Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 38

Cryogenic and Metal Hydride based Hydrogen Compressors

In the previous classes we have seen the different mechanical compressors which can be used for Hydrogen Compression. We have also noticed that they have several disadvantages like they have many moving parts as such there as lot of vibration, noise being created, at the same time these systems are quite complex and bulky require a larger footprint area, they have a high energy consumption and it is very difficult to get the heat transfer being done use in these compressors.

However, another option could be use of non mechanical compressor and these non mechanical compressors as against the mechanical compressors have advantage, that they do not have moving parts. And as such the operation is very quiet, it is noise free, at the same time the OPEX-the operation and maintenance cost in such non mechanical compressor is comparatively lower.

The design of these compressors is simple they are more compact, even some of the compressors which are thermally driven compressors the energy input which is required for the compression process can come from the waste industrial heat. So, in today’s class we will start with looking at the non-mechanical compressors. The first of this type is a cryogenic compression.

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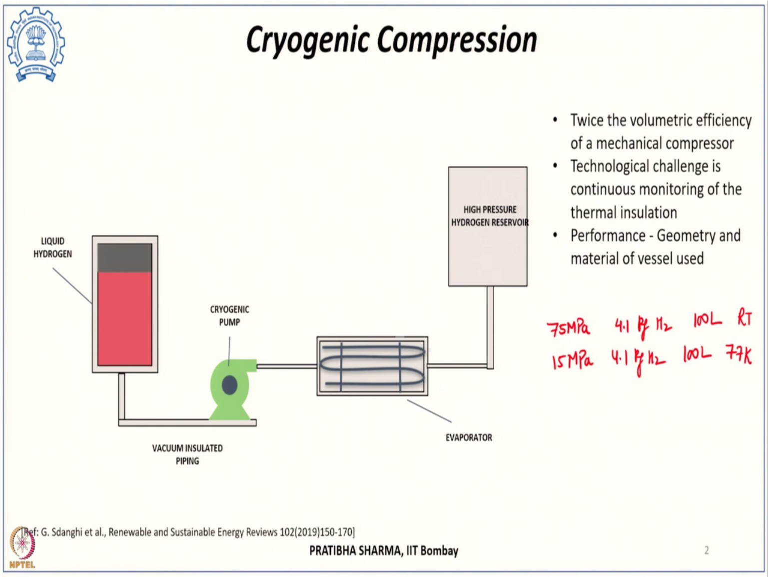

Now in Cryogenic compression this is actually a combination of hydrogen liquefaction and compression and as such there are benefits of both liquefaction and compressed storage of hydrogen. At the same time there are challenges also associated with both the processes. Now in this method instead of compressing gas at ambient temperature to higher pressure, liquefied hydrogen is a pressurized and then it is stored in a cryo-compressed tank. So, again the cryo compressed tank has to hold higher pressure at the same time liquid hydrogen temperatures.

So, in this particular method the amount of fuel that can be stored is 2 to 3 times more then it could be stored at ambient temperature in a compressed gas. For example, if at 75 MPa we need to store about say 4.1 kg of hydrogen and that requires say 100 litres at room temperature. In that case if we reduce the temperature of the gas to 77 kelvin. So, the same volume same amount we can store at a reduced pressure of 15 MPa.

So, as such the volumetric density improves when it is a cryo compressed method of storage. However, the cryogenic compression this involves technologically sophisticated modular elements and these are sequentially connected, like there will be a liquid hydrogen storage tank which is connected by means of an vacuum insulated piping to a cryogenic pump.

Now, all these accessories the containers needs to be well insulated. So, that there should not be any heat inflow from the surroundings into the system. And as an when there is a requirement of hydrogen it can pass through a vaporizer or an evaporator and downstream we can get a high pressure hydrogen.

But this method has volumetric efficiency which is twice as high as a mechanical compressor, the major challenge that remains with this cryogenic compression method is that we have to continuously monitor the thermal insulation and this is because the holding temperatures are low and there should not be a heat inflow into the system.

