Natural Gas Engineering
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Module No # 03
Lecture No # 14
Sweetening of Natural Gas

Hello everyone, in today's lecture, we will continue our discussion of processing natural gas. So in today's lecture, we will discuss sweetening process in the previous lecture, we were discussing about removing the water vapor from the natural gas.

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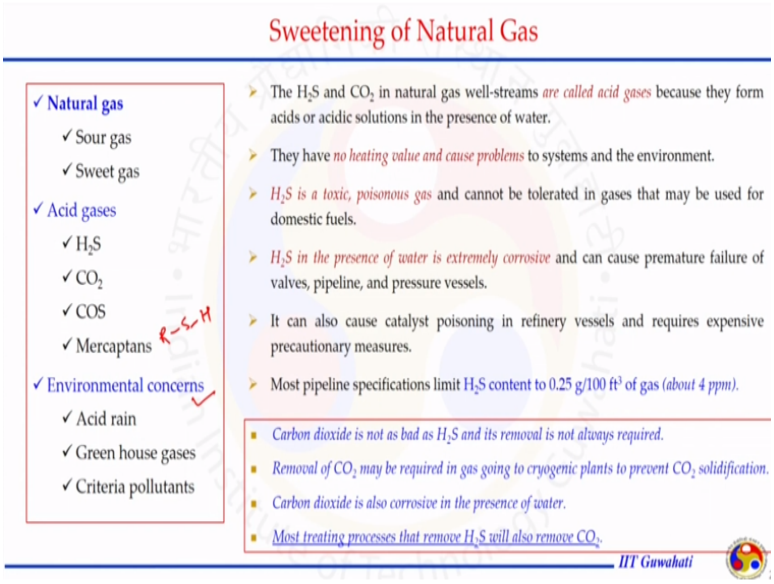

So in this lecture the acid gases present in the natural gas will be discussed. So the H2S and CO2 in natural gas well-streams are called acid gases because they form acid or acidic solutions in the presence of water. They have no heating value that is why they should be removed because when we are transporting natural gas along with these acid gases.

A was the case in the water removal process also water was not having any energy value similarly H2S and CO2 are also not having any energy, we are unnecessary transporting more amount of the natural gas which is having the less energy. Not only the energy content, but these gases are corrosive in the nature in the presence of the water and they create lot of problem for the equipment and pipeline design for handling the natural gas.

H2S in the presence of water becomes very extremely corrosive and cause permanent failure of valves, pipeline and pressure vessels. It can also cause catalyst poisoning in refinery, so if the natural gas is sent to further processing unit where the catalyst is being used and in that process, if H_2S is there, water vapor is there, then H_2S will create the poisoning for the catalyst and the catalyst deactivation will occur.

In most of the cases, the pipeline specification limits H_2S content to 0.25 gram per 100 feet cube of gas that is approximately around 4 ppm. So the gases CO_2 and H_2S make the natural gas sour gas and if we removing these gases, along with the water we are having the gas that is termed as sweet gas. The acid gases are H_2S, CO_2, COS as well as Mercaptans.

Mercaptan is a kind of a structure RSH. This is also called (()) (03:09) and they are having very bad odour, they should also be removed along with the other acid gases to make the gas feasible in the domestic purpose. The removal of the H_2S, CO_2, COS and Mercaptans not only because of the pipeline requirement, but they create a major problem in terms of the acid rain, greenhouse gases and the product of these acid gases when they are combusted fall in the criteria pollutant also.

So the environmental concern should also be taken care when we are using the natural gas. So sweetening of natural gases means removing the acid gases the presence of acid gases makes the natural gas sour gas and after removing this natural gas becomes the sweet gas. The product of sulfur compounds when it is oxidized, SO_2 is one of the criteria pollutant that were this should be removed and most of the process those are used to remove the H_2S also remove this CO_2.

But the selectivity of a process should be chosen because carbon dioxide is not as bad as H_2S removal of CO_2 may be required when we are going to send this gas for the cryogenic application, where because of the low temperature is CO_2 is getting solidified and creating problem. Carbon dioxide is also corrosive in the presence of the water and as mentioned most of the process those remove the H_2S, also remove CO_2.

