Upstream LNG Technology
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Lecture – 43
Acid gas removal in natural gas system- I

Welcome now we shall learn about another processing methods related to the removal of the acid gases and this lecture will be divided into a few parts.

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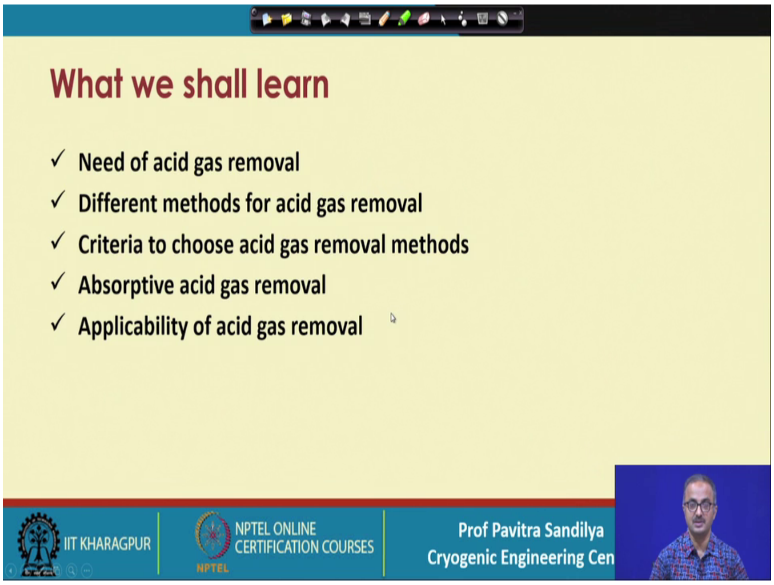

What we shall learn

- ✓ Need of acid gas removal
- ✓ Different methods for acid gas removal
- ✓ Criteria to choose acid gas removal methods
- ✓ Absorptive acid gas removal
- ✓ Applicability of acid gas removal

First we shall see in this particular lecture that the what are the various types of as removal methods of the acid gases. And then we shall see the various criteria to see these to choose these methods and then we shall be focusing on the absorptive acid gas removal.

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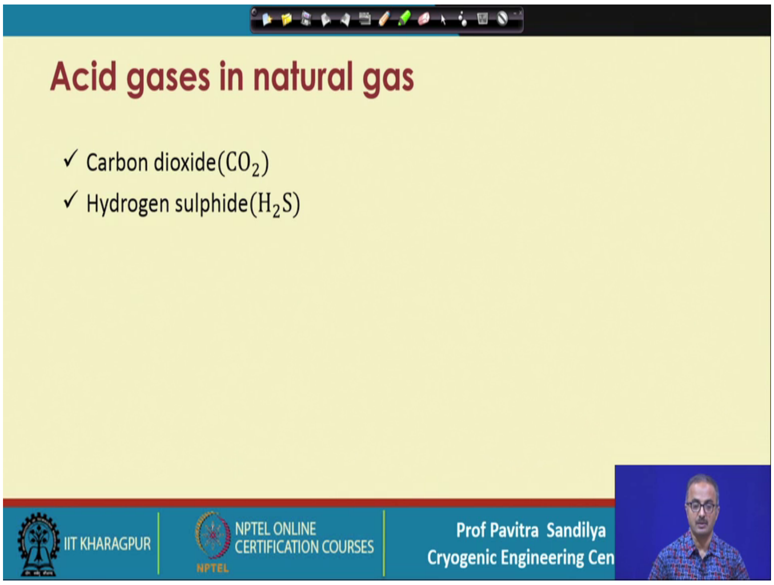

Acid gases in natural gas

- ✓ Carbon dioxide(CO_2)
- ✓ Hydrogen sulphide(H_2S)

So first, let us see what are the acid gases in natural gas? They are carbon dioxide and hydrogen sulfide.

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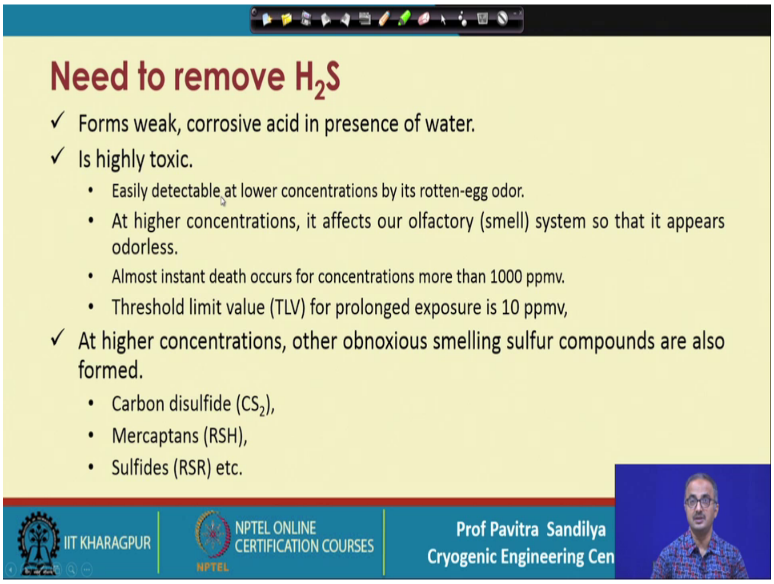

Need to remove H_2S

- ✓ Forms weak, corrosive acid in presence of water.
- ✓ Is highly toxic.
  - Easily detectable at lower concentrations by its rotten-egg odor.
  - At higher concentrations, it affects our olfactory (smell) system so that it appears odorless.
  - Almost instant death occurs for concentrations more than 1000 ppmv.
  - Threshold limit value (TLV) for prolonged exposure is 10 ppmv,
- ✓ At higher concentrations, other obnoxious smelling sulfur compounds are also formed.
  - Carbon disulfide (CS_2),
  - Mercaptans (RSH),
  - Sulfides (RSR) etc.

Now, why do we need to remove hydrogen sulfide? Because it forms weak corrosive acid in presence of water it is very toxic. And though it can be detected easily at low concentrations because it gives a rotten egg smell, but at high concentration it numbs our olfactory system. Olfactory means that our smelling system is affected so that we cannot smell it that at high concentration, but and when we cannot smell it, but it is going inside our system and then it can prove little to us. So, it may cause death for concentrations more than 1000 ppmv and the threshold limit is a prolonged exposure is 10 ppmv for long exposure we at as low as 10 ppmv of this H 2 S can cause death.