Also the performance of such systems that depends upon the geometry as well as the vessel material which we have used. So, insulation compression both the phases of the compressed gas and the liquid are stored as such the geometry and the material matters here in cryogenic compression.

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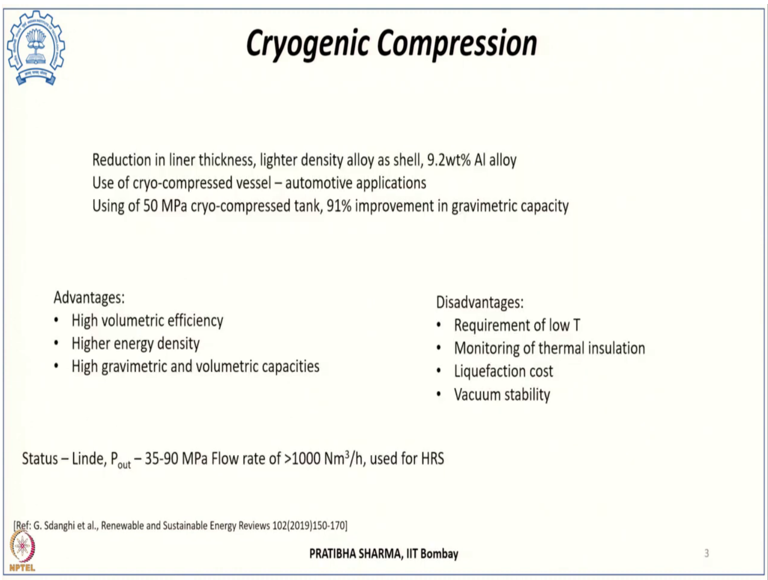

Now there have been several advancement in the whole process of compression, like the inner composite tank it is liner its thickness has reduced over a period of time, then the use of lighter density alloys like aluminium. As a shell material that also improves on to the gravimetric capacity like with aluminium alloy it is 9.2 weight percent, besides if say for example we are using a 50 Mpa cryo compressed tank. Then it is observed that as against the compressed hydrogen tank the improvement in gravimetric capacity of about 91 percent is observed.

At the same time the mass of carbon fibre and composite which is required for such tanks in a cryo-compressed hydrogen tank reduces by about 46 percent and cost reduces by 21 present. So, that is an advantage of storing in a cryo compressed form. Now the use of cryo compressed vessels that has already been demonstrated in different automotive applications, there have been several prototypes already being demonstrated like there have been hybrids like by Toyota Prius and BMW.

Now, there are different advantages of cryogenic compression it not only ensures higher volumetric efficiency, but higher energy density at the same time higher gravimetric and volumetric capacities. But the major disadvantages are since there is a requirement of low temperature as such the process is cost intensive as well as energy intensive. At the same time continuous monitoring of the thermal insulation is required, since we need to liquefy hydrogen as such the cost of liquefaction adds up to the process and the biggest challenge is the vacuum stability.

So, if it is desirable at ten years of vacuum stability that is very difficult to attain the reason being usually these vacuum stability is obtained when it is a metal which is being baked for a higher temperature, but here we are using a composite tank.

Now there if we look at the status Linde is well known for manufacturing such cryo compressed containers and they have already manufactured like with the pressure output which we can get of 35 to 90 MPa for flow rates of higher than even 1000 normal meter cube per hour and these have been used at hydrogen refuelling stations to fill fuel cell electric vehicles.

So, this is one of the non mechanical type of compression, the another non mechanical type of hydrogen compressors are Metal Hydride Compressors. Now these are thermally driven devices they are like the thermal sorption type of compressors.

