Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 43
Liquid State Hydrogen Storage

In the previous class, we have seen the ways in which we can liquefy hydrogen. What are the different challenges associated with liquefaction of hydrogen, how much is the energy associated with liquefaction and we have also seen that what are different cycles which are based on either pre-cooling or by means of expansion expanding or expander or expanding device which is being used. Now, once we have liquid hydrogen we have to store it in a container. So, in this class, we will see what are the hydrogen storage options when it is in the liquid state.

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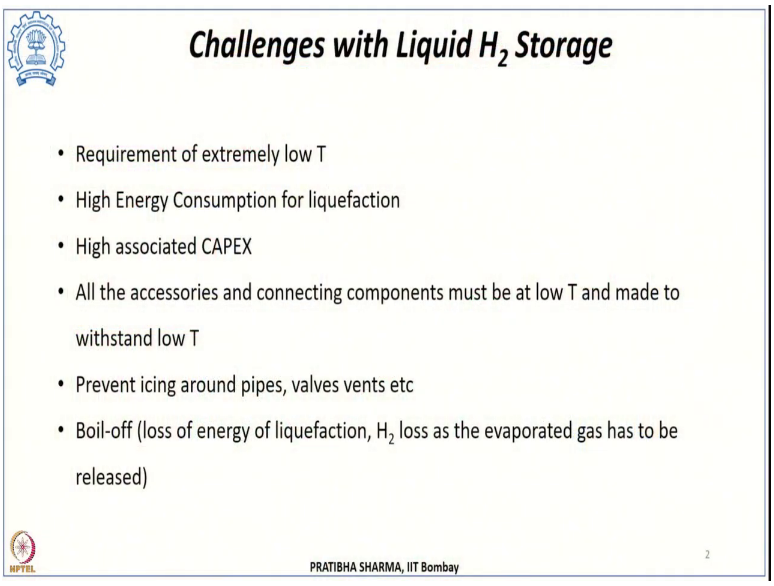

Now, the problems which are there when it comes to storing liquid hydrogen is we know that this hydrogen has to be stored at 20 K which is a very low temperature. We have already seen that it involves very high energy consumption when we liquefy it. At the same time the cost associated with liquefaction is also very high.

Now, once we are storing hydrogen which is at 20 K, all the accessories connecting components including tubings, pipes, valves, manifolds, all those must also be at that temperature. So, a chilling process is essential for all the connecting components. And it is essential that all these accessories should be able to handle that low temperature.

So, they should be made to withstand such a low temperature without undergoing major mechanical changes in the process. At the same time since the temperature involved are very low on these storage components on these valves, piping, vents, icing, should not take place because of the lower temperature. There should not be any condensation outside on the outer surface; icing should not take place, because that will unnecessarily increase the pressure and force. So, that should be as low as possible.

At the same time, the another major challenge associated with storing in liquid hydrogen form is the boil-off. Now, this boil-off is a process where in the liquid hydrogen which has been stored in a storage container tank or vessel. It evaporates subjected to several conditions that we will see. It evaporates, converts into gaseous hydrogen increasing the pressure inside the storage vessel. So, that increase of the pressure is known as pressure build-up and the process by which the liquid hydrogen converts or evaporates to gaseous hydrogen is known as boil-off.

Now, this boil-off is a major challenge, because it not only results into loss of energy which we have fed into liquefy hydrogen. So, that is not only an energy loss, but at the same time it is the loss of hydrogen because of the evaporation that has to be released into the environment, if it is not being used. So, that itself is a loss of hydrogen. So, energy loss at the same time loss of hydrogen results because of the boil-off.

