# Upstream LNG Technology
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## Lecture – 55
## Trace components in natural gas

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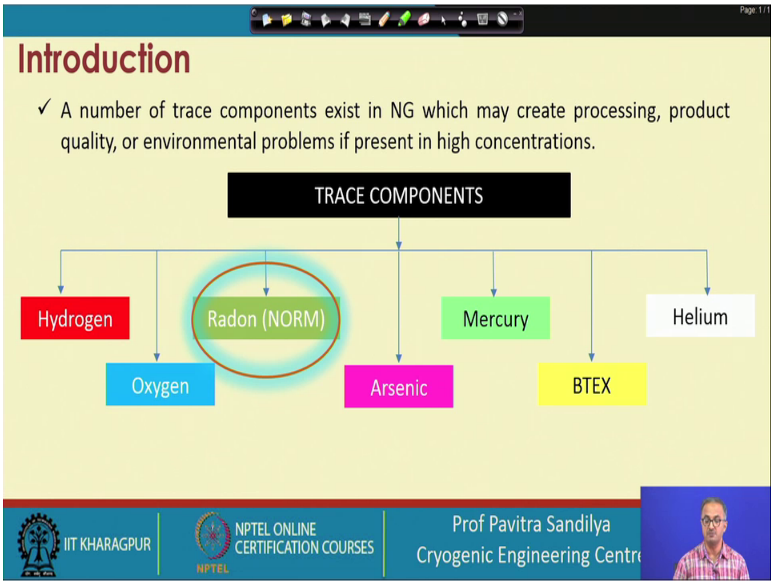

## Introduction

- ✓ 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

Welcome. Today, we shall be learning in this lecture the trace components which are present in the natural gas systems and some of the removal processes. So, first let us see that in number of trace components exist in natural gas which may create processing, and product quality, and environmental problems if present in high concentration even that that is why we need to remove them and know about them. So, these are the various types of trace components present in the natural gas like hydrogen, oxygen, radon, arsenic, mercury, BTEX and helium. So, this radon is a radioactive material this is normal normally radioactive material; whereas, BTEX is the benzene, toluene, ethyl benzene and xylem. We shall be taking up helium separately in a separate lecture.

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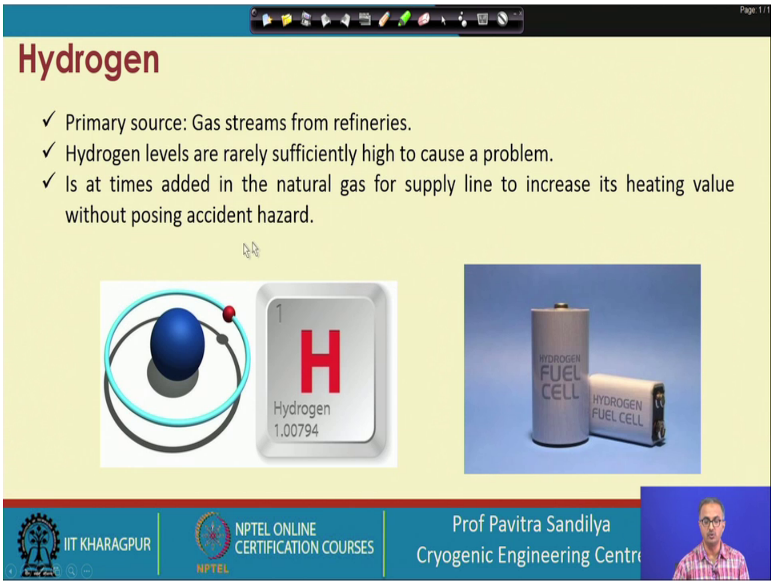

## Hydrogen

- ✓ Primary source: Gas streams from refineries.
- ✓ Hydrogen levels are rarely sufficiently high to cause a problem.
- ✓ Is at times added in the natural gas for supply line to increase its heating value without posing accident hazard.

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So, first we shall see the hydrogen. Now, hydrogen we know this primary source is the gas streams from the refineries. And hydrogen's levels are rarely sufficient high to cause any problem rather sometimes the natural gas is added with hydrogen to increase its heating value without causing any accidental hazard and this is the one use of the hydrogen in the fuel cell.