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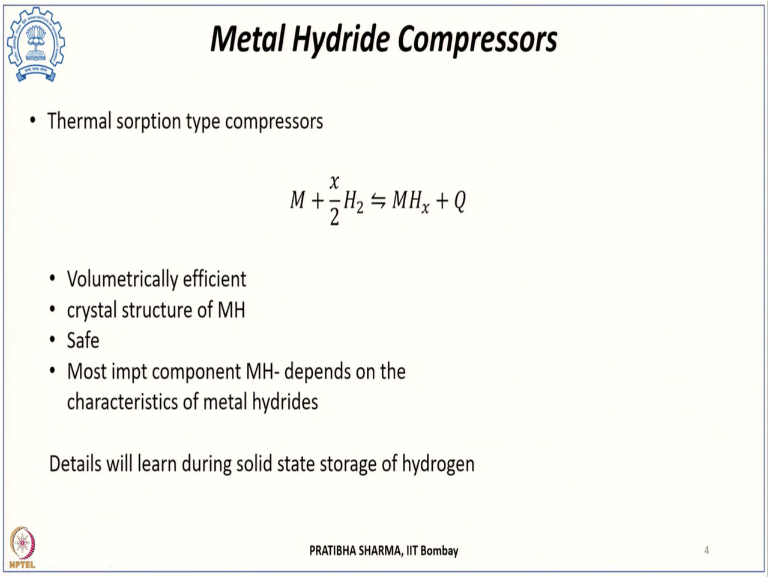

And in them the heat energy is converted into gas energy. So, the basically the driving reaction is a metal which could be a metal or an alloy or it can be an intermetallic compound it reacts with hydrogen to form metal hydride and heat is evolved in the process. So, this forward reaction is an exothermic reaction. However, when the required heat is supplied to the metal hydride the reverse reaction of desorption occurs wherein we get the hydrogen back.

So, this is a reversible reaction and the advantage of this reaction is that the reaction is highly volumetrically efficient. So, we can store large quantities of hydrogen in these metal hydrides roughly like if could be even 100 grams per litre and the storage of this hydrogen or the hydrogen gets into the metal hydride crystal structure occupying the place inside the crystal this method is quite safe in storage. The reason being if there is a leak in case of any accident then the reversible reaction we know it is endothermic reaction.

So, for the release of hydrogen certain amount of heat has to be provided. So, even if in case of a leak there is a hydrogen evolution taking place with time the temperature of the system will drop and that will reduce the rate of hydrogen evolution and as such it is a safe method. Now the in this reaction the major at the most important component in the metal hydride based compressors is the metal hydride itself and it depends upon the characteristics of the metal hydride the compression, like the characteristics like what is its gravimetric and volumetric capacity. It also depends on the kinetics of this reaction, it depends upon the thermodynamics of the process, it depends upon the thermal conductivity of these metal hydrides.

Now, we will study much more detail about these type of hydrides when we will study the solid state storage of hydrogen. Here we will just look at some of the fundamentals which are essential to know when we study these type of compressors. Now to understand some of the Fundamentals related to these metal hydrides if we see this reversible reaction.

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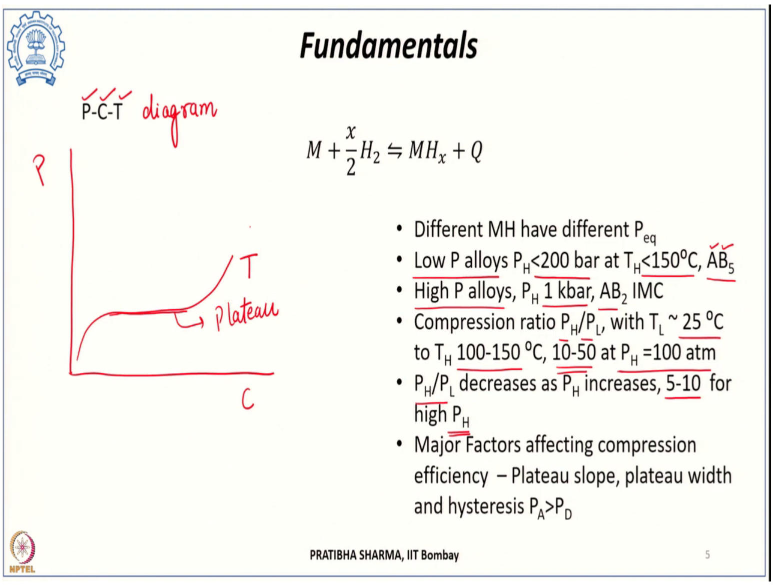

In that case the equilibrium of this reaction is interrelated to the pressure, the composition, the concentration of hydrogen in the solid phase and the temperature and this is represented by a pressure composition temperature diagram PCT diagram.