Then we for high concentrations what happens this H 2 S can form other foul smelling sulfur compounds like carbon disulfide, mercaptans and sulfides.

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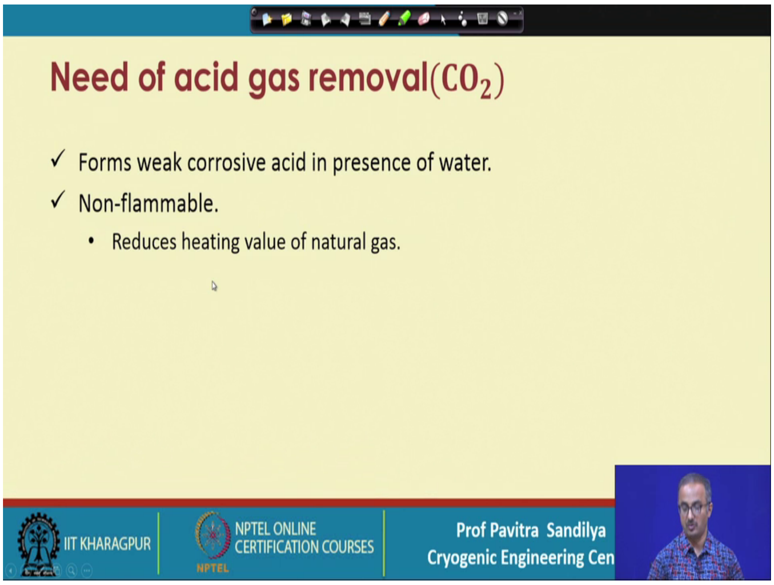

Need of acid gas removal(CO_2)

- ✓ Forms weak corrosive acid in presence of water.
- ✓ Non-flammable.
  - Reduces heating value of natural gas.

Why we need to remove carbon dioxide? Because it again forms weak corrosive acid in presence of water like H 2 S and it is non flammable and that is how it reduces the heating value of the natural gas.

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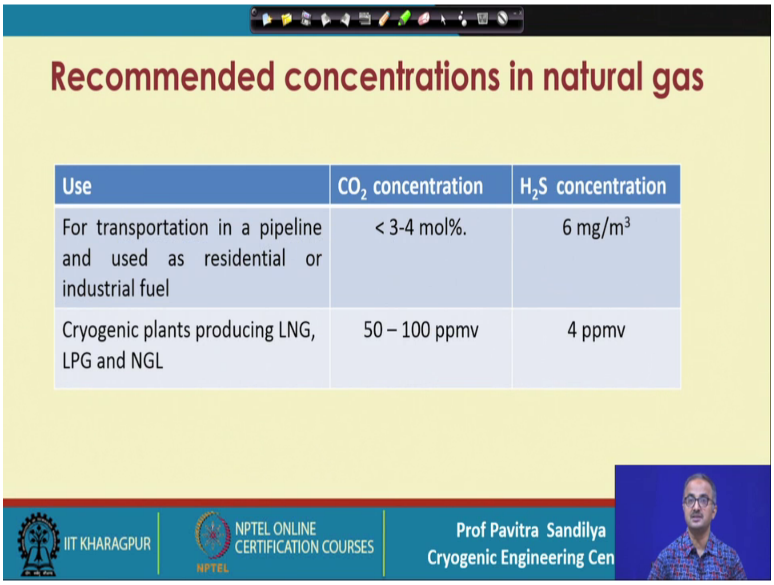

Recommended concentrations in natural gas

Use	CO_2 concentration	H_2S concentration
For transportation in a pipeline and used as residential or industrial fuel	< 3-4 mol%.	6 mg/m^3
Cryogenic plants producing LNG, LPG and NGL	50 – 100 ppmv	4 ppmv

So, for these reasons we need to remove this 2 gases and here in this table we find the maximum limit permissible limit in this natural gas. For transportation in a pipeline or used for residential industrial fuels, we find that the carbon dioxide should be less than 3 to 4 mole percent whereas, H 2 S constant concentration should be less than 6 milligram per cubic meter; Whereas, for cryogenic plants in which we are handling LNG that is Liquefied Natural Gas; liquefied a LPG refer to Liquefied Petroleum Gas and the NGL that is Natural Gas Liquid.

So, in these cases we find that the; these are the maximum limits which are permissible in these gases.

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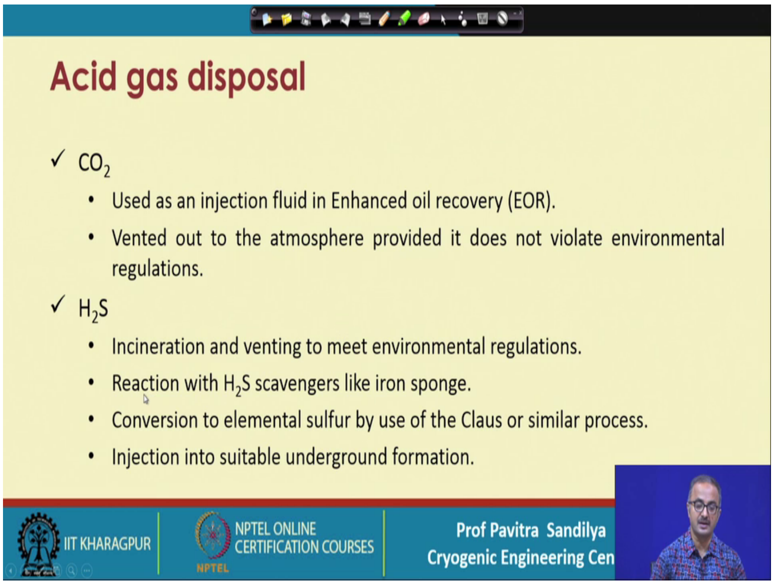

Acid gas disposal

- ✓ CO_2
  - Used as an injection fluid in Enhanced oil recovery (EOR).
  - Vented out to the atmosphere provided it does not violate environmental regulations.
- ✓ H_2S
  - Incineration and venting to meet environmental regulations.
  - Reaction with H_2S scavengers like iron sponge.
  - Conversion to elemental sulfur by use of the Claus or similar process.
  - Injection into suitable underground formation.

Now, when we talk of this acid gas disposal how we can dispose of carbon dioxide? That we can dispose of dispose it by injecting in an enhanced oil recovery system. And this is the method to recover any residual petroleum oil in which are entrapped in the rock formation in the sediment.