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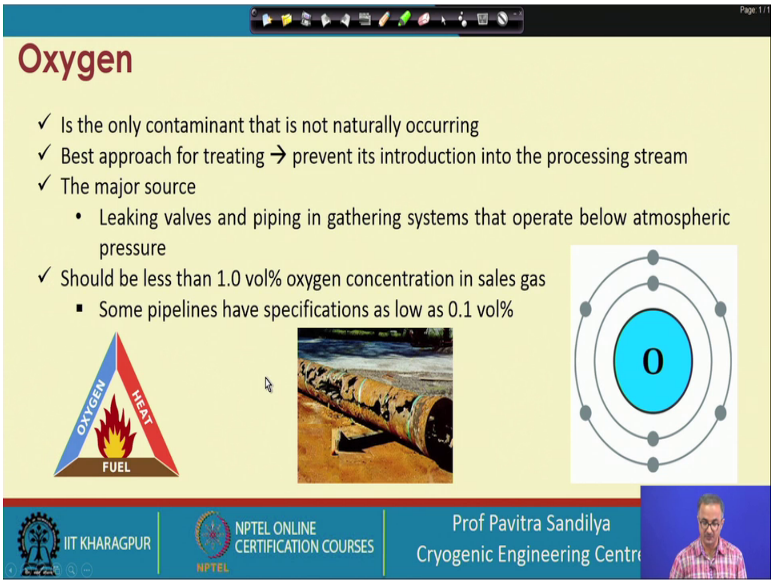

## Oxygen

- ✓ Is the only contaminant that is not naturally occurring
- ✓ Best approach for treating → prevent its introduction into the processing stream
- ✓ The major source
  - Leaking valves and piping in gathering systems that operate below atmospheric pressure
- ✓ Should be less than 1.0 vol% oxygen concentration in sales gas
  - Some pipelines have specifications as low as 0.1 vol%

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Then we come to the oxygen. Oxygen is the as you know that it can be a reactive gas. So, it is only contaminant that does not occur naturally and it is best appropriate is this prevent its introduction into the processing stream, because if it enters the processing stream it has many many hazards, like it can cause if there is leakage of oxygen through the walls and piping then there could be oxygen leakage from that if it is below atmospheric pressure and should be less than 1 percent is all kind of prescribed limit of oxygen in the sales gas. And these are the sum of the bad effects of oxygen it can it is causes emission; and if it is it reacts with the pipelines and it can cause corrosion, so that is why that we find at sometimes the specified limit is less than 1 percent to about 0.1 volume percent depending on the particular situation.

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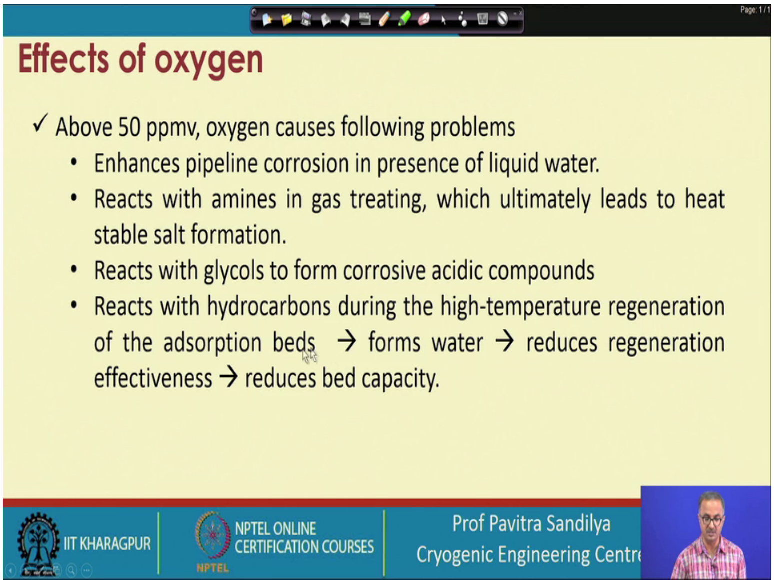

## Effects of oxygen

✓ Above 50 ppmv, oxygen causes following problems
- Enhances pipeline corrosion in presence of liquid water.
- Reacts with amines in gas treating, which ultimately leads to heat stable salt formation.
- Reacts with glycols to form corrosive acidic compounds
- Reacts with hydrocarbons during the high-temperature regeneration of the adsorption beds → forms water → reduces regeneration effectiveness → reduces bed capacity.

Now, above 50 ppm, oxygen causes these problems. It enhances pipeline corrosion in presence of liquid water. It reacts with amines in gas treating which ultimately causes the formation of the salt, and if this salts are formed they can cause scaling problem inside the particular equipment. And it can react with the glycols to form some corrosive acidic compounds which will be causing the corrosion to the equipment again.

It can remove with it can react with the hydrocarbons during high temperature regeneration of the adsorption beds. And then if it is react, it forms water; and if water is formed, it reduces the regeneration efficiency by causing cooling because with the regeneration we need high temperature, but water will be sub doing the heating effect that is why, that is how it will be reducing the regeneration efficiency and thereby it will reduce the bed capacity for regeneration.

