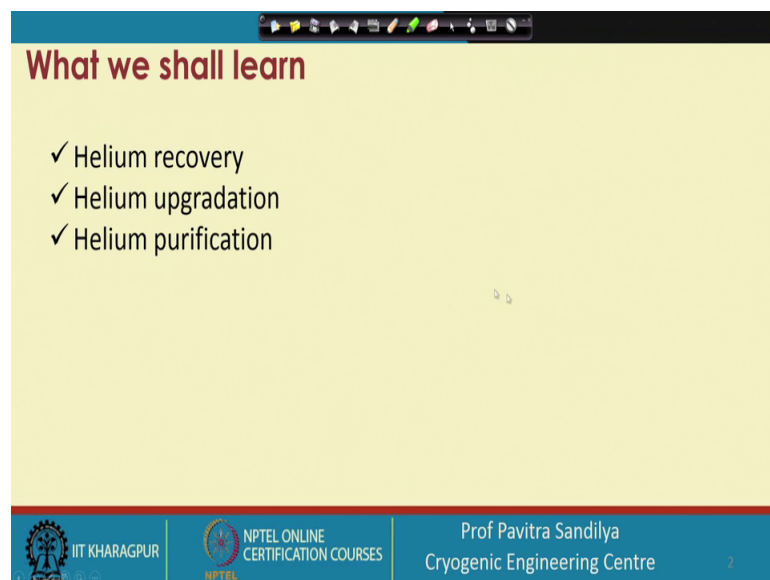


Upstream LNG Technology
Prof. Pavitra Sandilya
Department of Cryogenic Engineering Centre
Indian Institute of Technology, Kharagpur



Lecture – 56
Helium recovery, upgradation and purification

Welcome. Today, we shall be learning about something the helium recovery. Helium as we know that it is a trace components, so but this is very important component. So, this lecture will be on helium recovery upgradation and purification.

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The slide is titled "What we shall learn" and lists three bullet points: "✓ Helium recovery", "✓ Helium upgradation", and "✓ Helium purification". The slide is part of an NPTEL online certification course by Prof. Pavitra Sandilya at IIT Kharagpur's Cryogenic Engineering Centre. The slide number is 2.

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We shall be learning about all this three processes separately.

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Introduction

✓ A number of trace components exist in NG which may create processing, product quality, or environmental problems if present in high concentrations.

TRACE COMPONENTS

- Hydrogen
- Oxygen
- Radon (NORM)
- Arsenic
- Mercury
- BTEX
- Helium

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So, as we found that earlier that among the trace components helium is one of them and, but this has been treated separately, because this is a quite important component.

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Helium: Uses

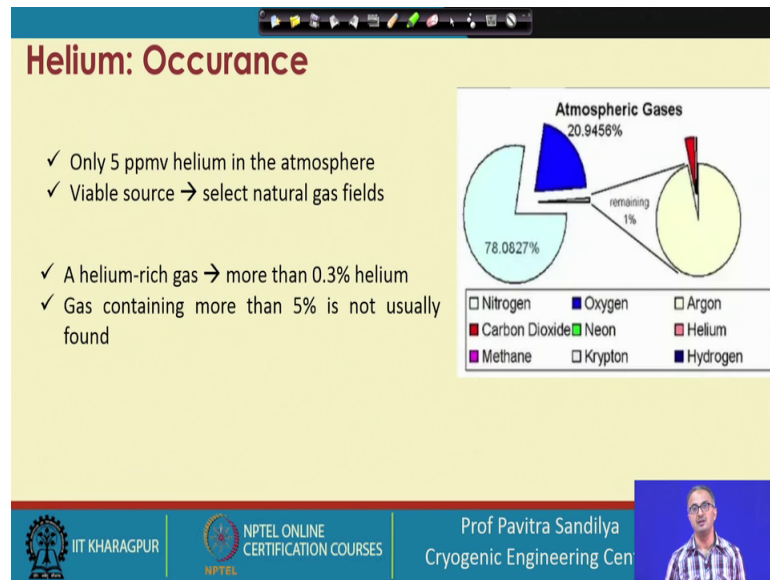
- ✓ Liquid coolant in
 - Superconductors for magnetic resonance imaging equipment in hospitals,
 - Particle accelerators and high-energy physics research,
 - Gas-cooled nuclear power reactors.
- ✓ Carrier gas in analytical equipment such as gas chromatographs,
- ✓ Blanket gas for welding,
- ✓ Helium/oxygen breathing gas mixtures to avoid nitrogen narcosis in deep-sea divers and operating-room patients.