So, there we can use carbon dioxide because it is important for us not only to capture the carbon dioxide, but also to find out a way so that it can be sequestered. So, this is one of the ways another way is to vent out to the atmosphere if the concentration does not exceed the environmental regulatory limit.

Then similarly for H 2 S gas; we have incineration that is burning and venting to meet the environmental regulations or we can react it with H 2 S scavengers; that means, like iron sponge then this can react with the H 2 S. And then we shall be learning more about them later then we have this conversion of the elemental sulfur by use of the Claus process and then we can inject this sulfur compounds in some underground formation.

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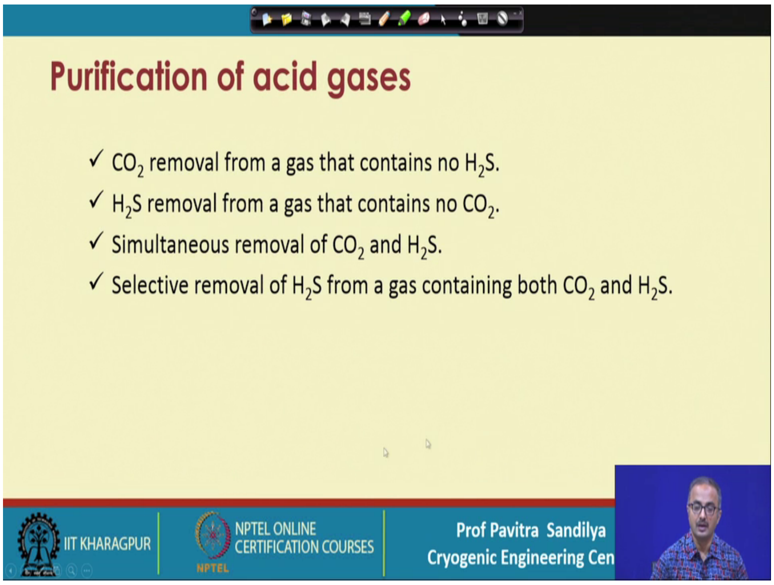

Purification of acid gases

- ✓ CO_2 removal from a gas that contains no H_2S.
- ✓ H_2S removal from a gas that contains no CO_2.
- ✓ Simultaneous removal of CO_2 and H_2S.
- ✓ Selective removal of H_2S from a gas containing both CO_2 and H_2S.

Now, let us see the various basis of this removal of this acid gases; we may remove carbon dioxide from a gas that contains no H 2 S or we can remove H 2 S from a gas which does not contain carbon dioxide; that is carbon dioxide and H 2 S are present alone. And then we can simultaneously remove these 2 gases or we can selectively remove H 2 S from a gas containing both CO 2 and H 2 S; depending on the requirement we will have to adopt suitable method to meet these conditions.

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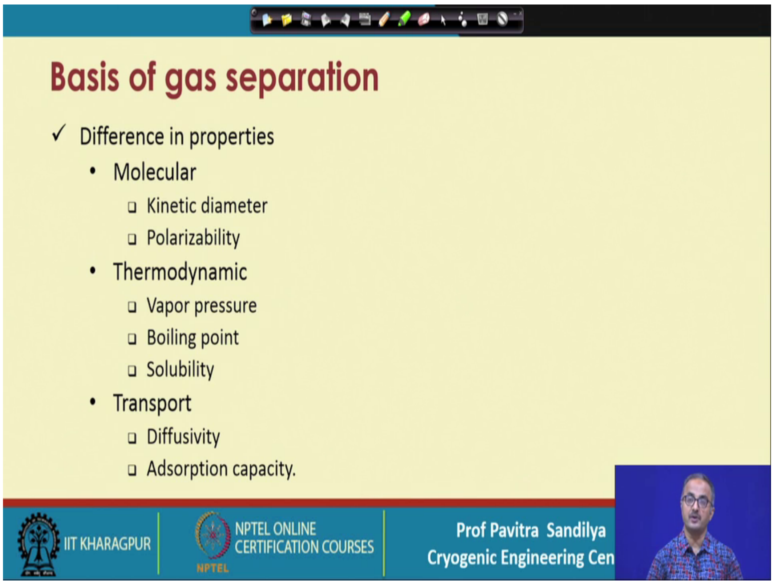

Basis of gas separation

- ✓ Difference in properties
  - Molecular
    - ❑ Kinetic diameter
    - ❑ Polarizability
  - Thermodynamic
    - ❑ Vapor pressure
    - ❑ Boiling point
    - ❑ Solubility
  - Transport
    - ❑ Diffusivity
    - ❑ Adsorption capacity.

Now, there are various basis of the gas separation; in this case either we go a molecular properties like kinetic diameter, polarizability; then thermodynamic properties like vapor pressure, boiling point, solubility, then transport property like diffusivity, adsorption property. So, all these properties will dictate that which type of method we have to adopt for a given application.

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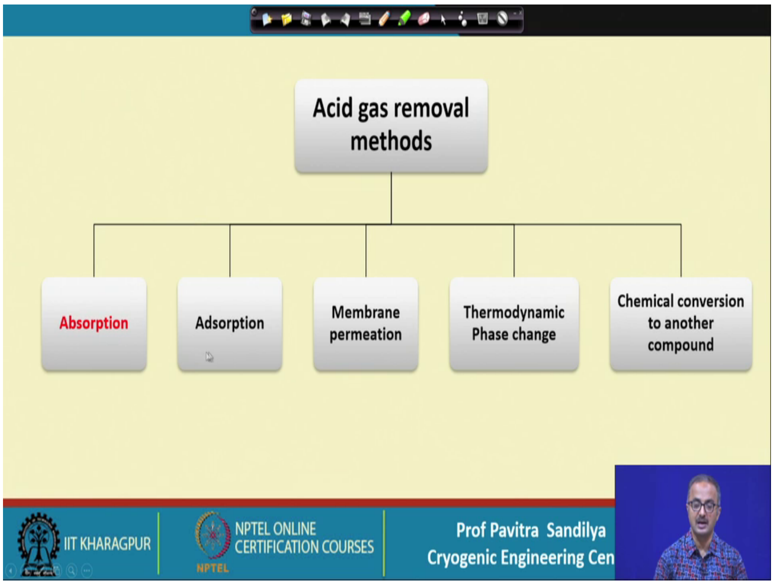

Acid gas removal methods

- Absorption
- Adsorption
- Membrane permeation
- Thermodynamic Phase change
- Chemical conversion to another compound

So, here are the various methods absorption, adsorption, membrane permeation, thermodynamic phase change and chemical conversion to another compound and in this particular lecture we shall be focusing on absorption.