Now, if we plot a PCT diagram wherein we can plot the pressure composition at a particular temperature we will get curves, these curves this is at a temperature T. Now if we see this curve there is a region which is flat this region which is flat this is also known as plateau region and different metal hydrides may have different this plateau pressure at different temperatures.

So in fact this PCT is a characteristic of different metal hydrides they have different equilibrium pressures at different temperatures and that depends upon the interaction of these hydrides with or these metals with the hydrogen. Now, we can get different this pressure is the equilibrium pressure, the plateau pressure and this can be different at a particular temperature for different metal hydrates.

Now if there are low pressure alloys in that case for them the pressure of desorption or the higher pressure can be less than 200 bar and that is at temperatures less than 150 degree centigrade. Now such metal hydrides which are which have this characteristic of a desorption pressure of less than 200 bar or at temperatures of 150 degree centigrade these are commonly the AB5 type of metal hydrides.

So, A and B we will see in more detail in solid state storage, that these are different metals which have either a higher hydrating tendency or a lower hydrating tendency. There can be even high pressure alloys where the pressure can be as high as 1 kilo bar and under this category comes the alloys AB2 type of alloys inter metallic.

Now using these different metal hydrides we can get a compression ratio like the higher pressure to the lower pressure ratio. Let us say if the starting temperature is 25 degree centigrade the lower temperature is 25 degree centigrade and it is raised to a temperature of 100 to 150 degree centigrade, we can even achieve pressures of 10 to 50. But this is when the higher pressure is only 100 atmosphere.

Now, as this desorption pressure or P_H increases the compression ratio also decreases and for higher pressures this compression ratio that can be achieved is 5 to 10. Now there are different factors which govern this compression process like the factors which govern is the plateau slope. So, this is an ideal curve which is showing a flat plateau; however, this may not be flat in the real cases for different hydrides, there are some hydrides which may have a sloping plateau.

So, this plateau may have a slope. So, the major factors on which this compression efficiency depends is the slope of the plateau, how much is the width of this plateau that will decide on to the reversible storage capacity of these metal hydrides. How much amount of hydrogen they can take reversibly, at the same time there may be hysteresis.

So, if this is the absorption curve then a desorption curve may be different. So, it may not return back into the on the same path, rather the absorption curve may be different from the desorption curve. So, the absorption pressure usually it is higher than the desorption pressure giving rise to a hysteresis. So, in all these 3 parameters also the equilibrium pressure, the compression efficiency depends on.

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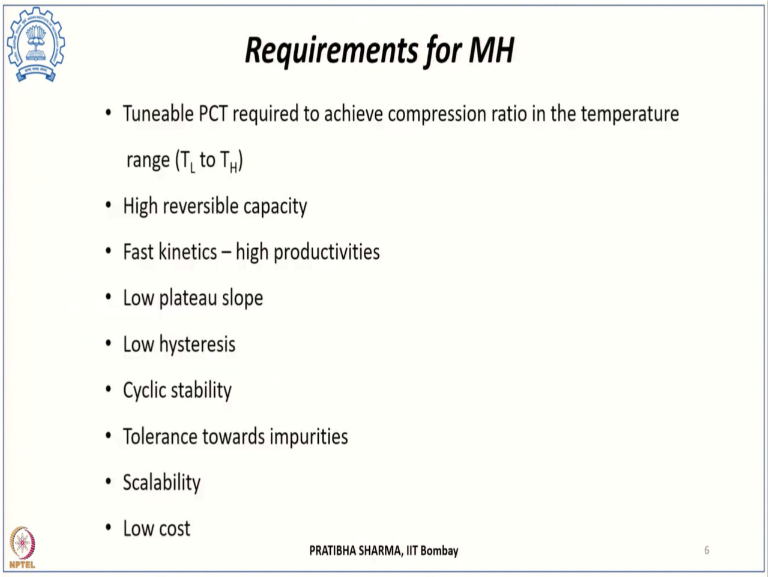