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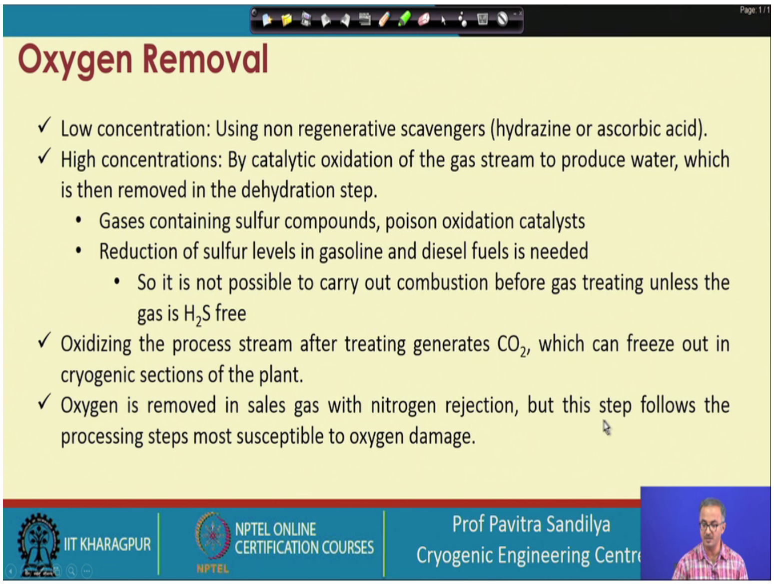

# Oxygen Removal

- ✓ Low concentration: Using non regenerative scavengers (hydrazine or ascorbic acid).
- ✓ High concentrations: By catalytic oxidation of the gas stream to produce water, which is then removed in the dehydration step.
  - Gases containing sulfur compounds, poison oxidation catalysts
  - Reduction of sulfur levels in gasoline and diesel fuels is needed
    - So it is not possible to carry out combustion before gas treating unless the gas is $H_2S$ free
- ✓ Oxidizing the process stream after treating generates $CO_2$, which can freeze out in cryogenic sections of the plant.
- ✓ Oxygen is removed in sales gas with nitrogen rejection, but this step follows the processing steps most susceptible to oxygen damage.

In the low concentration, oxygen is removed by non regenerative scavengers, for example hydrazine and ascorbic acid that means it is low concentration, so they will react irreversibly and we need not bothered to regenerate this particular scavengers. If we are having high concentrations oxygen, then by catalytic oxidation of the gas stream to produce water this oxygen is removed which is then removed in the dehydration step.

And we know that gases containing sulfur compounds, may poison the oxidation catalysts and the reduction of the sulfur levels in the gasoline and diesel fuels is needed. So, it is not possible to carryout combustion before gas treating unless gas is H 2 S free; otherwise what will happen if you do that then if the H 2 O will be absorbed more on the this adsorbents.

The oxidizing the process stream after treating generates carbon dioxide, which can freeze out in the cryogenic sections of the plant. So, we have to be cautions that we should not allow the carbon dioxide formation if we are taking the natural gas for liquefaction; otherwise the carbon dioxide can form the solid ice. Oxygen is generally removed from the cells get with the along with nitrogen rejection and but this step follows most susceptible to oxygen damage. As we have seen that in the sales gas, the amount of oxygen has to be very small has to be less than 1 percent or even 0.1 volume percent, so that is why in the sales gas we have to remove this oxygen along with the nitrogen; nitrogen because it reduces the heating value of the natural gas.

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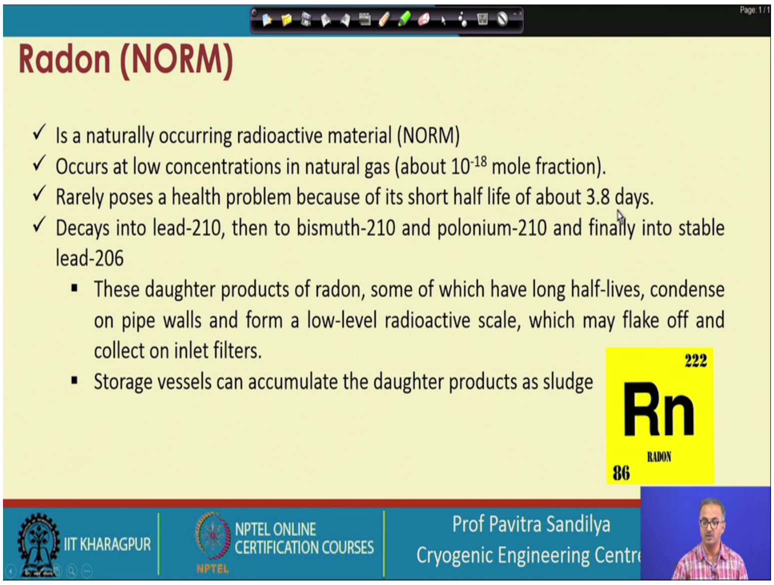