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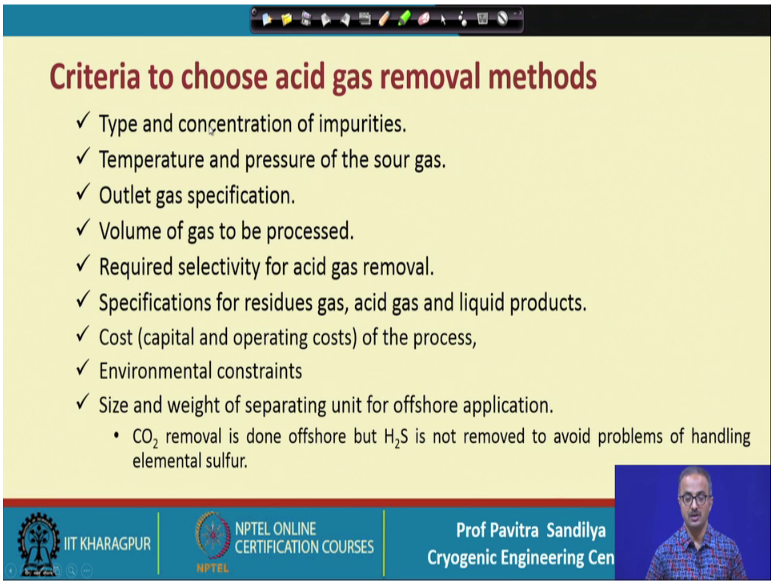

Criteria to choose acid gas removal methods

- ✓ Type and concentration of impurities.
- ✓ Temperature and pressure of the sour gas.
- ✓ Outlet gas specification.
- ✓ Volume of gas to be processed.
- ✓ Required selectivity for acid gas removal.
- ✓ Specifications for residues gas, acid gas and liquid products.
- ✓ Cost (capital and operating costs) of the process,
- ✓ Environmental constraints
- ✓ Size and weight of separating unit for offshore application.
  - CO_2 removal is done offshore but H_2S is not removed to avoid problems of handling elemental sulfur.

Now, first before that let us see what are the criteria to choose these acid gas removal methods? One is this that type and the concentration of the impurities that is how much amount of H 2 S and CO 2 are present. Then temperature and pressure of the sour gas and then outlet gas specification, the volume of the gas to be processed, the how much selectivity we want for the acid gas removal.

Then the specification of the residual gas, acid gas and liquid products; then the cost of the process in any environmental constraints and size and weight of the separating units in case we are talking of offshore application. And in this case carbon dioxide removal is done offshore, but H 2 S is not generally removed to avert problems of the handling the elemental sulfur on the offshore applications.

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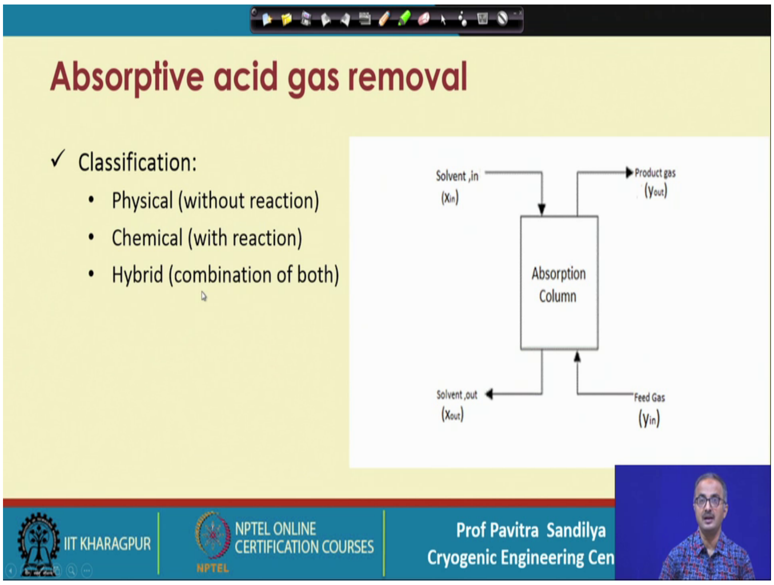

Absorptive acid gas removal

✓ Classification:
  - Physical (without reaction)
  - Chemical (with reaction)
  - Hybrid (combination of both)

Now let us come to the absorptive acid gas removal; here we find from this diagram a typical arrangement to remove these gases by absorption. Here we have an absorption column and we are feeding the gas from the bottom and the solvent some solvent is fed from the top, it comes down and it moves up and they are mixing counter currently in this particular column.

And during this mixing what is happening? The carbon dioxide and H 2 S are getting dissolved in the solvent and they are removed from the gas; the gas which is coming out will be having now less amount of these gases; Whereas, this solvent will be rich with the H 2 S and CO 2. So, that is how a typical absorption process looks like and we have various types of absorption processes which are physical; that means, without any kind of reaction, then chemical this is with reaction and hybrid which includes both physical and chemical absorption process.

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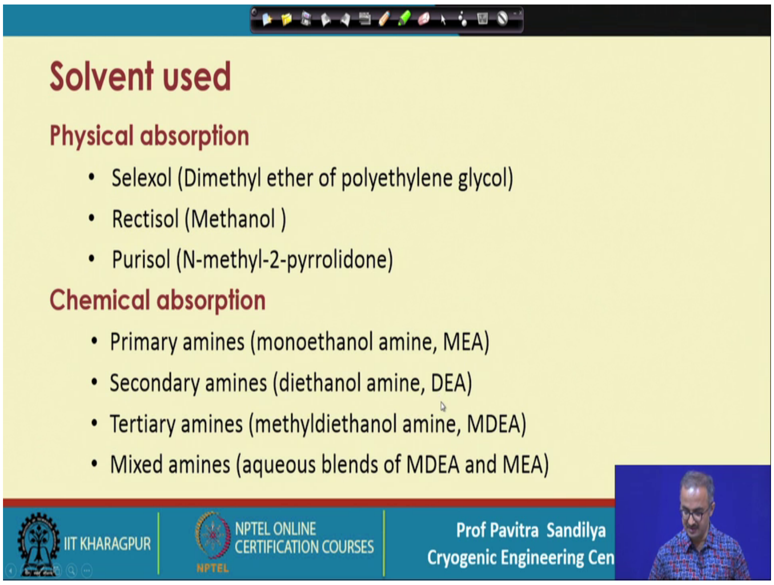