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So, first let us see the uses of helium, it is used as a coolant in the superconductor for MRI applications in the hospitals. Then particle accelerators also for a high-energy physics research, then gas-cooled nuclear power reactors. It is used as a carrier gas in analytical equipment like gas chromatographs. And, in the blanket for blanket gas for welding and it is also used by the divers because we are the divers; we are taking a

mixture of the helium oxygen. So, here we have shown in the figure this is the MRI application; and this is the application of the high energy physics. This is for the chromatograph. This is for the blanket gas, and this is for the diving. So, we find it is very important gas.

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And of course, we know that in the balloons also we put a helium and this balloons are used through conduct many experiments in the aerial way. So, here the occurrence of helium, so helium is generally very much abundant in the sun, but on the earth we do not have much; in the atmosphere we have only about 5 ppm in volume basis. And the viable sources for helium is natural gas. And here we have see that in the distribution of the various gas it in the atmosphere, the chunk of it is by the nitrogen then comes the oxygen and rest of the gases are here.

And if we magnify again a rest of the gases we find only a small amount of the rest of the gases is helium, that is why the atmospheric air is not a commercial source of helium. So, a helium gas rich source is supposed to be more than 0.3 percent helium and generally the gases have about 5 percent the rich source of natural gas have about 5 percent of helium and that is considered to be a commercial reserve for the helium gas.

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Helium Recovery

- ✓ Gas plant (Nitrogen rejection unit) produces raw helium stream containing roughly an equimolar mixture of helium and nitrogen
- ✓ If the LNG plant does not have a helium recovery unit any He in the feed gas will be vented to atmosphere with the N₂ vent stream.

Crude helium → Low temperature upgradation → Purification (Adsorptive/membrane) → High purity helium(99.995%)

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Now, for the helium recovery generally this is dump from this nitrogen rejection unit, the whatever gas you obtain from that that produces raw helium and that containing almost equimolar mixture of helium and nitrogen. And if the LNG plant does not have any helium recovery system, what is then, then we have to purge out the helium along with the nitrogen vent stream. By recovery what we mean that we have the crude helium which is first upgraded by some low temperature method and then it is purified further by either using adsorption or the membrane processes and this, so that we can get a very highly pure helium gas.

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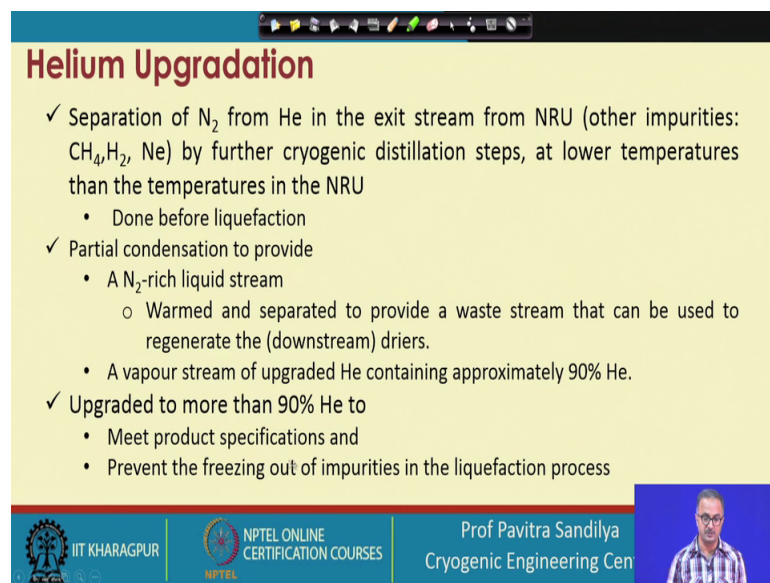
Helium Recovery

- ✓ Cryogenic distillation
 - Conventional
 - Energy intensive
 - Expensive
 - Currently there is no alternative commercially available process technology
- ✓ Alternate technologies
 - Pressure swing adsorption (PSA)
 - Membranes
 - ❖ Large capital and energy-cost savings compared with cryogenic distillation processes
 - ❖ Used in industrial applications like hydrogen production in chemical and petrochemical processes.