And when both the gases are present in the natural gas our process should be chosen that can remove both the gases, along with other acid gases like COS and Mercaptans,

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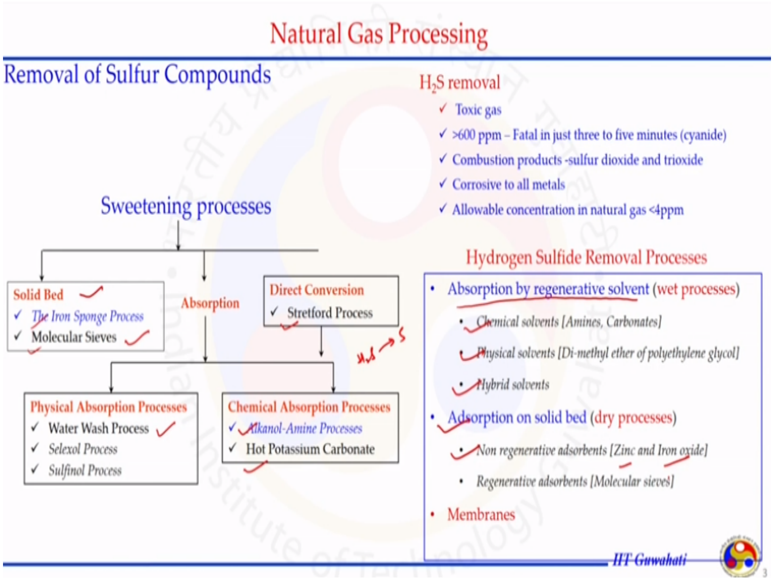

So the removal of sulfur compound is very much required when we are going to send natural gas for the end user applications. For example, the H2S removal is very much required because it is toxic gas, more than 600 ppm concentration in the natural gas is consider very fatal and its toxicity is compared with the cyanide. Combustion product like sulfur dioxide, trioxides they contribute to the acid rain, corrosive to almost all the metals and a level concentration in natural gas is less than 4 ppm.

That is why H2S must be removed from the natural gas and the removal process of H2S and other sulfur compound from the natural gas is called sweetening process. We can classified sweetening processes as we did for the dehydration process like there are ways where the physical processes can be adopted.

Like in case of the dehydration process the direct cooling the compression followed by the cooling where the physical processes where the just changing the operating condition the water could be separated and specifically designed processes like the adsorption and absorption processes are widely used.

Similarly for removing the acid compound or performing the sweetening processes, if we look in the literature, there are several processes more than 100 processes are there those can be employed or those where employed to remove the sulfur compounds from the natural gas. If we broadly classify them we can say they are solid based means the adsorption kind of processes they can be the absorption kind of the processes or could be the direct conversion when sulfur compounds are directly getting converted to elemental sulfur.

So if we look on the solid bed processes, the processes like the irony sponge processes and the molecular sieves processes are similar to adsorption processes for the dehydration where the packing of solid bed is used to remove selectively the compound from the natural gas. In case of the sweetening process it is H2S or carbon dioxide or some other gases those are present in the natural gas.

So this solid bed processes like the irony sponge, molecular sieves, there could be some other solid packing also in the tower that can be used to perform the sweetening processes in the absorption processes. Further it can be classified in two parts physical absorption processes and chemical absorption processes.

So the physical absorption processes the solvent is used that is not reacting with the H2S, CO2 or other acid gases, but physically it is having certain affinity to these gases selectively or in a combined manner for both CO2 and H2S, they are getting separated from the natural gas. The processes could be water wash process, Selexol processes, Sulfinol processes.

On the other side chemical absorption processes, the reaction between the solvent chosen and the acid gases present in the natural gas occur and the separation of acid gases from natural gas can be accomplished. There are again several processes, some of them are highlighted here like the amines based processes or the hot potassium carbonate processes.

In the direct conversion process the process is called Stretford process that is used long time back for the direct conversion of H2S to sulfur, it be looked based on the other criteria how to classify the processes, we can see for the hydrogen sulfide removal processes, we can lump the processes in the form absorption by regenerative solvents also called the wet processes.

In this kind of the processes, the solvent that is used for the absorption purpose is getting regenerated either it is a physical solvent or chemical solvent, both the solvents are getting regenerated in their respective processes and being re-circulated for perform the continuous operation. The solvent like the chemical solvent could be the amine or the carbonate solvent.