Solvent used

Physical absorption

- Selexol (Dimethyl ether of polyethylene glycol)
- Rectisol (Methanol)
- Purisol (N-methyl-2-pyrrolidone)

Chemical absorption

- Primary amines (monoethanol amine, MEA)
- Secondary amines (diethanol amine, DEA)
- Tertiary amines (methyldiethanol amine, MDEA)
- Mixed amines (aqueous blends of MDEA and MEA)

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First we come to the physical absorption; here we have the solvents used here that selexol; these are the selexol, rectisol and purisol; they are the names of the commercial names. And they are basically all these compounds chemistry wise and they are compositions are proprietary that is why they have been given some commercial names. And similarly for the chemical absorption we have this basically amine based, we have primary amines, secondary amine, tertiary amine and mixed amine and here are the names of some of these amines.

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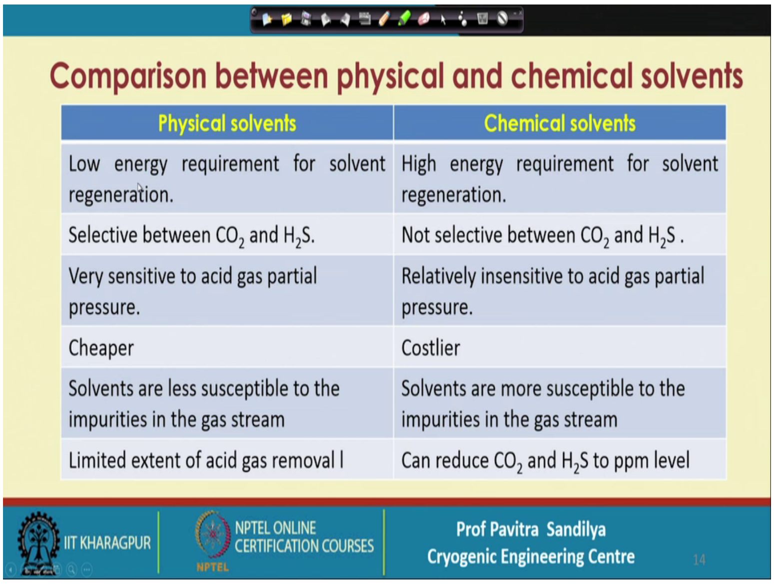

Comparison between physical and chemical solvents

Physical solvents	Chemical solvents
Low energy requirement for solvent regeneration.	High energy requirement for solvent regeneration.
Selective between CO_2 and H_2S.	Not selective between CO_2 and H_2S .
Very sensitive to acid gas partial pressure.	Relatively insensitive to acid gas partial pressure.
Cheaper	Costlier
Solvents are less susceptible to the impurities in the gas stream	Solvents are more susceptible to the impurities in the gas stream
Limited extent of acid gas removal	Can reduce CO_2 and H_2S to ppm level

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Now, if we compare the physical and the chemical solvents; we find that the physical solvents have low energy requirement for solvent regeneration. Because the H 2 S and CO 2 are weakly held by the solvent whereas, the energy requirement for the chemical solvents is high because a much stronger bond due to the chemical reaction between H 2 S, CO 2 and the solvent. Then this selective between CO 2 and H 2 S whereas, in chemical solvent they are not selective between these 2 gases; that means, these 2 gases are absorbed almost the same extent.

Then physical solvents are very sensitive to acid get partial pressure whereas, chemical solvents are relatively insensitive to the partial pressure of the acid gases; that means, the concentration of the acid gases in the feed mixture. Physical solvents are cheaper, chemical solvents are costlier then physical solvents are less susceptible to the impurities in the gas stream whereas, chemical solvents are more susceptible to the presence of the impurities.

Because the impurities again may get reacted with these solvents and they will reduce the solvent capacity. And then we have limited extent of the acid gas removal; whereas, in case of chemical solvent they can reduce the, this acid gas to a very very low extent and even they can go to PPM level.

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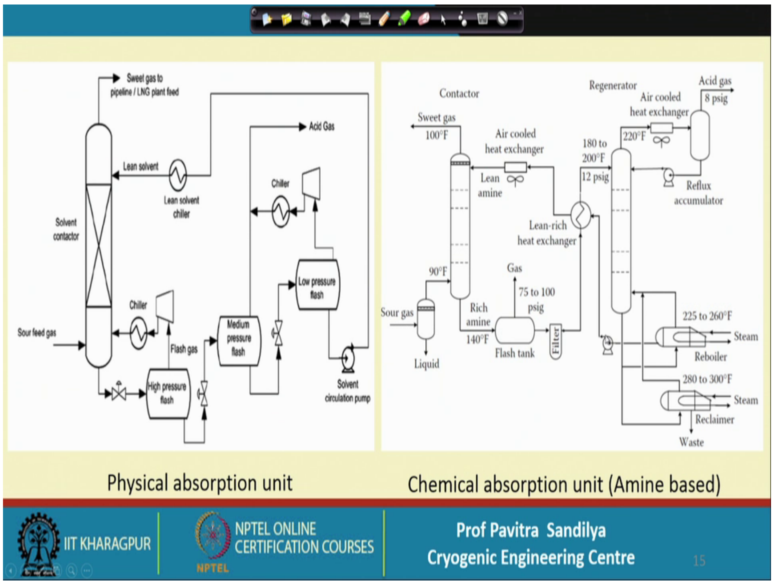

Physical absorption unit

Chemical absorption unit (Amine based)

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Next, we come to a typical physical absorption unit; in this we find that we have the suburb feed gas here which is fed from the bottom of the absorption column. And from the top we are inputting the lean solvent; lean means this solvent does not have much of carbon dioxide and H 2 S. If it is fresh solvent it is does not have any, but if it is regenerated the amount of carbon dioxide and CO 2 and H 2 S will be less.

So, this is why this called lean solvent and when it contacts with the up going gas; then what happens? It takes up the carbon dioxide and H 2 S and that is how it becomes a rich solvent. And then it is flashed twice at two different pressures and because of flashing only and flashing does not take much energy; so, because it is flashing we can do a multiple cascaded flashing high pressure medium pressure low pressure and by reducing the pressure we are able to recover the solvent more and more.