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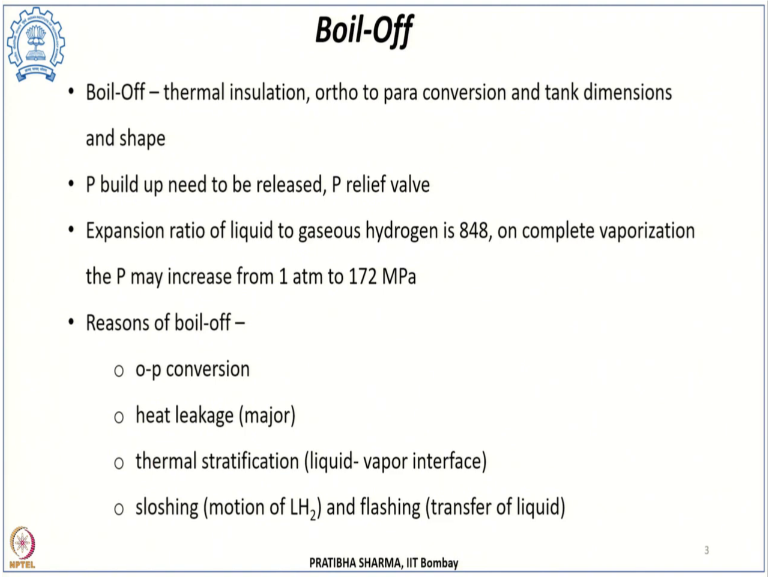

Now, this boil-off is in fact, correlated with the thermal insulation, how well is the tank insulated, because we have to stop any heat inflow from the surroundings into the storage vessel. The reason is we are storing hydrogen at 20 K and there is a very large temperature difference between the ambient and the temperature at which we store. So, we have to use very good thermal insulation, so as to prevent any heat inflow into the storage system.

At the same time the another reason for boil-off could be ortho to para conversion. Now, we have already studied in the previous class that this ortho to para conversion it is a very slow process. And it is essential that when it is stored in a storage vessel or tank, then this conversion should have already occurred.

Reason, the ortho to para conversion is an exothermic process. And if it has been incomplete while we have liquefied hydrogen, and still there is certain amount of ortho hydrogen, remaining in the storage tank that will finally, convert into parahydrogen, releasing heat and that will evaporate the hydrogen liquid, hydrogen into convert it into gaseous hydrogen. And that is highly undesirable.

So, this boil-off also depends upon what is the tank dimension, how large is the tank size, what is the capacity of the tank, what is the shape of the tank. The reason being the surface of the tank will be in the environmental conditions. So, higher, in that case we have to reduce the boil-off losses. So, we need to have lower surface to volume ratio. That means, the higher capacity tanks will have lower boil-off and shapes like spherical surface which has a lower surface to volume ratio will have lower boil-off.

But constructing a sphere is from the manufacturing point of view, does not have many advantages it is little complicated. So, usually these are either even cylindrical tanks also available. Now, these can be hold either horizontally or vertically. So, basically boil-off depends upon what is the quality of thermal insulation, ortho to para conversion and on the tank dimension and on to the shape because of this boil-off process because of evaporation of liquid hydrogen converting into gaseous hydrogen in the storage tank.

The pressure will start to increase it will build-up and that process is the pressure building up inside the tank. Now, once it has reached to a certain pressure which is the maximum allowable pressure of the tank, it has to be released. So, that gas has to be released and then a pressure relief valve is essential in such storage tanks.

Now, if we consider the expansion ratio, so from liquid hydrogen, if it converts into gaseous hydrogen, then the expansion ratio is 848. So, if the liquid hydrogen, it completely vaporizes from initially, let us say it is in the liquid state at 1 atmosphere if it vaporizes, then the pressure that will increase inside a storage vessel will be about 172 MPa and that is substantial.

We have to also understand that the in liquid hydrogen storage vessels they are meant for holding lower temperatures like 20 K but not very high pressures. So, these tanks they are made up of to have a very good insulation, these are super insulated vessels. But unlike the compressed hydrogen storage, they do not hold very high pressures. So, as such this increase in the pressure which is because of the pressure build-up that has to be released and that is the loss of hydrogen.

Now, there are different reasons for this boil-off, like as mentioned ortho to para conversion. However, the major reason is the heat leakage. So, from the surroundings into the system, however, good insulation we may use there may always be some amount of heat inflow and that is unavoidable. And that could be the major reason for the boil-off.

At the same time thermal stratification like because of the heat inflow, the density of the liquid hydrogen will be different and the one which is at a slightly higher temperature will come on to the top. And then there will be a stratification. So, there will be a interface which will be created.

