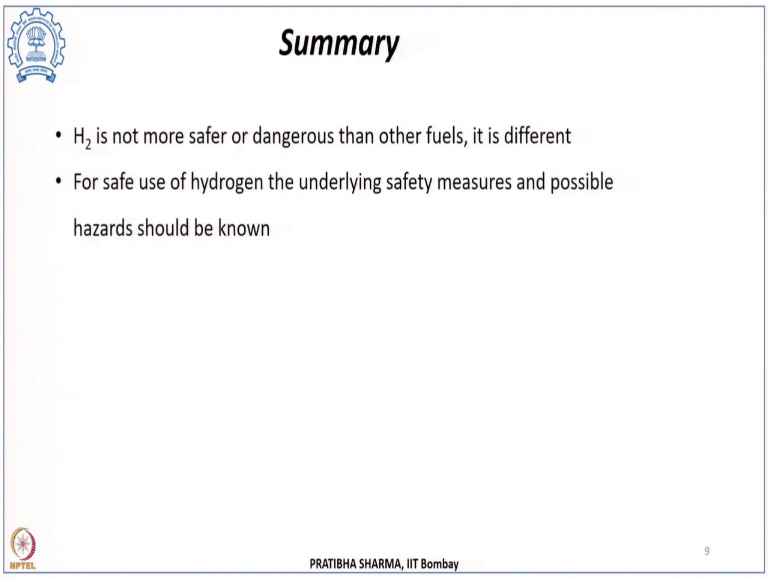

So, to summarize this part we have seen the different properties associated with hydrogen, we have seen past accidents some of the past accidents that have occurred when hydrogen was being used. It would not be correct to say whether hydrogen is more safe or more dangerous than other fuels, best would be to say that it is different from other fuels.

And for safe use of hydrogen the underlying safety measures and possible hazards we should know, and these should be taken care of at all the points in the hydrogen energy value chain.

Thank you.