## Radon (NORM)

- ✓ Is a naturally occurring radioactive material (NORM)
- ✓ Occurs at low concentrations in natural gas (about $10^{-18}$ mole fraction).
- ✓ Rarely poses a health problem because of its short half life of about 3.8 days.
- ✓ Decays into lead-210, then to bismuth-210 and polonium-210 and finally into stable lead-206
  - These daughter products of radon, some of which have long half-lives, condense on pipe walls and form a low-level radioactive scale, which may flake off and collect on inlet filters.
  - Storage vessels can accumulate the daughter products as sludge

Next we come to the radon, which is a radioactive material and its concentration in natural gas is very very small about 10 to the power minus 18 mole fraction. And it does not generally causes health problem because it has a short half life about 3.8 days. And this radon the decays into lead 210, then bismuth-210 and polonium-210 and which up to the ultimately it goes to a stable lead-206. So, these are the in between radioactive materials which are form from the radon.

The daughter products of radon, which some of which are have long half lives condense on the pipe walls and form a low-level radioactive scale, which may flake off and collect on the inlet filters that is why it is important for us to remove radon so that the intermediate radioactive materials which have a longer life period or not formed and causes this kind of radioactive scaling. And storage vessels can accumulate the daughter products as sludge.

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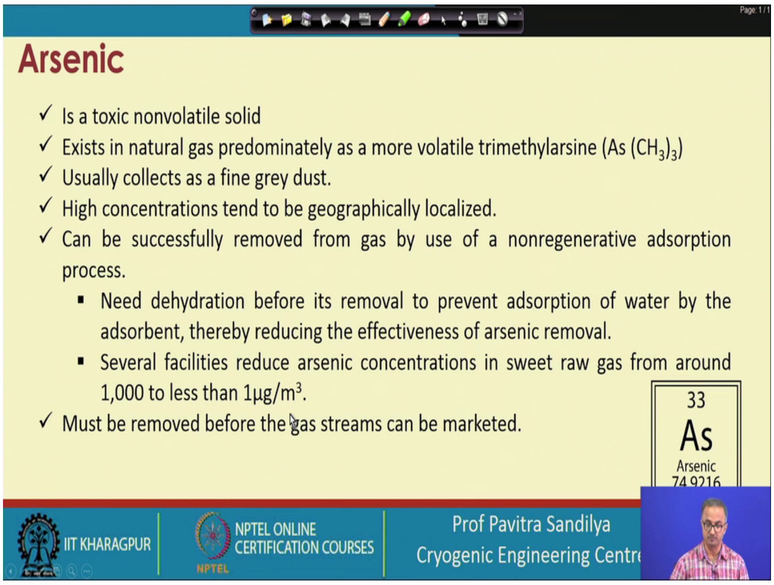

## Arsenic

- ✓ Is a toxic nonvolatile solid
- ✓ Exists in natural gas predominately as a more volatile trimethylarsine (As $(CH_3)_3$)
- ✓ Usually collects as a fine grey dust.
- ✓ High concentrations tend to be geographically localized.
- ✓ Can be successfully removed from gas by use of a nonregenerative adsorption process.
  - Need dehydration before its removal to prevent adsorption of water by the adsorbent, thereby reducing the effectiveness of arsenic removal.
  - Several facilities reduce arsenic concentrations in sweet raw gas from around 1,000 to less than 1μg/$m^3$.
- ✓ Must be removed before the gas streams can be marketed.

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Next we come to arsenic. In the arsenic, we know that arsenic pollution in the water at various areas is very, very critical. So, in similarly arsenic is also there in natural gas, it is a toxic nonvolatile solid that means it will tend to stay in the sludge; it will not be vaporizing along with the natural gas. And it exists in natural gas predominantly has a more volatile trimethylarsine that is this is the formula of the trimethylarsine. And, it usually collects as a fine grey dust and high concentrations leads to geographical localized, so that is why we find that there could be some problem with arsenic of the so health problems are caused by the arsenic.

It can be removed by some non regenerative adsorption process. It needs hydration before its removal to prevent the water absorption. Because if water is not removed before arsenic removal what will happen when it goes to the adsorption column because arsenic is present in a low amount and lot of water is present at high amount, the adsorbent will be collecting mode of the water than arsenic. So, we will not be able to separate the arsenic from the natural gas. And their several facilities reduce the arsenic concentrations in sweet raw gas from 1000 two less than 1 microgram per cubic meter. And the arsenic must be removed before marketing the gas.