So, just by flashing we recover the, these gases and from then with that take the solvent back to the column after regeneration. So, this cycle is continued until unless we find that the capacity of the solvent has not come below the requisite capacity; so this is quite simple. And but in case of the chemical solvent we need more elaborate arrangement for the regeneration. Because the bonding between the solvent and the acid gases are much stronger; in this case simple flashing does not work.

So, in this case what happens the regeneration is done by steam stripping; that means, we put the steam. And this steam again it has it is a external heating we do to get the steam. And the steam is put in another column regenerator column and in this regenerator column, we take the rich amine rich solvent from the top and stream from the bottom. And then we get this particular amine from this column and it is sent back to the actual absorption column.

So, this is how we are operating the chemical absorption unit and here we are needing the steam and not simple flash.

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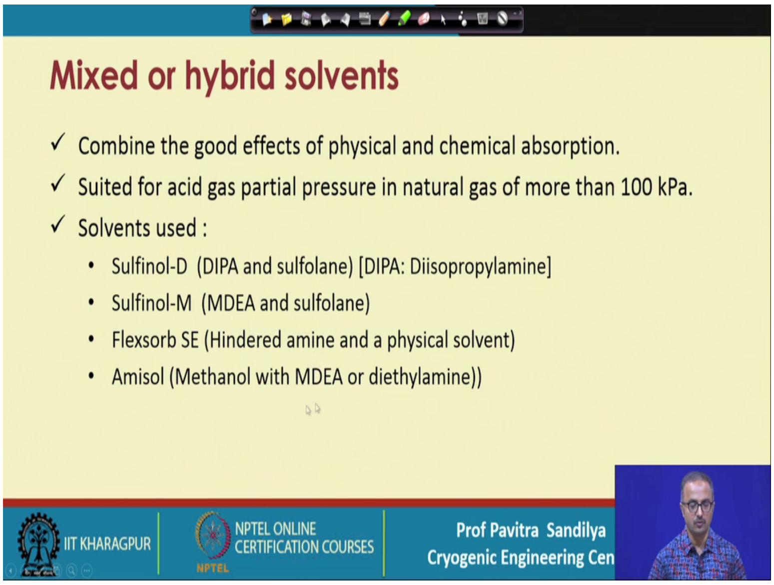

Mixed or hybrid solvents

- ✓ Combine the good effects of physical and chemical absorption.
- ✓ Suited for acid gas partial pressure in natural gas of more than 100 kPa.
- ✓ Solvents used :
  - Sulfinol-D (DIPA and sulfolane) [DIPA: Diisopropylamine]
  - Sulfinol-M (MDEA and sulfolane)
  - Flexsorb SE (Hindered amine and a physical solvent)
  - Amisol (Methanol with MDEA or diethylamine))

And then we have mixed hybrid or mixture hybrid solvent in and why we use this? Because they are having the combining the good effects of both the physical and chemical absorption processes; which we shall see just a while later. And then we have their suitable for acid gas partial pressure in natural gas more than 100 kilopascal and these are the various mixed solvents used sulfinol; D is something like a DIPA and sulfolane sulfinol M is MDEA and sulfolane and so on and so forth. So, we are using different types of mixed amines.

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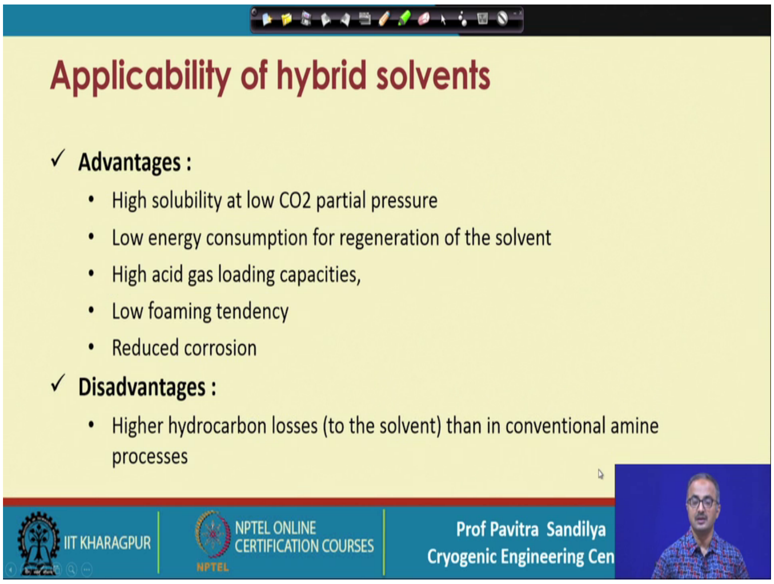

Applicability of hybrid solvents

- ✓ **Advantages :**
  - High solubility at low CO2 partial pressure
  - Low energy consumption for regeneration of the solvent
  - High acid gas loading capacities,
  - Low foaming tendency
  - Reduced corrosion
- ✓ **Disadvantages :**
  - Higher hydrocarbon losses (to the solvent) than in conventional amine processes

And these are the applicability of solvents and advantages are that; there are high solubility at low carbon dioxide partial pressure, they are low energy consumption for regenerating the solvent. And they have very high capacity to remove the acid gases, they do not form much and they have very low corrosion tendency. These are the advantage are that there will be high hydrocarbon loss to the solvent than the conventional amine processes.