At the same time certain amount may get evaporated. So, there will be a gas liquid interface which will be created, a liquid vapor interface which will be created, liquid is having a very poor thermal conductivity. So, all that can also increase the boil-off. There could be sloshing, now because of some movement of the liquid storage tank, it could be acceleration, deceleration, while transporting because of the movement of liquid hydrogen, motion of liquid hydrogen tank, their kinetic energy it gets converted into the thermal energy.

And because of this thermal energy, there will again be a boil-off. At the same, if we are transferring liquid hydrogen from one tank to another tank, so from a tank which is at a higher pressure to a tank which is at lower pressure usually like the main storage tank and then we are filling another auxiliary storage tank. Then, during the transfer of liquid there could be a process is, which is known as flashing that can also result into boil-off.

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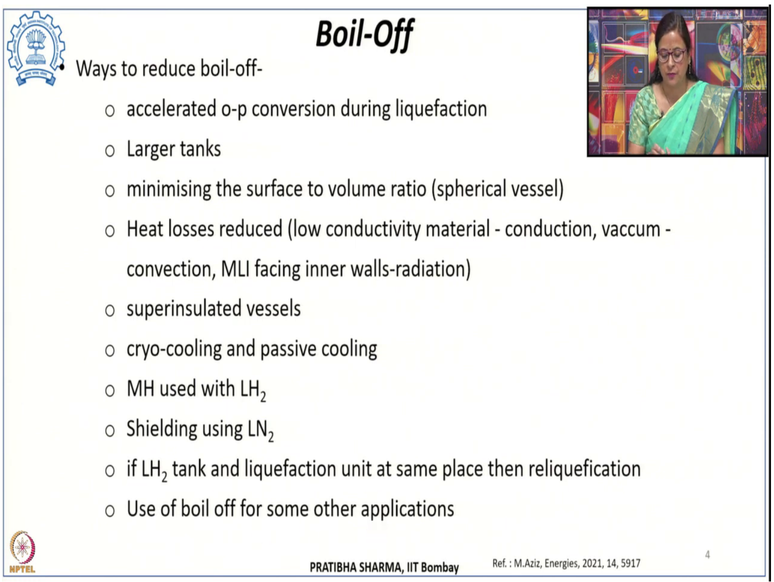

So, we can we have to consider the ways in which we can reduce this boil-off which is the major challenge when storing hydrogen in the liquid state. So, there can be ways in which we can reduce that. During liquefaction we have to convert it into parahydrogen. So, the equilibrium composition should be 99.8 percent of parahydrogen at the liquefaction temperature. So, it should be an accelerated ortho to para conversion which needs to be done during liquefaction.

And this can be achieved with the use of various oxide based catalysts. Another possibility is we can use larger tanks, this is because the smaller surface to volume ratio and that will result into lower heat inflow. So, we can have even spherical vessels that will again minimize the surface to volume ratio and reduce the boil-off losses.

There can be various heat losses that needs to be reduced in the process, like the design of the tank itself should be such that the heat inflow to the liquid hydrogen should be as low as possible. And this can be done that the conduction heat flow could be reduced by using a low conductivity material for the tank.

We can have a vacuum insulation provided vacuum provided in between the two tanks that we will see the design of these tanks and that vacuum will prevent the convective heat flow. And then, we can include multilayer insulation which faces the inner wall to reduce the radiation related heat losses.

And important is that these should have very good insulation. So, we have to use superinsulated vessels for hydrogen storage in the liquid form. At the same time we can provide cryocooling or passive cooling, we can have shielding using liquid nitrogen. So, in very large sized tanks a liquid nitrogen flow is maintained, so as to reduce the heat inflow and maintain the outside temperature to a liquid hydrogen temperature.

At the same time like, there are certain studies wherein they have shown that the losses which are there because of the boil-off that can be used in a metal hydride, so as to use it for different applications; so, whatever hydrogen which is released after the pressure build up because of the boil-off that can be taken up by a metal hydride and then that can be used for other applications.

If the storage tank for liquid hydrogen storage and the place where liquefaction is being done they are at the same location then whatever is the loss of hydrogen the boil-off, the gaseous hydrogen which has to be released, that can be again re liquefied and then we can again store back into that liquid hydrogen tank. Also, it is proposed that the boil-off which occurs or the hydrogen loss which has to be released, that can be used for various other applications.