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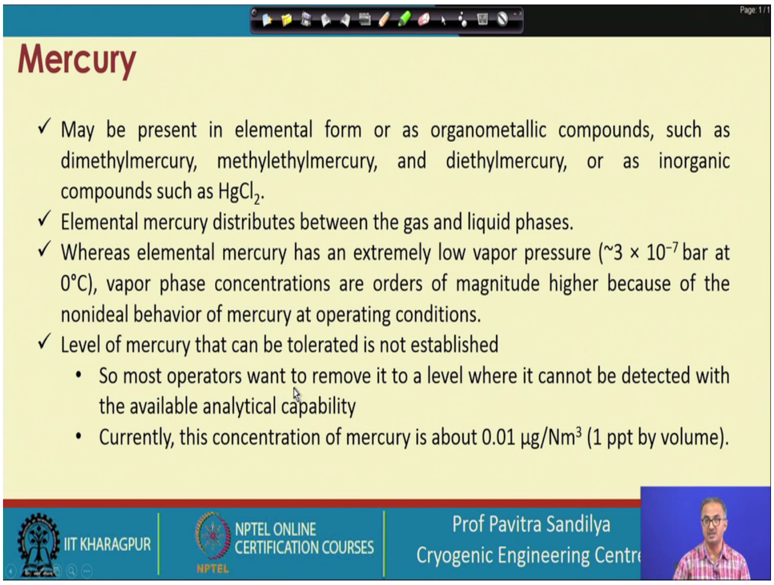

## Mercury

- ✓ May be present in elemental form or as organometallic compounds, such as dimethylmercury, methylethylmercury, and diethylmercury, or as inorganic compounds such as $HgCl_2$.
- ✓ Elemental mercury distributes between the gas and liquid phases.
- ✓ Whereas elemental mercury has an extremely low vapor pressure (~$3 \times 10^{-7}$ bar at 0°C), vapor phase concentrations are orders of magnitude higher because of the nonideal behavior of mercury at operating conditions.
- ✓ Level of mercury that can be tolerated is not established
  - So most operators want to remove it to a level where it cannot be detected with the available analytical capability
  - Currently, this concentration of mercury is about 0.01 μg/$Nm^3$ (1 ppt by volume).

Next we come to mercury. Mercury is another hazardous component. It may be present in the elemental form or as organometallic compounds like methylethylmercury, dimethylmercury, diethylmercury, or in organic form like in terms of HgCl 2 that is mercury chloride. Now, elemental mercury distributes it still between the both gas and the liquid. Mercury has very low vapor pressure about 3 into 10 to power minus 7 bar at 0 degree centigrade, but vapor phase concentration order of magnitude higher because of the non ideal behavior of mercury at operating conditions. So, at 0 degree, it has a very low pressure, but a operating conditions which is very high temperature, the vapor pressure is quite substantial. So, it needs to be removed.

Now, most operators want to remove this mercury to the extent that it cannot be detected by the available analytical techniques. So, there is no particular level up to which mercury has to be removed, but it depends on the how much capable we are able the capable to detect the mercury. If we cannot detect it by some available analytical methods, then we assume that we are safe. And the concentration of mercury is to be 1 parts per trillion by volume ppt is 1 parts per trillion by volume that is about 0.01 micro gram per normal cubic meter of the gas.

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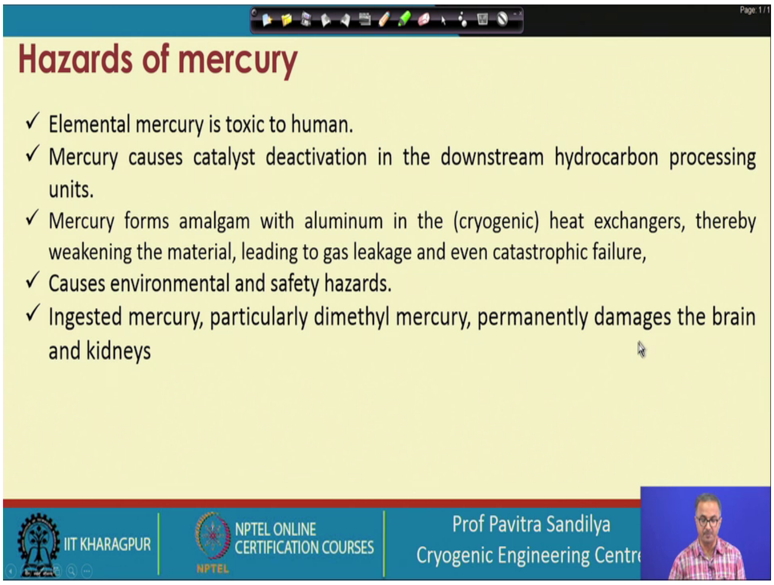

## Hazards of mercury

- ✓ Elemental mercury is toxic to human.
- ✓ Mercury causes catalyst deactivation in the downstream hydrocarbon processing units.
- ✓ Mercury forms amalgam with aluminum in the (cryogenic) heat exchangers, thereby weakening the material, leading to gas leakage and even catastrophic failure,
- ✓ Causes environmental and safety hazards.
- ✓ Ingested mercury, particularly dimethyl mercury, permanently damages the brain and kidneys

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And these are some of the hazards caused by the mercury. We know that it is hazardous for the human then mercury causes catalyst deactivation in the downstream hydrocarbon processing. So, it has to be removed and it forms amalgam with aluminum; and these aluminum is generally used in the cryogenic heat exchangers. So, if amalgam is formed then what will happen it will weaken the material of construction of the heat exchanger and if the material is weakened, then what will find that there could be gas leakage or even catastrophic failure; it causes environmental and safety hazards. And if mercury is ingested goes into our system, then they will permanently damages the brain and the kidney.