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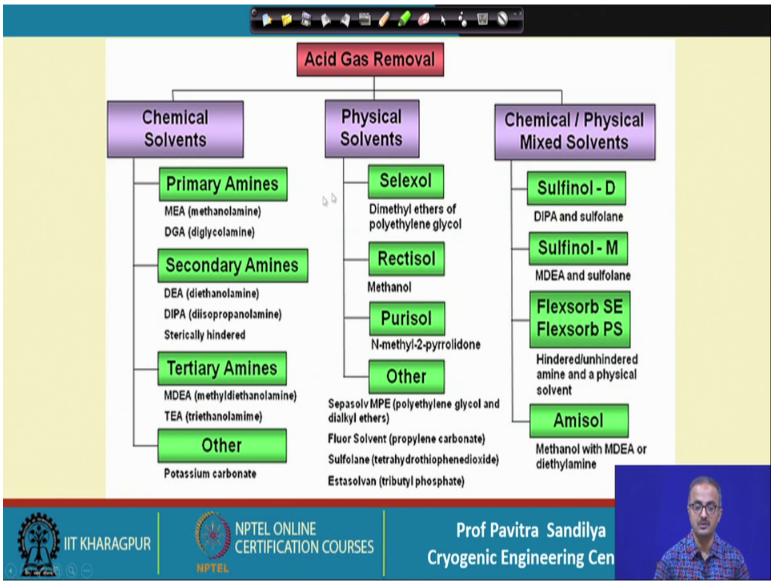

Acid Gas Removal

- Chemical Solvents
  - Primary Amines
    - MEA (methanolamine)
    - DGA (diglycolamine)
  - Secondary Amines
    - DEA (diethanolamine)
    - DIPA (diisopropanolamine)
    - Sterically hindered
  - Tertiary Amines
    - MDEA (methyldiethanolamine)
    - TEA (triethanolamime)
  - Other
    - Potassium carbonate
- Physical Solvents
  - Selexol
    - Dimethyl ethers of polyethylene glycol
  - Rectisol
    - Methanol
  - Purisol
    - N-methyl-2-pyrrolidone
  - Other
    - Sepasolv MPE (polyethylene glycol and dialkyl ethers)
    - Fluor Solvent (propylene carbonate)
    - Sulfolane (tetrahydrothiophenedioxide)
    - Estasolvan (tributyl phosphate)
- Chemical / Physical Mixed Solvents
  - Sulfinol - D
    - DIPA and sulfolane
  - Sulfinol - M
    - MDEA and sulfolane
  - Flexsorb SE
Flexsorb PS
    - Hindered/unhindered amine and a physical solvent
  - Amisol
    - Methanol with MDEA or diethylamine

And here in this particular figure; we find that we are listing the various types of solvents used for the acid gas removal. In this we have chemical solvents, we have primary amine, secondary amine, tertiary amine and others like these are not amine potassium carbonate is not an amine. And those these are the various chemical solvents and these are the physical solvents the selexol, rectisol, purisol and others. All these things are given the commercial names and then we have the mixed solvents like sulfinol-D, sulfinol-M flexsorb, amisol etcetera.

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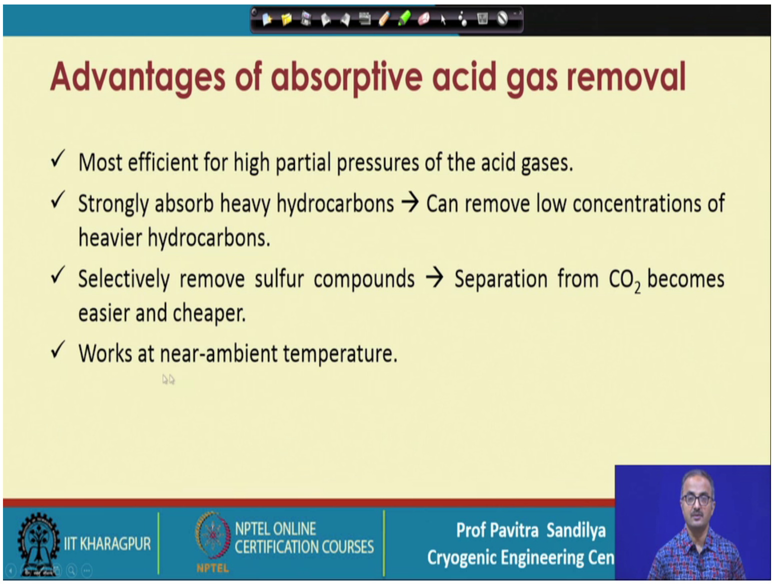

Advantages of absorptive acid gas removal

- ✓ Most efficient for high partial pressures of the acid gases.
- ✓ Strongly absorb heavy hydrocarbons → Can remove low concentrations of heavier hydrocarbons.
- ✓ Selectively remove sulfur compounds → Separation from CO_2 becomes easier and cheaper.
- ✓ Works at near-ambient temperature.

The advantages of the whole absorptive acid gas removal in comparison to the other processes like adsorption, membrane etcetera. That we find that they are most efficient for high partial pressure of the acid gases; that means, if the acid gases amount come down; they may not be that economical and they adsorb; they absorb very high heavy hydrocarbons that they can remove the low concentration of heavier hydrocarbons. And they can selectively remove the sulfur compounds so, that we can separate carbon dioxide easily and cost effectively and they can work at near ambient temperature.

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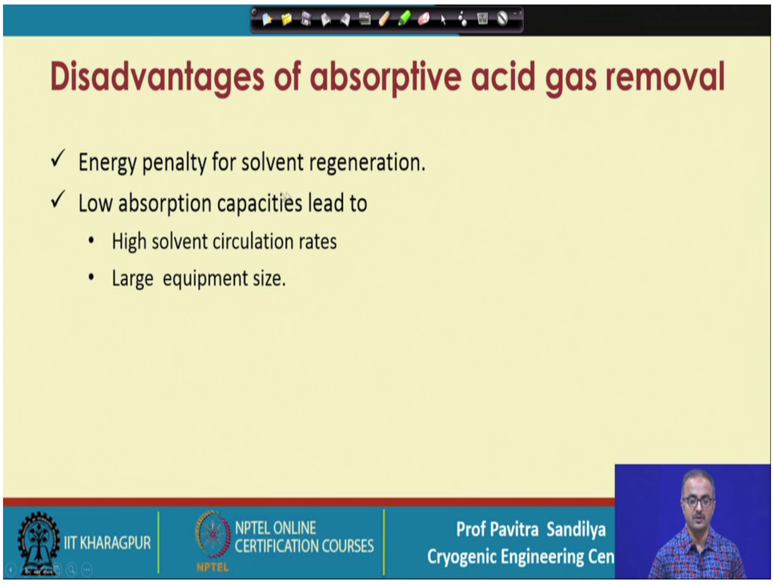

Disadvantages of absorptive acid gas removal

- ✓ Energy penalty for solvent regeneration.
- ✓ Low absorption capacities lead to
  - High solvent circulation rates
  - Large equipment size.

However, the disadvantages are that we have to spend energy for the solvent regeneration and they have low absorption capacity that that leads to high solvent circulation rate and large equipment size.