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Now, in a helium recovery, first we have the cryogenic distillation. And this is very conventional method, but it is quite energy intensive like any other distillation process. So, it is quite expensive. And currently there is no alternative commercially available process technology for helium recovery. And other technologies are being developed that is membrane and the pressure swing adsorption. And they have a large capital and energy-cost saving compared with the cryogen distillation. And they used in industrial applications like hydrogen production in chemical and petrochemical processes, but not so much for the helium recovery.

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Helium Upgradation

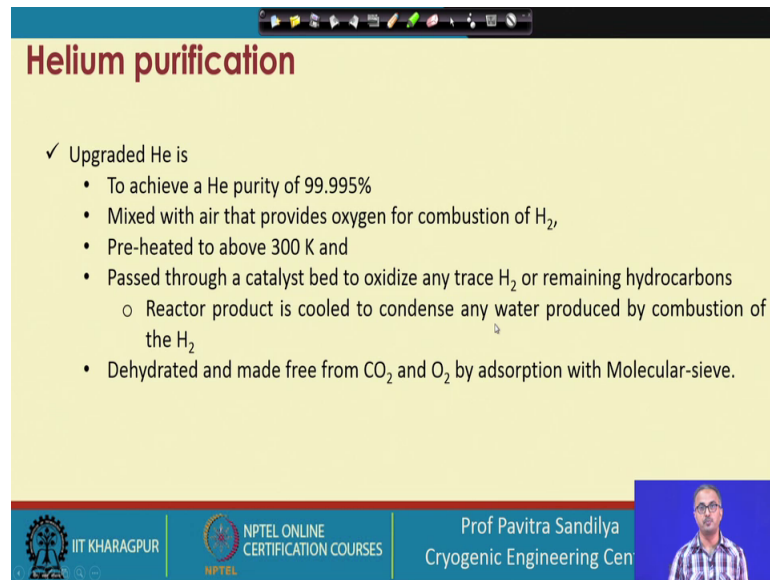
- ✓ Separation of N_2 from He in the exit stream from NRU (other impurities: CH_4, H_2, Ne) by further cryogenic distillation steps, at lower temperatures than the temperatures in the NRU
 - Done before liquefaction
- ✓ Partial condensation to provide
 - A N_2 -rich liquid stream
 - Warmed and separated to provide a waste stream that can be used to regenerate the (downstream) driers.
 - A vapour stream of upgraded He containing approximately 90% He.
- ✓ Upgraded to more than 90% He to
 - Meet product specifications and
 - Prevent the freezing out of impurities in the liquefaction process

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First we come to the helium upgradation. In this what we mean that we want to separate the nitrogen from the exit gas stream of the nitrogen recovery unit; other impurities in the exit gas streams are methane, hydrogen, neon, etcetera. And for this what we do we further cool it down to the cryogenic temperatures and that is lower than the temperature which is used in the NRU. And this is done before the liquefaction of the helium. And here we have the first the things that what you partially condense to obtain what to obtain a nitrogen rich liquid stream because nitrogen is less volatile compare to helium. So, it will be coming as a liquid stream. And this nitrogen stream may be warmed up and separated to provide a waste stream that can be used to regenerate the downstream driers. We shall see about it later. And then we have a vapor stream which is upgraded helium containing about 90 percent helium.

So, this upgraded helium is taken for further purification. And this more than 90 percent required, because it will be meeting the product specification; and to prevent the freezing out of impurities in the liquefaction process because any other impurities remaining there we will get frozen because helium has the lowest boiling point among all the fluids.