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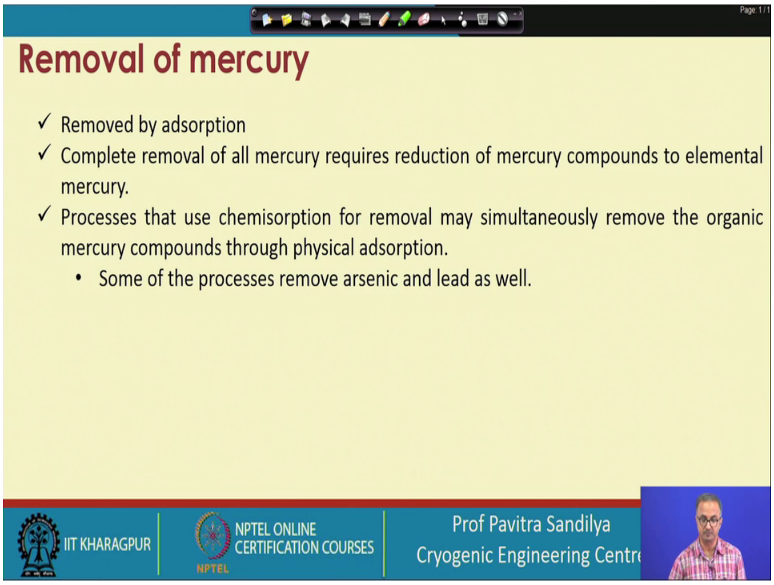

## Removal of mercury

- ✓ Removed by adsorption
- ✓ Complete removal of all mercury requires reduction of mercury compounds to elemental mercury.
- ✓ Processes that use chemisorption for removal may simultaneously remove the organic mercury compounds through physical adsorption.
  - Some of the processes remove arsenic and lead as well.

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So, mercury has to be removed. It is removed by adsorption. And it is complete removal of mercury requires reduction of the mercury compounds into elemental mercury. So, we have to convert the all the compound compounds of mercury into the elemental mercury to ensure its complete removal. And generally these processes use chemisorption for removal and to remove also the organic mercury compounds to physical absorption. So, both chemical absorption adsorption and physical adsorption are used for the removal of the mercury. And during this removal of mercury some of the arsenic and lead also get removed.

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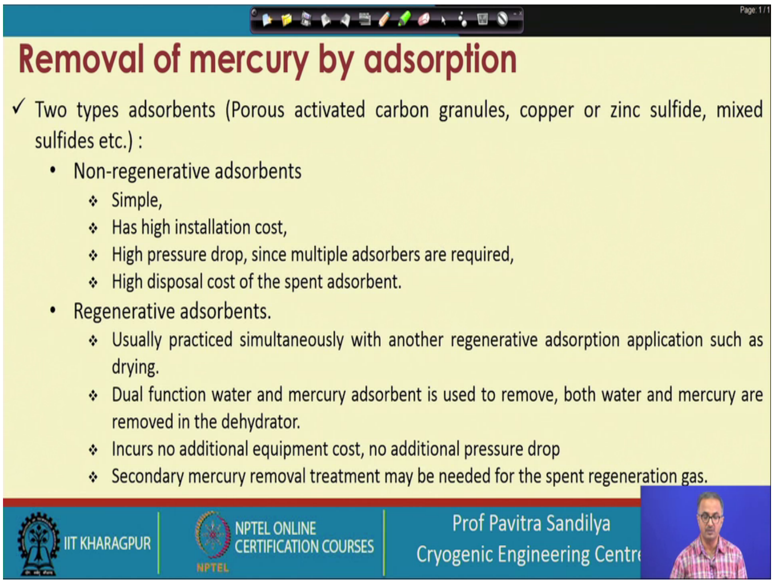

## Removal of mercury by adsorption

- ✓ Two types adsorbents (Porous activated carbon granules, copper or zinc sulfide, mixed sulfides etc.) :
  - Non-regenerative adsorbents
    - ❖ Simple,
    - ❖ Has high installation cost,
    - ❖ High pressure drop, since multiple adsorbers are required,
    - ❖ High disposal cost of the spent adsorbent.
  - Regenerative adsorbents.
    - ❖ Usually practiced simultaneously with another regenerative adsorption application such as drying.
    - ❖ Dual function water and mercury adsorbent is used to remove, both water and mercury are removed in the dehydrator.
    - ❖ Incurs no additional equipment cost, no additional pressure drop
    - ❖ Secondary mercury removal treatment may be needed for the spent regeneration gas.