In the category of physical solvent this could be the Di-methyl ether of polyethylene glycol or some other. There are several chemical and physical solvents have been reported in the literature to perform the sweetening process or there is a possibility also to use both chemical and physical solvent to perform the absorption process in a regenerative mode like the process where we are choosing chemical solvent as well as physical solvent in a particular proportionality and performing the absorption process.

On the other side the adsorption on the solid bed also called the dry process classified as non-regenerative adsorption processes where the packing material or the material which is used to selectively remove the acid gases like the Zinc, iron oxide or there might be some other materials cannot be regenerated or not regenerated and there could be processes where the material is regenerated like molecular sieves are used to perform the adsorption process to remove the acid gases.

There are certain other processes those are based on the membranes, so the membrane are designed those are having very specific selectivity to separate out some of the compounds from a particular gas stream, in this case the membranes can be selected those are alloying to pass through H2S and CO2 gases selectively and retaining the other gases on the other side. All together we can see there are several processes

Those are similar to what we did for the dehydration processes. We are having the solid bed or the absorption tower where the liquid is been circulated and the gas is in the contact with the liquid and the selectively H2S, CO2 or other sulfur compounds are getting separated out from the natural gas. Further the industry sweetening process can be classified as non-regenerative process, generating process with recovery as H2S or recovery with the elemental sulfur.

The H2S removal processes again can be classified based on the process name like the cryptal process it is the combination of several processes which use the amine solvent that could be MEA, DEA, DGA and MDEA. The Benfield Corporation process that is the carbonate, potassium carbonate and this selexol process that is the physical solvent MPEG.

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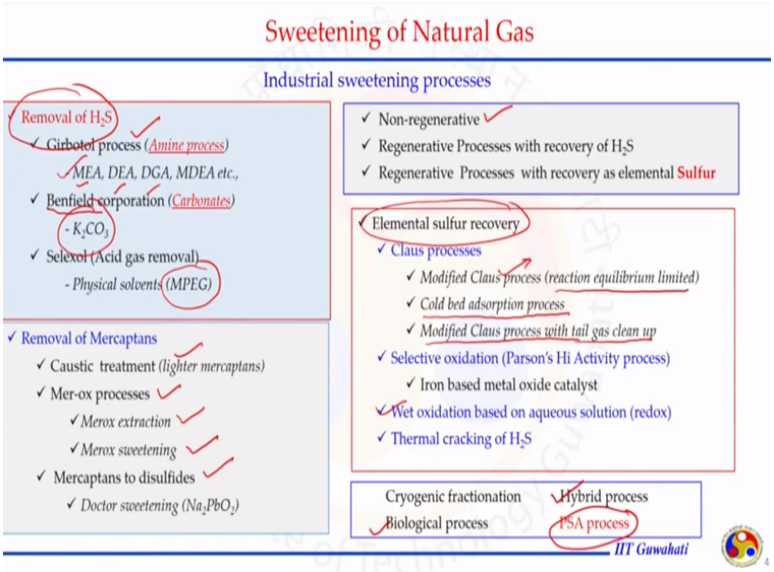

Similarly for the removal of Mercaptans, the processes are named as caustic treatment process which is used for lighter Mercaptans compound removal, Merox process that is further classified in a Merox extraction and Merox sweetening processes and converting Marcaptans to disulfide the process named as doctor sweetening process or the sodium plumbide process

On the other hand when we talk about the elemental sulfur recovery the processes are classified as Claus processes. In Claus processes we can have the option of modified Claus processes that work from the reaction equilibrium Limited concept. Cold bed adsorption process or modified Claus process with tail gas clean up.

This selective oxidative process is also there which generate elemental sulfur while removing the acid gases from the natural gas and that can also be accomplished by wet oxidation based on aqueous solution this process is named as redox process or Bi- thermal cracking of H2S. In advance side, we are having the processes that could be the hybrid process where the combination of one or two processes are being used to remove the acid gases from the natural gas either in the form of the H2S or in the form of elemental sulfur.

Biological processes are getting advanced, another process that is PSA preserving adjacent process that is just a physical process where the operating condition like the pressure is changing in such a manner the acid gases are getting separated out from the natural gas. Let us discuss some of the processes those are widely used to perform the sweetening process at the industrial level. We are not going to discuss each and every process but some of the process goes use the concept of physical separation or chemical separation or converting the acid gases to elemental sulfur will be discussed in a brief manner.