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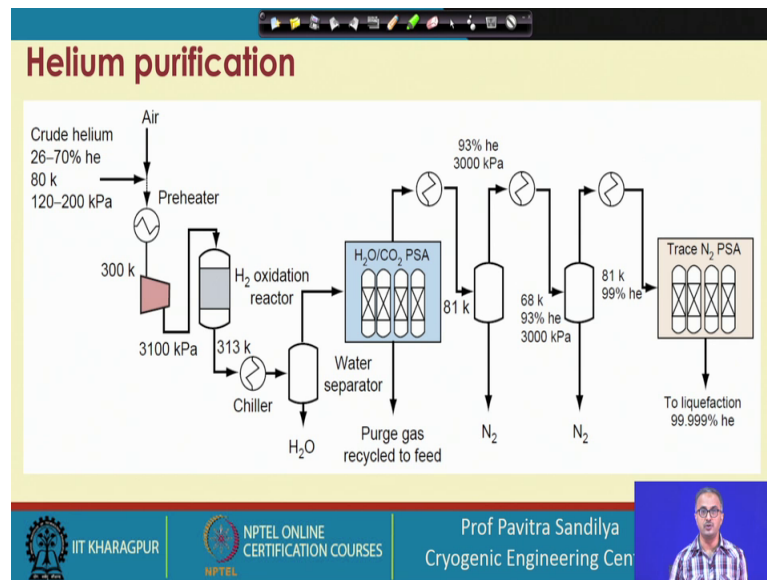
Helium purification

- ✓ Upgraded He is
 - To achieve a He purity of 99.995%
 - Mixed with air that provides oxygen for combustion of H_2 ,
 - Pre-heated to above 300 K and
 - Passed through a catalyst bed to oxidize any trace H_2 or remaining hydrocarbons
 - Reactor product is cooled to condense any water produced by combustion of the H_2
 - Dehydrated and made free from CO_2 and O_2 by adsorption with Molecular-sieve.

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After upgradation, we get a highly pure helium gas as we saw earlier. So, how do you do it that first we mix the upgraded helium with air that an air provides a oxygen required to combust hydrogen. And then, it is pre-heated to about 300 Kelvin. And then it is passed over a catalyst bed to oxidize any trace of hydrogen and remaining hydrocarbon. The reactor product is cooled to condense the water produced due to the combustion of the hydrogen and the hydrocarbon and this water is drained out. And the dehydrated it is dehydrated and made free from carbon dioxide, oxygen by adsorption with molecular-sieve.

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So, here we show this whole process here. Here we get the crude helium which is coming to about say 70 percent maximum at this temperature pressure; it is mixed with air. Then pre-heated it is compressed, compressed and then taken to this reactor it is being reacted. And then this cool down and cool down by cooling down we are condensing the water vapor into liquid water; the water is drained out. Then it is put in a PSA unit then this purge gas is recycle to the feed here. And then we keep on cooling down in stepwise manner to take out the nitrogen. And ultimately we again take it to adsorption columns based on the psa and so that we get the trace amount of nitrogen is removed and we get a highly pure helium. So, this is how we carry out the helium purification.

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Adsorption based He recovery

- ✓ PSA based
- ✓ Remove trace N_2 from upgraded He (>90 mol%) to achieve 99.999% He product streams.
 - All impurities are adsorbed because He generally has the lowest affinity for adsorption
- ✓ Needs upgraded feed stream (90% He).
- ✓ Generally uses **zeolites** and **narrow pore-activated carbons**.

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Now, let us see that what how the adsorption is used for the helium recovery this is it is PSA based that is pressure swing adsorption then it removes trace amount of nitrogen from the update helium that is more than 90 percent to achieve this much percentage of helium in the product streams. And the all the impurities are adsorbed because helium does not get generally absorbed because it does not have much affinity towards the adsorbents. And this adsorption needs updated feed stream. And it generally uses zeolites and narrow pore activate carbons.