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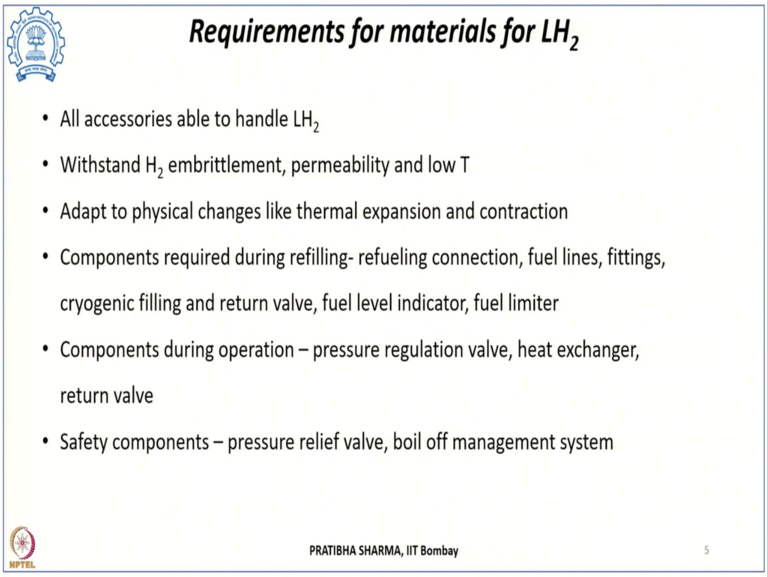

Now, there are materials requirement when we talk about liquid hydrogen storage. The important requirement is that all the accessories, the storage tank, the peripheral equipments, components, all needs to be able to withstand that temperature of the liquid hydrogen. So, they should be able to handle that liquid hydrogen temperature.

They should withstand hydrogen embrittlement, permeability, and low temperature. Now, hydrogen embrittlement as against the gaseous hydrogen storage or compressed hydrogen storage is much less in case of liquid hydrogen storage because hydrogen embrittlement that decreases as the temperature reduces. At the same time, the permeability is also lower and the materials which are selected are such that they have very low permeability.

Important is there will be physical changes like thermal expansion and contraction, subjected to pressure change. While filling the tank there will be a temperature change or while emptying the tank there could be a temperature change, all that could lead to thermal expansion and contraction. So, the material which is used for manufacturing the liquid hydrogen tank or the other components, they should be able to handle this thermal expansion and contraction, these physical changes.

Now, there are different components which are there other than the hydrogen storage tank, they should also have such characteristics. Like the components which will be required while refilling of the tank it will have a connection, that will be connected to the refuelling station or the refuelling device.

So, refuelling connection there will be fuel lines that will allow the fuel to flow through it. There will be fittings cryogenic filling and return valve, fuel level indicator, there will be fuel limiter. There will be several components which will be there along with the storage vessel. During operation there will be pressure regulation valve, heat exchanger and the return valve, and other safety components like the pressure relief valve and the boil-off management system.

So, all these components should also be able to handle liquid hydrogen temperature.

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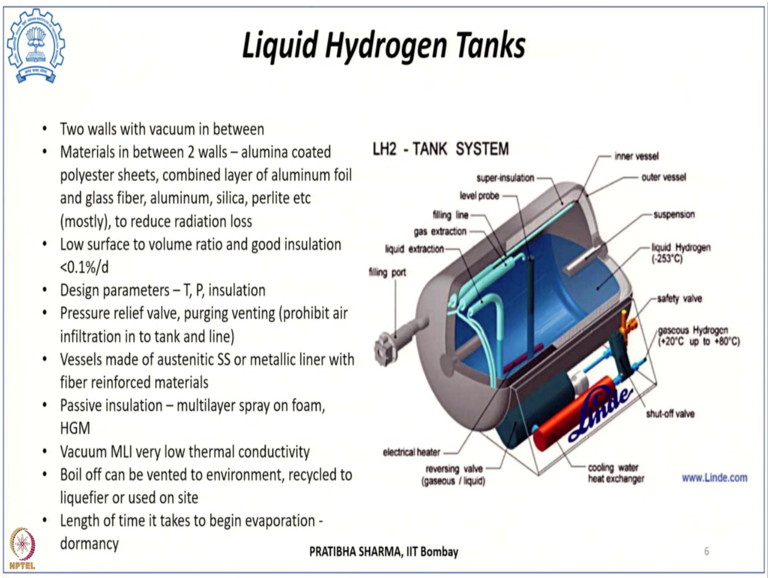

Now, if we see the design of a liquid hydrogen tank, it is basically made up of two tanks or it is two walls in the tank. So, an outer wall and an inner wall and in between is the vacuum in such tanks. So, these are super insulated vessels. There are two walls with vacuum in between.