Now the major requirement when we select particular metal hydride as mentioned this is the most important component of the hydrogen compression, in the metal hydride based compressors. So, the requirement in terms of the metal hydride when we select a particular metal hydride is that it is pressure composition temperature curves these should be tuneable.

So, that we can achieve the desired compression ratio when the temperature is changed from T_L to T_H. At the same time they should have a high reversible capacity, they should have fast kinetics, faster absorption and desorption and that could lead to higher productivities. They should have a lower plateau slope, lower hysteresis, good cyclic stability they should be operational for large number of cycles the material should be tolerant towards impurities.

So, these impurities can be present in the hydrogen gas and it should not change it is characteristic when subjected to these impurities or it its performance should not degrade in the presence of these impurities, that is under idealistic condition required. The materials that are used should be scalable and of low cost. So, these are the desired properties of the metal hydrides which can be used for hydrogen compression application.

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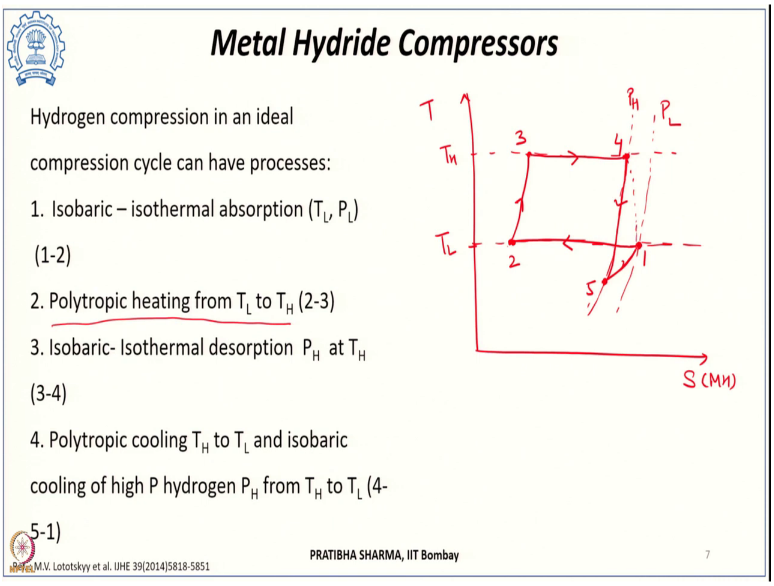

Now, if we look at the metal hydride compressor then in case of an ideal metal hydride compressor cycles it need to have different processes. Now if we draw it on a T-S plot let us say the higher temperature T_H the lower temperature T_L, then we can represent it by a process let us say these are the isobars if we draw a T-S diagram for the compression cycle considering it an ideal cycle.

So, starting from point 1 to point 2 this is an isobaric isothermal absorption by the metal hydride taking place from at a temperature which is T_L and pressure P_L. So, this is an isobaric isothermal absorption taking place when the system moves from state 1 to state 2, so this is absorption.

Now, then there occurs a poly tropic process that is the heating process, wherein the system moves from 2 to 3 and this is the heating which is done from T_L and the temperature rises from T_L to T_H in the process from 2 to 3. Now the third step involves an isobaric and isothermal desorption at this point 3 to 4 there occurs an isobaric isothermal desorption at a temperature of $T_{H,}$ at a pressure of P_H and the process is represented by 3 to 4. And finally there is a poly tropic cooling that occurs from point 4 to 5 and then to 1.