Like for example the iron sponge sweetening process it is batch process also known as dry box process in which the sponge being a hydrate iron oxide supported on a wood chip is used and the natural gases just passed through this batch Mode packing and we are going to get the gases those are present in the natural gas. Like the H2S is getting separated on the bed of this wood chip iron sponge.

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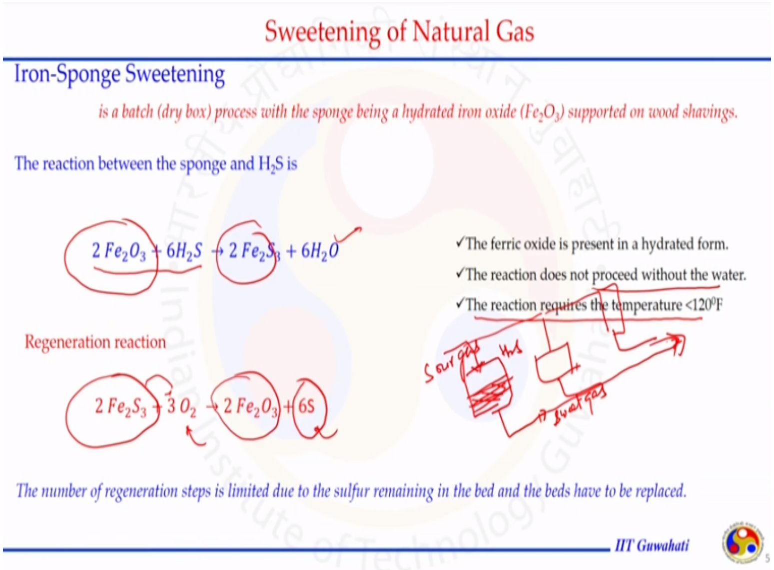

In iron sponge sweetening process there is a tank which is filled with this iron sponge on the support of wood chips and the natural gas which is having the sour gases is passed over it and after passing through this bed we are getting the sweet gas. This is sour gas, so the packing inside his tank is Fe2O3 and when the gas which is having the H2S is passing the reaction is happening between this ferric oxide with H2S and we are getting ferric sulfide as the product on this bed and the water is removed.

In the regeneration mode, we can regenerate this bed which is in operated under the batch mode, in that mode we are going to perform the regeneration process by passing the oxygen through this bed and because of the reaction happening here we are going to get Fe2O3 bed along with elemental sulfur on the bed.

So the reaction does not proceed without the water so some amount of the water along with alkalinity should be present in the tank that is where the process will occur and the reaction will cause the temperature to be lower than 120 degree Fahrenheit, then only this reaction will occur at a high temperature, it will not occur if the water is not present or alkalinity is not present in the tank, the iron sponge reaction will not be effective to remove the H2S compound.

So this is based on the chemical reaction process where the ferric oxide is reacting with H2S getting converted into some sulfur compound Fe2S3 and during the regeneration process we are going to get this elemental sulfur as the product. The number of regeneration process is limited because this sulfur or the elemental sulfur remains in the bed and after certain regeneration is stepped, this bed may not be useful for performing the H2S removal process thus we have to replace the bed.

If we want to perform this irony sponge process at a larger scale, as it is a batch mode when we are having this packing just passing the natural gas over it, we can put the multiple unit in parallel to perform the reaction at a larger scale.

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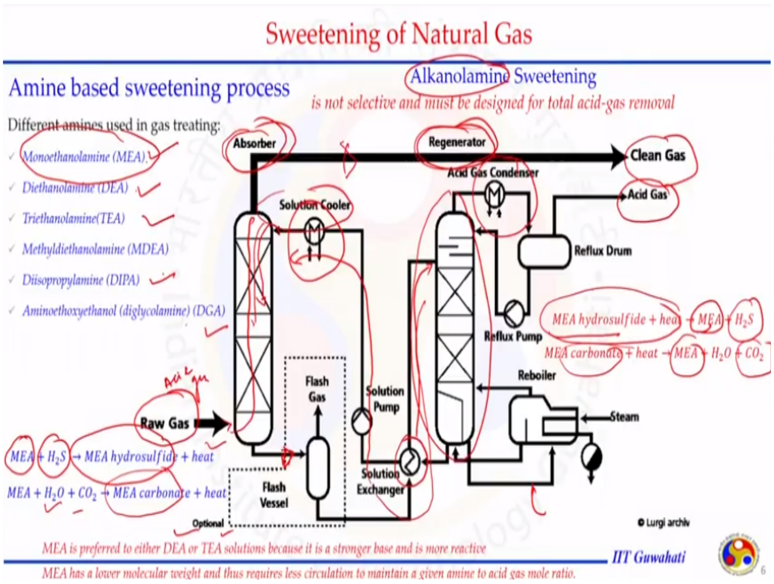