Now, in between the two walls, the outer wall and the inner wall there are materials which are used, these are alumina coated polyester sheets or combined layer of aluminium foil and glass fiber. It could be aluminium or it could be silica or it could be perlite. Perlite is mostly used. There could be multilayer insulation which could be used and all this is introduced into the vacuum region, so as to reduce the radiation losses.

At the same time, the lower surface to volume ratio including very good insulation can reduce the boil-off losses to less than 0.1 percent per day. Now, that is there are several design parameters for such tanks what is the temperature, what is the pressure and insulation that needs to be considered.

There has to be a pressure relief valve, there has to be purging or venting arrangement. And this purging and venting arrangement is to prohibit any air infiltration into the tank and line and that could be very much detrimental. So, if there is a pressure difference, air can enter inside the tank and that can condense and that when it evaporates then it can form a mixture of hydrogen and the air later. So, it is essential that purging and venting arrangement should be provided.

Usually, the vessel is made up of either aluminium or stainless steel. So, austenitic stainless steel is used or it is it could be a fibre reinforced tank with metallic liner. So, as to hold the liquid hydrogen, and the passive insulation, it could be provided, it could be multilayer spray on foam, it could be hollow glass microspheres or it could be vacuum which has multilayer of insulation and that multilayer of insulation should have very low thermal conductivity.

Whatever is the boil-off that takes place or the gaseous hydrogen which is being formed in the tank because of the boil-off losses that has to be vent to the environment. Or it can be recycled to the liquefier or it can be used on site. Now, there is one more term which is used associated with the liquid hydrogen tanks is dormancy. This is defined as the length of time which it takes to start evaporation so, in the entire process, when there is a heat inflow initially the liquid hydrogen tank that is a closed system.

Now, with the flow of heat, certain amount of liquid hydrogen will evaporate to convert it into gaseous hydrogen. With time this amount will increase because of the heat inflow which is unexpected, undesirable, in spite of being a super insulated vessel. Now, this increase in the gaseous hydrogen content will start to increase the pressure inside the storage tank. They are meant to have a certain maximum allowable pressure; beyond that they cannot hold. So, that increase in the pressure is known as pressure build-up.

Thereafter, once it reaches to that pressure, the pressure relief valve vents off the gaseous hydrogen pressure from inside the tank. And that time when this evaporation starts, the length of the time when it begins to evaporate that is what is known as dormancy and that should be as high as possible.

So, if we look at the tank, then there are several other components we can see in the tank. There is a filling port, then we can see there is a liquid extraction port, gas extraction port, then there are filling line, there is a probe to check the level inside. Then there is a inner vessel, there is insulation in between, there is an outer vessel, there is a suspension and in between the tank is the liquid hydrogen which is being filled, there is a safety valve, shut off valve. There are cooling water heat exchanger, reversing valve and electrical heater. So, if it is gaseous hydrogen which is being desired for the utility.

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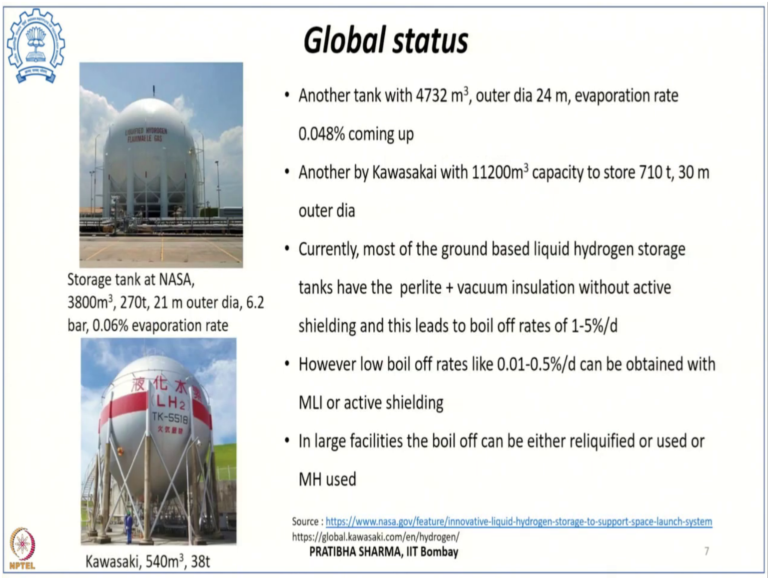