So, here in this poly tropic cooling from T_H to T_L and then isobaric cooling of high pressure hydrogen occurs from P_H point and from temperature T_H to T_L. So, this is a step 4-5-1. So, this is a cycle compression cycle being represented on a T-S plot.

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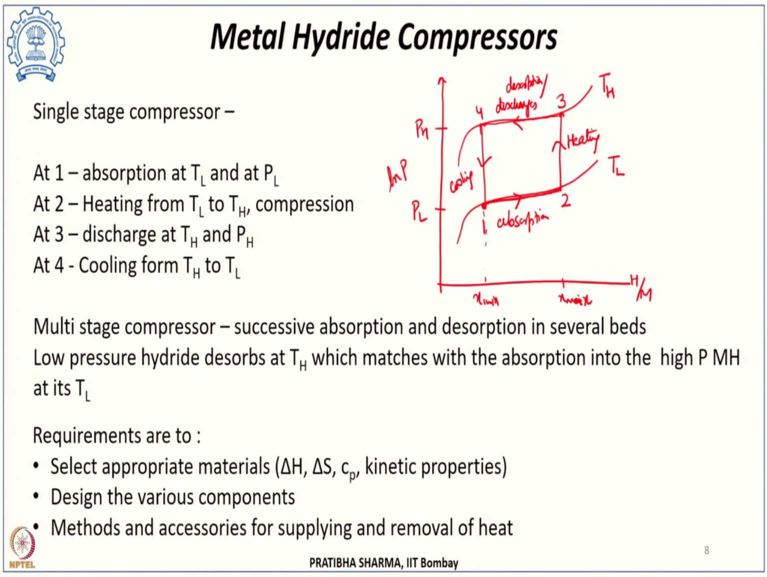

The same we can represent on a PCT curve on a pressure composition isotherm. Let us say we have 2 different isotherms, so the lower T_L temperature, higher temperature is TH and in this process ln of P is being plotted here. So, in the entire process from point 1 to point 2 this is an absorption that is going to take place in the metal hydride hydrogen is being absorbed this is the minimum and this is the maximum concentration.

So, in the absorption process as the system absorbs hydrogen and it moves from the state 1 to state 2 at a temperature of T_L and at a pressure of P_L. At point 2 there is heating of the metal hydride bed, so that its temperature rises from T_L to T_H and this results into the compression of hydrogen at and it reaches a pressure of P_H.

So now, the pressure P_H is attained at point 3 then the discharge occurs at a temperature T_H and pressure P_H. So, this is absorption 1 to 2 then heating to take its temperature from T_L to TH, then there is desorption from 3 to 4 or discharge or delivery at temperature TH and pressure PH and finally it is cooled from point 4 to point 1.

So, that its temperature falls back to its initial temperature TL. So, TH to TL, 4 to 1 step this is cooling. So, this is a single stage compressor a pressure composition isotherm in a demonstrated in a pressure composition isotherm. So, there are 4 steps involved in absorption of hydrogen, then when it is heated that heated then the pressure increases the temperature increases of the system.

Then at that when it attains the discharge pressure which is PH the hydrogen is discharged and then it is being cooled from 4 to 1. So, that it attains the pressure which is lower after discharge and at the same time the temperature of the bed also reduces.

Now, this is a single stage compressor, but usually with a single stage compressor the final pressures attained, the delivery pressures attained are not very high. So, multi stage compressors are required in which similar absorption and desorption cycle takes place and that is successive absorption and desorption cycles takes place but in several beds.

These are matched in such a way that the low pressure hydride which desorbs at a temperature T_H that is in synchronization with the absorption of the next stage. So, the second stage will be superimposed and synchronized in such a manner that the desorption temperature of the first stage matches with the absorption temperature of the second stage and in this way we can couple these stages together.