If we talk about amine based sweetening process. This is the process which is widely used to perform the sweetening of natural gas in this, process also known as alkanolamine sweetening process, which is not selective towards choosing one particular type of the acid gas but it removes both CO2 and H2S.

Different amines are used to perform this alkanolamine sweetening process, those could be MEA Monoethanolmine, Diethanolamine, Trietanolamine MDEA, DIPA or DGA on the combination of them. There are several studies performed where the combination of them maybe performing better than Individual.

But all together MEA is considered as one of the best options to choose as solvent. In this process, the things are almost similar what we have for the dehydration process, so far any absorption or adsorption process we are having the two units, one is to perform the absorption and adsorption process and the other unit to have the regeneration of either the solvent or the solid packing material.

Similar to those processes in the amine based sweetening process the raw gas which is having the acid gases along with it is entering to this absorber tower and passing through from bottom to top. We are circulating this solvent, the chosen solvent could be individual amines or the combination of the amines that is passing through this absorber tower from top to bottom.

And the gas and the solvent are coming into contact and the chemical reaction is happening as amine is having the affinity to H2S and MEA + H2S are going to form MEA hydrosulfide and releasing some heat in this process. The MEA also reacts with CO2 in the presence of H2O and we are going to get MEA carbonate along with the heat.

So this two reactions are happening in this absorber tower and selectively both H2S and CO2 are going to convert in another chemical form along with the heat release, and after that so the gas that is passing from the top is clean gas because these acid gases are removed with the help of this solvent.

And the solvent which is coming out of this absorber tower from the bottom part, may go to a flash gas drum kind of a is cover or a separator or a flush separator that is an optional device where it is separating the just free gases out of the solvent. Otherwise, the gases those are with the solvent are going through some heat exchanger unit and after that they are going to regeneration unit.

In regeneration unit, we are going to separate this solvent from this chemical which is form in the absorption tower. Either it is a physical or it is a chemical reaction the region the reasons to perform to recover the valuable solvent and the valuable solvent can be sent back to the absorber tower to perform the continuous operation and reducing the cost of supplying the fresh solvent every time.

In that case, in the regenerator we are increasing the temperature, it means we are supplying the heat and this chemically formed chemical in the absorber is going to release the MEA from both hydrosulfide and carbonate compound along with the H_2S and CO_2. So the reverse reaction whatever was happening in the absorber where you will be able to separate this CO_2 and H_2S from the natural gas.

The reverse reaction is happening in the regenerator where the CO_2 and H_2S along with water also getting liberated and the MEA, the solvent chosen to perform this process is getting recovered and the recovered solvent is going back through this heat exchanger through the pump and getting circulated at temperature which is required to perform this process to absorber and perform the continuous operation.

The heat exchanger like the cooler is required because during this regenerated process, we are using the higher temperature to remove the MEA from this chemically formed compound like the MEA Hydrosulfide and MEA carbonates, that is why the coolers and the other assemblies are required.

On the other side if we see a this is kind of a unit regenerated unit where we having the heating options through the re-boiler and similarly whatever is getting on the top we are having the condenser type of the assembly where we are able to recover the acid gases and the remaining solvent is going back to the tower like a distillation column.

So altogether depends upon whatever the solvent we are using, we are always going to have the absorber and the regenerator facilities to perform the sweetening process. As already mentioned MEA is preferred to DA or TA solution because it is stronger base and more is attractive. MEA as a lower molecular weight, thus the circulation is easy to maintain the ratio of amine to acid gases.