If we see the global status, there are tanks available from very small size to very large size of liquid hydrogen storage. Like, some of the representative examples are like the largest tank which is at NASA. So, that storage tank has a volume of 3800 meter cube and that can store 270 tons of liquid hydrogen that has an outer radii of 21 meter. And the pressure it can hold is 6.2 bar. So, as we have already seen spherical tanks and larger capacity tanks have a lower evaporation rate, for this particular tank the evaporation rate is 0.06 percent.

Another tank which is at Kawasaki, this is having a volume of 540 meter cube, and it can store 38 tons of liquid hydrogen; one more tank which is coming up at NASA that has a volume of 4732 meter cube and outer diameter of 24 meters, and in evaporation rate that will be 0.048 percent.

Similarly, another tank which is coming up at Kawasaki that will have 11200-meter cube of capacity which could store 710 tons of liquid hydrogen, and it will have an outer diameter of 30 meters.

Currently, if we see most of these ground based liquid hydrogen tanks they have the insulation which is perlite or vacuum insulation in the perlite and vacuum insulation without they do not have active shielding. And because of that there are boil-off which are in the order of point 1 to 5 percent per day.

However, we can reduce this boil-off losses to like of the order of 0.01 to 0.5 percent per day by using either multilayer insulation or active shielding. In very large scale facilities, either we can use metal hydride for capturing that hydrogen, which is released on boil-off. Or we can if the tank is located at the same place where liquefaction is done, then it can be re-liquefied or it can as such be used for various applications to reduce the boil-off losses or the losses which are involved because of boil-off.

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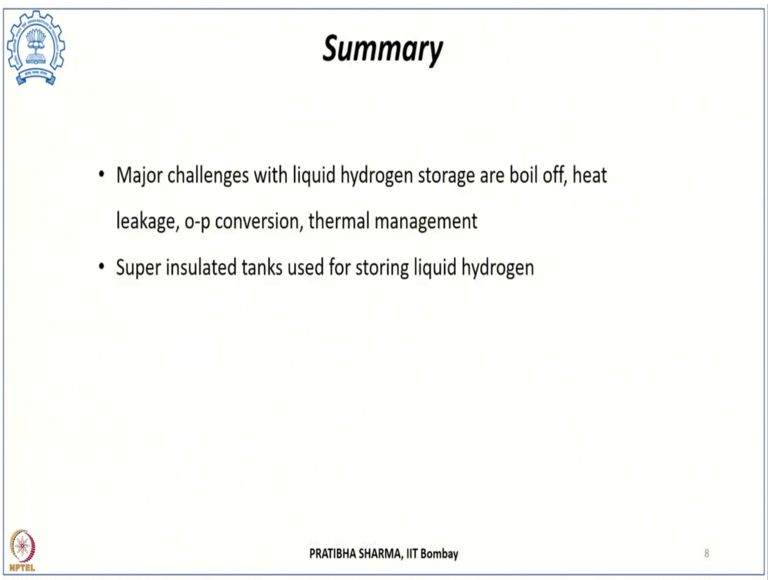

To summarize this part, we have seen in the various liquid hydrogen storage systems, what are the major challenges associated with that. The major challenge being like boil-off, if there is any heat input, or the incomplete ortho to para conversion that can also lead to an exothermic reaction.

So, thermal management becomes very essential. These tanks which are designed for holding hydrogen, these are super insulated tanks and they can store large quantities of hydrogen. They can be found in various capacity from small to large capacity tanks are available.

Thank you.