So, as to achieve a multi stage compression and we can get the desired pressure ratio or the compression ratio. Now what is desired in such metal hydride based compressors is we need to have an appropriate metal hydride which is the key component, such that it should have the desired thermodynamic properties.

The ΔH, ΔS values, it should have the required heat capacity, the kinetic properties, so as to have this compression having a better productivity faster kinetics. We need to also design the different components of the compressor and there should be different methods and accessories, so as to supply the required amount of heat and remove the required amount of heat.

Usually these metal hydrides they have poor thermal conductivity, as such we need to improve on to their thermal conductivity or we need to have a better heat exchange surfaces involved, so that the reaction does not stop. Now usually when we talk about these metal hydride storage vessels or these tanks these are tubular in nature they could be cylindrical.

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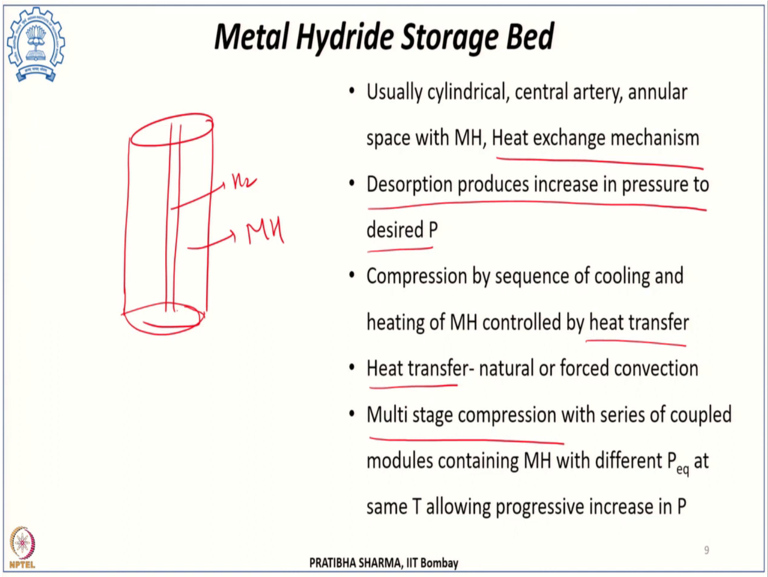

So, if we consider a cylindrical metal hydride bed in that case there is a central artery which can which carries hydrogen and the annulus that has the metal hydride being stored. And there could there should be a heat exchange mechanism being integrated, such that during the forward reaction when the metal hydride is being formed when metals are subjected to hydrogen pressure.

In that case the heat which is formed in the metal hydride bed needs to be removed, at the same time during the reverse reaction when hydrogen needs to be desorb that amount of heat has to be supplied uniformly. So, for that a heat exchange mechanism need to be there for in for more details when we will look at the metal hydride hydrogen storage systems design.

Now, absorption takes place and then when the when the required pressure we need to get the required pressure desorption is carried out, so that there is an increase in the pressure and finally we can get the desired pressure. Now here in the whole process a series of cooling and heating of metal hydride bed is done.

So, as to achieve the compression and that entire process is being controlled by the heat transfer. So, here heat exchange or thermal management plays an important role and this heat transfer can be either by means of natural or forced convection, it can be either air cooled or heat transfer fluid can be either air it can be water or it can be oil depending upon what temperatures are desired.

And with the help of multi stage compression with a series of such coupled modules having metal hydride or such metal hydride beds with different equilibrium pressure at the same temperature. We can have incremental pressure between the different stages or we can have progressive increase in the pressure with several such stages being added or in a multi stage compression process.