We did not discuss in detail how the factors going to affect this process, those factor could be the concentration of the acid gases, the circulation rate of the solvent, the temperature and pressure at which the absorber and regenerator are being operated. So we had discussed the flow sheet where we are having different unit assembled to perform the sweetening process.
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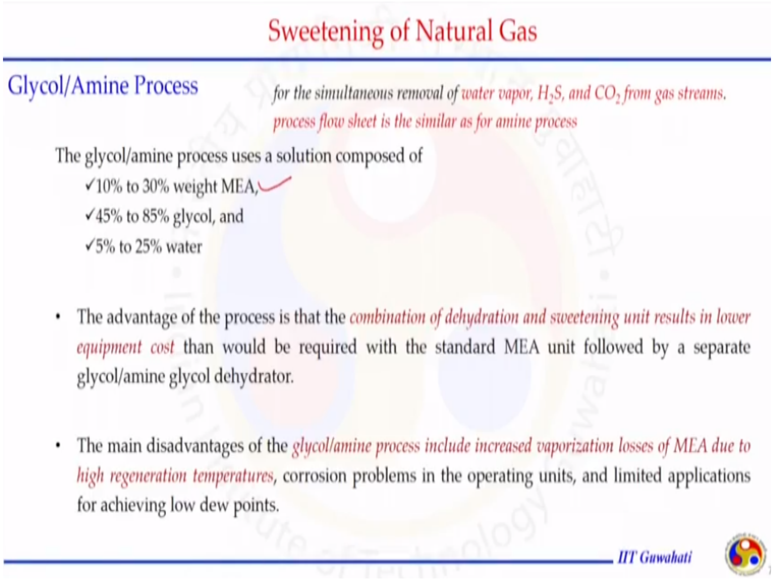

In glycol amine process, this process removes simultaneously water vapor, H2S and CO2 from the gases stream. The process flow sheet for the glycol amine process is similar to what we are having for the amine process in any type of the absorption process, we are going to have the two tower.

One is for the absorption process and the other for the regeneration process. And the other accessories like heat exchanger knock out drum, pump going to be placed to perform the process effectively. Similarly to amine processes are solvent is used in the glycol amine process is also, but here the solvent is a combination of glycol and amine.

Most of the time the solution or the solvent concentration goes like 10 % to 30% by weight MEA, 45 % to 85 % glycol, 5 % to 25 % water. The advantage of the process is that combination of dehydration and sweetening can be performed in a single unit. If you remember in the dehydration process we were using the glycol to separate the water vapor from the natural gas.

And the previous slide, we discussed how amine is going to help us to remove the acid gases. So the glycol amine process is a combination of both glycol process for the dehydration and the amine process for the acid gas removal and in this process both dehydration and sweetening process are performed simultaneously.

This is the advantage of choosing this glycol amine process however the disadvantage is that increased vaporization losses of MEA because in the regeneration unit the glycol is having the higher boiling point, we have to go at a higher temperature to regeneration unit and because of the boiling point difference in the MEA and the chosen glycol, we are going to lose MEA.

So compare to amine process, glycol amine process offer certain advantages as well as certain disadvantages are there. However, the efficiency of a particular process or the selectivity of a particular process depends on the other factors.

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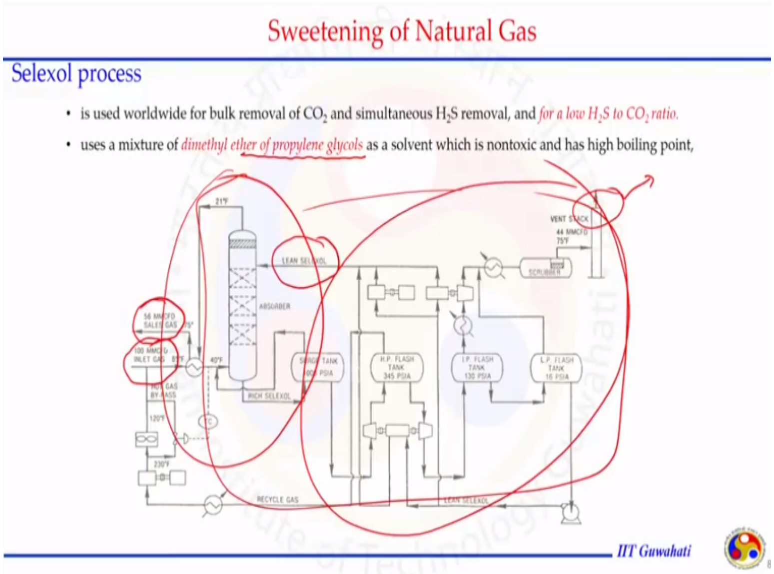

Next is a selexol process, it is based on the physical solvent which is used to remove the acid gases from the natural gas. So selexol process is used worldwide for bulk removal of CO2 and simultaneous H2S remover and this process is more effective when we are having low H2S to CO2 ratio.