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And these are the two types of adsorbent process of mercury removal one is non regenerative and regenerative and we find that for the non-regenerative processes; that means, in this case we are not regenerating the adsorbent. And it can happen that if it is we are not going for regeneration then it becomes the process become simple. And there is a high installation cost is there; the pressure drop is high and the disposal cost is also high.

On the other hand, this regenerative process is in the other way it has lower and pressure drop and no addition equipment cost. And it can remove both mercury and the water and the in the dehydrator. And it is generally practice simultaneously with some regenerative adsorption application such as drying, that means both for dehydration and this mercury removal are done simultaneously. And we may need a secondary mercury removal treatment for the spent regeneration gas.

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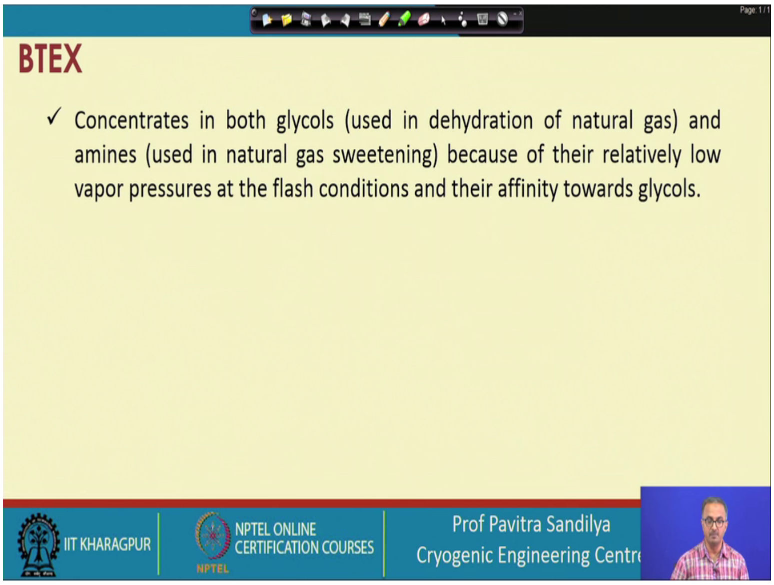

BTEX

- ✓ Concentrates in both glycols (used in dehydration of natural gas) and amines (used in natural gas sweetening) because of their relatively low vapor pressures at the flash conditions and their affinity towards glycols.

Next we come to BTEX. In the BTEX, we have the benzene, toluene, ethyl benzene and the xylem. So, this is concentrates both in the glycols that is used in dehydration of natural gas and amines which is used in the natural gas sweetening because of their low vapor pressure at the flash conditions and their affinity towards glycol.

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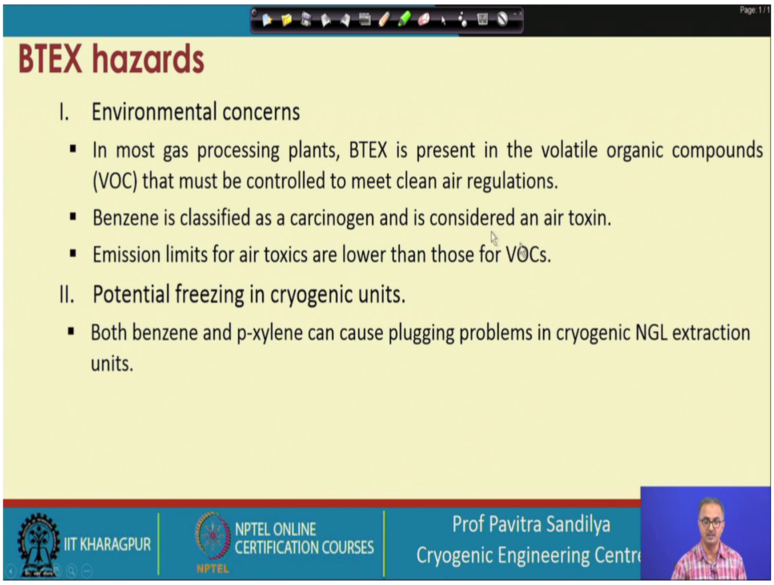

## BTEX hazards

I. Environmental concerns
- In most gas processing plants, BTEX is present in the volatile organic compounds (VOC) that must be controlled to meet clean air regulations.
- Benzene is classified as a carcinogen and is considered an air toxin.
- Emission limits for air toxics are lower than those for VOCs.

II. Potential freezing in cryogenic units.
- Both benzene and p-xylene can cause plugging problems in cryogenic NGL extraction units.