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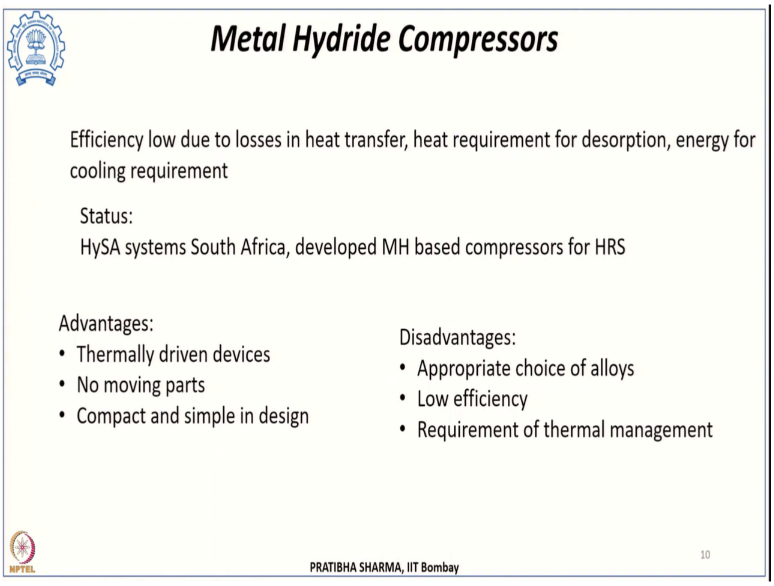

Now, metal hydride compressors they have efficiencies like less than 25 present at 423 kelvin, but there are several losses also involved. The efficiency of these metal hydride compressors further reduces because there are several losses involved in the heat transfer, at the same time during the desorption there is a heat requirement for the desorption and for the cooling there again energy has to be supplied.

So, overall the efficiency reduces and it is at times less than even 10 present. Now, the status is that HySA systems they in South Africa they have developed several metal hydride based compressors and these have been integrated for hydrogen refuelling stations which is used for fuel cell powered forklifts.

There are several such demonstration on these metal hydrides based compressors. Now if we look at the advantages of these metal hydride compressors these are thermal driven devices. So, as such the waste heat from any a process heat or an industrial waste heat can be used to drive the process and improve the efficiency. There are no moving parts as such they are compact and simple in design, but the major disadvantages are that an appropriate choice of alloy is required and a proper selection determines the efficiency of the process.

The overall efficiency of compression is a low because of the several losses as mentioned and there is a requirement of efficient thermal management system for the removal as well as supplying the required heat of the reaction.

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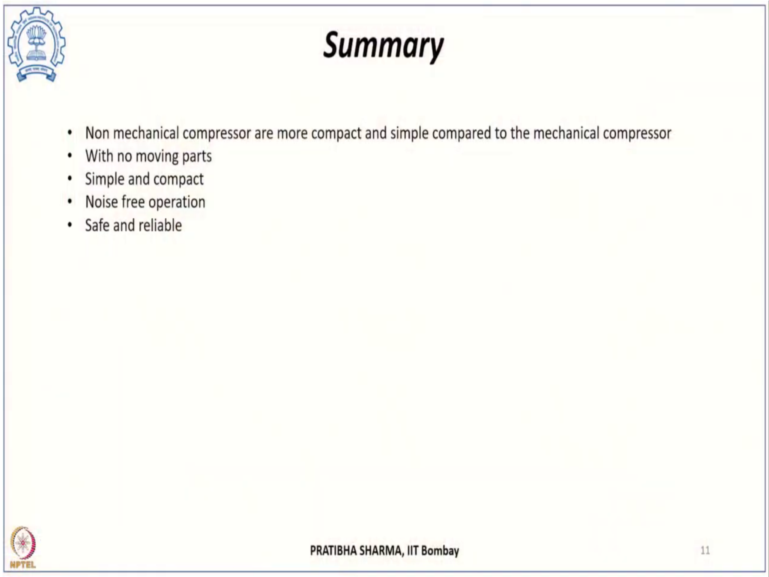

So, to summarize the non-mechanical compressors they are more compact and simple in design, compared to the mechanical compressors they do not have moving parts they are simple and compact they have noise free operation and they are much more safe and reliable.

So, other than the metal hydride based compressors and the cryogenic compression, we have seen today there are electrochemical compressors, there are adsorption based compressors which we will learn in the next class.

Thank you.