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Adsorption based He recovery

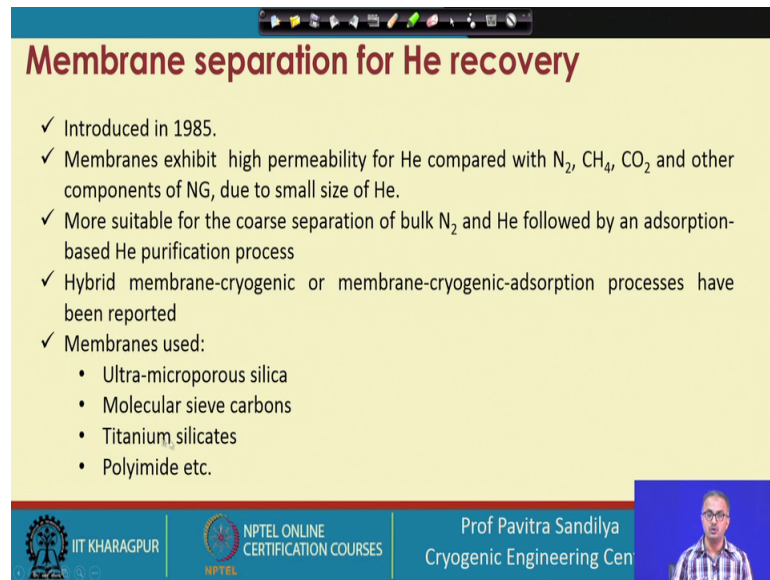
- ✓ Commonly used adsorbents in natural gas processing:

Adsorbent type	Trade names	Species adsorbed
Zeolites	ZSM-5 HISIV 3000 (UOP) Zeolite 5A (UOP, Sigma) Zeolite 13X (UOP)	CH_4 , CO_2 , N_2
Wide pore-activated carbons	BAX-1100 (Westvaco) RB3, R2030, GAC 1240 (Norit) BPL 4 × 10 (Calgon) Acticarb EA1000 (Activated Carbon Technologies, Australia and New Zealand)	CH_4 , CO_2 , N_2
Narrow-pore activated carbons Ca- and Li-exchanged 13X (Baksh 2010; Das <i>et al.</i> 2010)	Maxsorb (Kansai Coke & Chemicals Co)	N_2 in final purification stage N_2 in final purification stage

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And here in this particular table we show the various types of adsorbent used, their trade names and the kind of species they adsorbed. So, we find that if we want to adsorb methane, carbon dioxide, nitrogen, we can use zeolite and widely pore-activated carbons. If you want to remove nitrogen, we can use this kind of adsorbents.

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Membrane separation for He recovery

- ✓ Introduced in 1985.
- ✓ Membranes exhibit high permeability for He compared with N_2 , CH_4 , CO_2 and other components of NG, due to small size of He.
- ✓ More suitable for the coarse separation of bulk N_2 and He followed by an adsorption-based He purification process
- ✓ Hybrid membrane-cryogenic or membrane-cryogenic-adsorption processes have been reported
- ✓ Membranes used:
 - Ultra-microporous silica
 - Molecular sieve carbons
 - Titanium silicates
 - Polyimide etc.

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Now, next we come to the membrane separation for helium recovery, membrane is membrane processes came later than adsorbent and it is not very old process so about in 1980s it was introduced. And in this membranes have high permeability for helium, because helium happens to be smallest of all the components. So, the membrane will be permeating the helium through pass through it and other components will be retained, so that is how we are able to use membrane for the helium purification.

And these membranes are suitable for coarse separation of bulk nitrogen and helium, and then this is followed by the adsorption based helium purification. We are also having nowadays hybrid membrane-cryogenic or membrane-cryogenic adsorption processes for the helium recovery. And these are some of the membranes which are used for the helium recovery.

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Membrane material	Temperature, °C	Selectivity α	
		P_{He}/P_{N_2}	P_{He}/P_{CH_4}
<i>Inorganic membranes</i>			
Porous glass, Vycor type	25	2.5	1.8
Molecular sieve carbon (3–5 Å)	25	20	–
<i>Organic membrane materials</i>			
Ethyl cellulose	20	11	2.8
Polytetrafluoroethylene	20	31	42
Polycarbonate	20	14.2	18.6
Aromatic polyimide	35	74	165

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And now we find that in this particular table, we find that we have the various types of membranes that are proposed that some are inorganic membranes; some are organic membranes, and the kind of temperature they can work at. And here in this particulate columns, we are finding the selectivity that is the this is a partial pressure, the permeability of the helium to the permeability nitrogen. So, this is with respect to helium nitrogen and helium methane. So, we find that in this particular thing, we find that is aromatic polyimide based membranes are giving the highest selectivity of helium with respect to both nitrogen and methane. So, this table may be used as a guideline to select the membrane.