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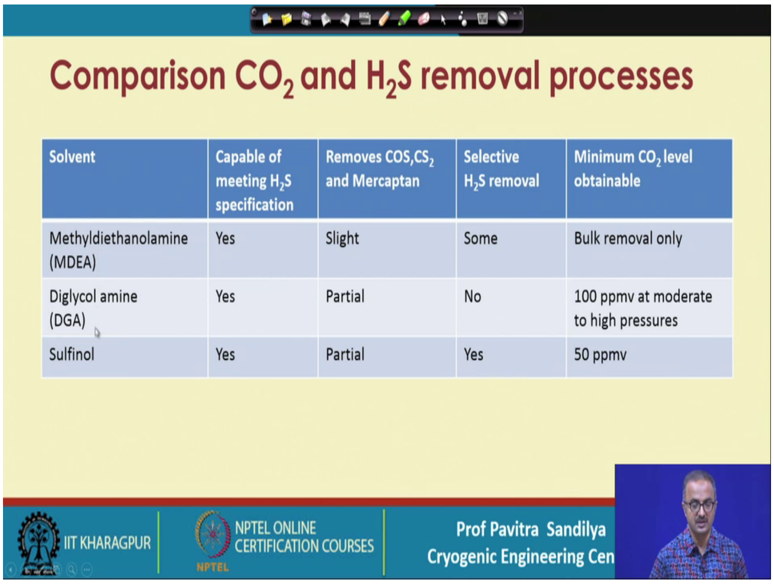

Comparison CO_2 and H_2S removal processes

Solvent	Capable of meeting H_2S specification	Removes COS,CS_2 and Mercaptan	Selective H_2S removal	Minimum CO_2 level obtainable
Methyldiethanolamine (MDEA)	Yes	Slight	Some	Bulk removal only
Diglycol amine (DGA)	Yes	Partial	No	100 ppmv at moderate to high pressures
Sulfinol	Yes	Partial	Yes	50 ppmv

Now, here are the comparison of the carbon dioxide and H 2 S removal processes using the various solvents here. We find that the various solvents we are putting in terms of the capability of meeting the H 2 S specification, whether they can remove these sulfur compounds or not and how selective are they about the H 2 S removal. And the minimum amount of CO 2 level that can be obtained and in this way we find that the various kinds of solvents are capable of removing sulfur to different extents and sulfur compounds. And we find that the amount the minimum amount of carbon dioxide level reached by this solvent also differ.

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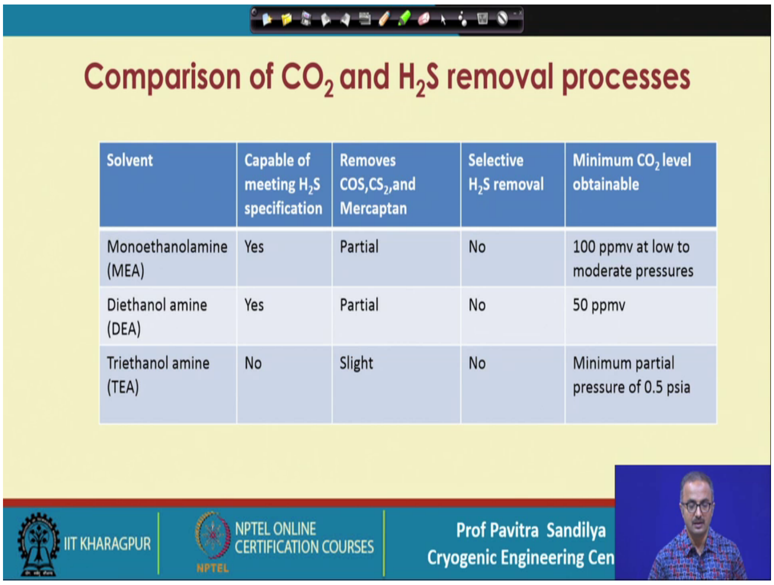

Comparison of CO_2 and H_2S removal processes

Solvent	Capable of meeting H_2S specification	Removes COS, CS_2, and Mercaptan	Selective H_2S removal	Minimum CO_2 level obtainable
Monoethanolamine (MEA)	Yes	Partial	No	100 ppmv at low to moderate pressures
Diethanol amine (DEA)	Yes	Partial	No	50 ppmv
Triethanol amine (TEA)	No	Slight	No	Minimum partial pressure of 0.5 psia

And here it continues with the other solvents here.

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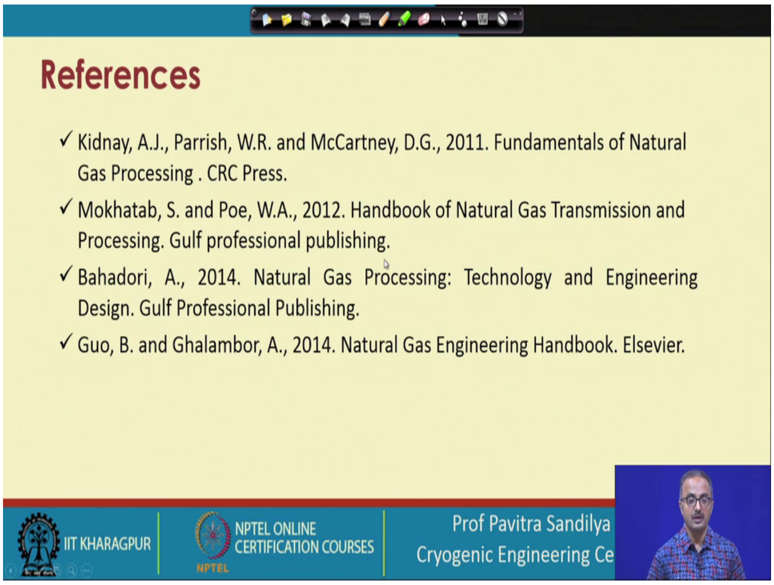

References

- ✓ Kidnay, A.J., Parrish, W.R. and McCartney, D.G., 2011. Fundamentals of Natural Gas Processing . CRC Press.
- ✓ Mokhatab, S. and Poe, W.A., 2012. Handbook of Natural Gas Transmission and Processing. Gulf professional publishing.
- ✓ Bahadori, A., 2014. Natural Gas Processing: Technology and Engineering Design. Gulf Professional Publishing.
- ✓ Guo, B. and Ghalambor, A., 2014. Natural Gas Engineering Handbook. Elsevier.

So, you can find more detail about these processes from these references.

Thank you.