So, BTEX hazards are that they have environmentally concerns are that BTEX is present they are there in the volatile organic compounds. So, if they go into the air, so that will be causing many problems. And these are this benzene is considered to be a carcinogenic that means, it can cancer and it is also considered to be toxic to the air. And the emission limits for the air toxic and lower than that for the volatile organic compounds, so that is why this BTEX have to be removed they are more (Refer Time: 14:09) than the volatile organic compounds. And these BTEX can also get frozen in the cryogenic plants. And if they freeze then what will happen they will cause plugging problems in the various cryogenic equipment and the pipelines, so that is why this BTEX have to be removed.

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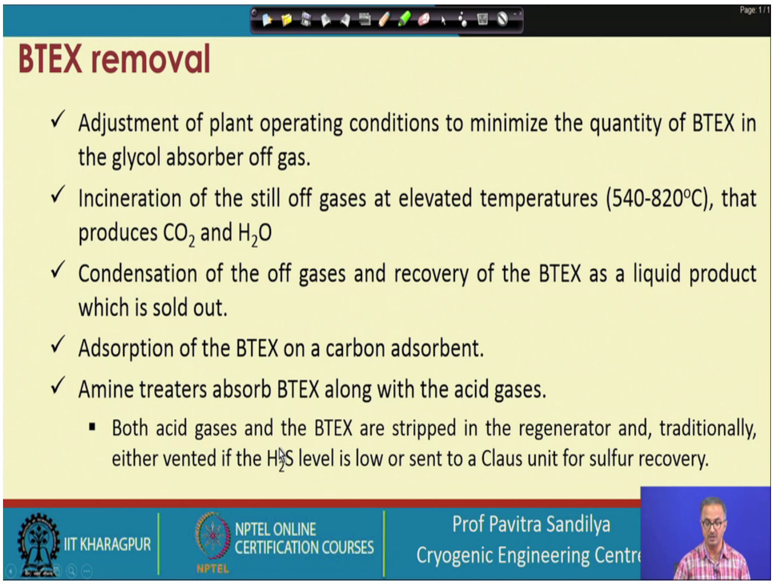

## BTEX removal

- ✓ Adjustment of plant operating conditions to minimize the quantity of BTEX in the glycol absorber off gas.
- ✓ Incineration of the still off gases at elevated temperatures (540-820°C), that produces $CO_2$ and $H_2O$
- ✓ Condensation of the off gases and recovery of the BTEX as a liquid product which is sold out.
- ✓ Adsorption of the BTEX on a carbon adsorbent.
- ✓ Amine treaters absorb BTEX along with the acid gases.
  - Both acid gases and the BTEX are stripped in the regenerator and, traditionally, either vented if the $H_2S$ level is low or sent to a Claus unit for sulfur recovery.

And for removal what we do sometimes, we adjust the plant operating conditions so that to minimize the quantity of BTEX in the glycol absorber. Then the gas is incinerated; and by incineration of the BTEX we get the carbon dioxide and water. And sometimes this BTEX is condensed and recovered as BTEX liquid and which is also sold out for making other chemical, so that is how we are able to remove the BTEX from the natural gas. BTEX can also be removed by using the carbon adsorbents. And amine absorption is also done to remove the BTEX. And if in case we are absorbing the BTEX, then both acid gas and BTEX are stripped in the regenerator and, traditionally, vented if the H 2 S level is low or sent to Claus if the H 2 S level is high for the sulfur recovery.

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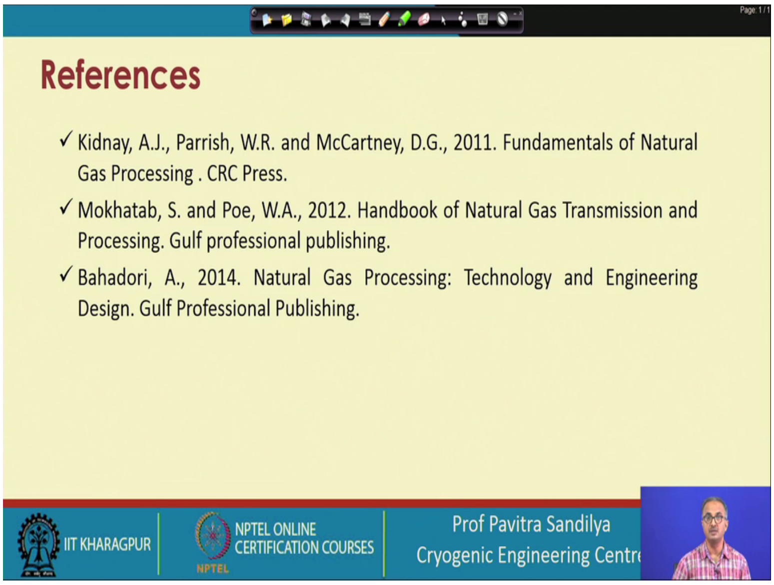

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These are the references for more details on these trace components.

Thank you.