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Industrial membrane system for He recovery

- ✓ To increase the purity of He, several membrane stages can be operated in series as shown in the two-stage process in the figure.
- ✓ Due to the large pressure drop (often 1500-3000 kPa) of the He-rich permeate across the membrane unit, multistage membrane processes require inter-stage compressors

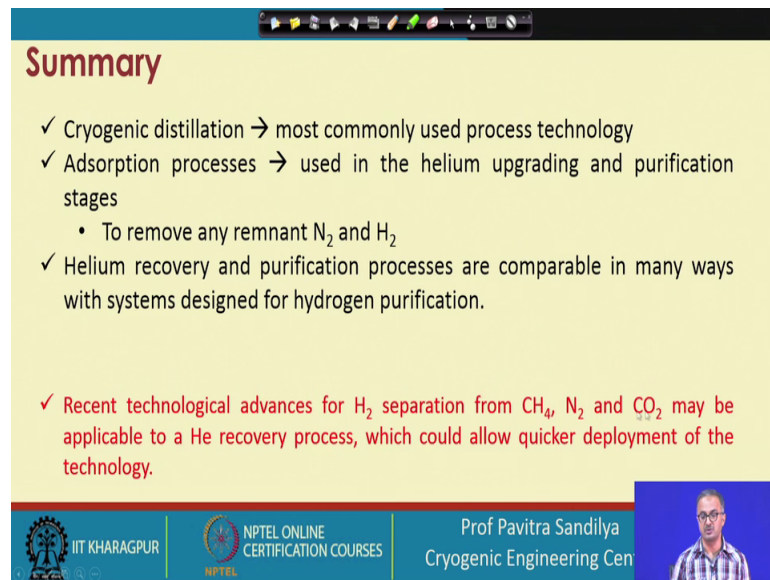
Feed: 2.4% He, 77.7% CH₄, 0.01% CO₂, 0.20% C₂+
Membrane stage 1 permeate: 11.2% He, 49.1% CH₄, 0.1% CO₂, 0.01% C₂+
Crude helium: 59.33% He, 39.2% CH₄, 0.1% CO₂, 0.01% C₂+
CH₄ + N residue

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Now, industrial membrane process is like this that we need to increase this purity of helium. So, we need several membrane stages about the stages we learnt earlier separately under the membrane separation methods. So, I will not be going to details of it. And here we find that we have about 2.4 percent of helium. And then we are having about by first membrane stage, we are able to increase the purity from 2.4 to 11.2 percent. And ultimately we are able to raise it to about for 59.33 percent that means, if we are using two membrane stages then from 2.4 percent we are going up to say 60 percent.

So, this is a typical some representative value of this membrane kind of separation. And due to the large pressure drop of the helium rich permeate, helium pressure drop 1500 to 3000 kilo Pascal; that means, about 1.5 to sorry 15 to about 30 bar. So, we use multistage membrane processes. And for multistage whenever be multistage, we need to compress, because always we compress we shall not be having enough driving force for the separation through the membranes, so that is why after each stage we need to use a compressor for the for going to the next stage.

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Summary

- ✓ Cryogenic distillation → most commonly used process technology
- ✓ Adsorption processes → used in the helium upgrading and purification stages
 - To remove any remnant N_2 and H_2
- ✓ Helium recovery and purification processes are comparable in many ways with systems designed for hydrogen purification.

✓ Recent technological advances for H_2 separation from CH_4 , N_2 and CO_2 may be applicable to a He recovery process, which could allow quicker deployment of the technology.

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And in summary, we can say then cryogenic distillation is the most common of the processes. Adsorption is used both for upgrading and for purification and to remove any residual amount of the nitrogen and hydrogen. And helium recovery and purification processes are comparable in many ways with those for the hydrogen purification. So, what happens that any development in the hydrogen separation from these gases like methane, nitrogen, carbon dioxide will be also be affecting the progress in the helium recovery systems.

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And these are some references which you may refer for detail on this helium separation and recovery.

Thank you.