It means this process is more effective when we are going to remove the CO2 and along with CO2, H2S is also getting separated out. This used a mixture of Dimethyle ether of propylene glycols as a solvent which is non-toxic and as high boiling point. Process flow sheet is similar again where we are having one the absorption tower where the separation is happening and the another combination of the unit where we are having the regeneration facilities to recover the solvent.

In this process selexol also, we can see the inlet gases here which is having the acid compound and after the absorber process we are going to get the gas that is ready to sell and we can call this sales gas it is having the very low concentration of acid gases and the acid gases are removed during this entire process.

And after regeneration, we are having the least selexol bed to the process and the acid gases are vented out from this part. So like amine and glycol amine process and selexol process, it is just different in case of the solvent is chosen to perform the absorption process. The selexol is the physical solvent another process is sulfinol process, this is used to remove H2S, CO2, COS, CS, Mercaptan and polysulfide from the natural gas.

So all sort of the acid gases can be removed using this sulfinol process, again the process flow diagram is similar to what we have for the amine process like we are having the absorption tower and regeneration tower. This process uses a mixture of solvent which allow us to perform both physical and chemical absorption process simultaneously.

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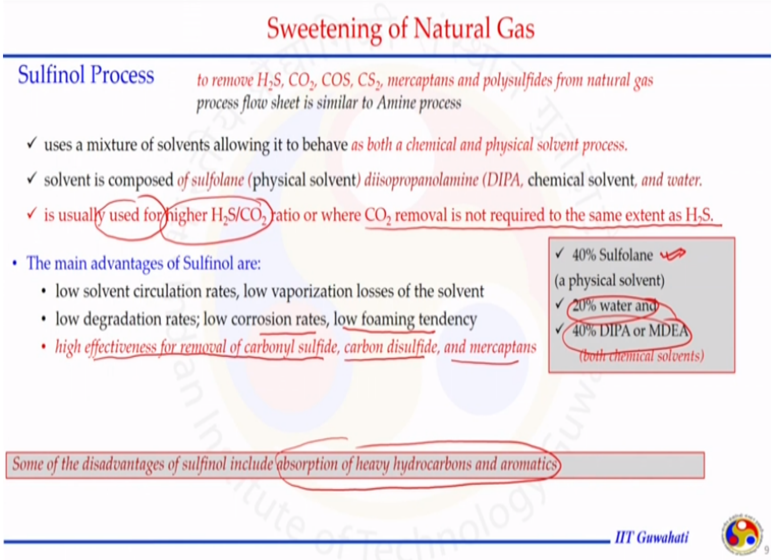

This solvent is composed of 40% sulfolane that act as a physical solvent and 20% water and 40% DIPA or MDEA that act as a chemical solvent. Because of having physical and chemical solvents, the operation of sulfinol process can be very selective to remove certain type of the gases either they are getting separated in the form physical solvent process or in the chemical absorption process.

This process is usually used for higher H2S to CO2 ratio or where CO2 removal is not required to the same extent as H2S. So this selexol process was used when we are having the ratio of H2S to CO2 at low level and when this ratio of H2S to CO2 is higher, we should use this sulfinol process.

The advantage of sulfinol process, it use both physical and chemical solvent, so it's a hybrid solvent process. The other advantage it offers we can use a low circulation rate of the solvent to perform the separation of sour gases. The solvent is having the low vaporization losses. Its degradation rates is also low, the corrosion rates is also low and it as the less tendency of forming.

The high effectiveness of removal of carbonyl sulfide, carbon disulfide and marcaptans along with H2S and CO2 makes sulfinol process as a good candidate when we are having the natural gas that contains all these kind of the sulfur compound. The disadvantage of this sulfinol process includes absorption of heavy hydrocarbons and aromatic compound.

So if the natural gas is having the higher hydrocarbon compounds in it and this sulfinol process should not be used because the physical and chemical solvent uses to perform the sweetening process. They may interrupt with the aromatic and the heavy hydro-carbonate compound and will become contaminate and the efficiency of the process will get reduced.

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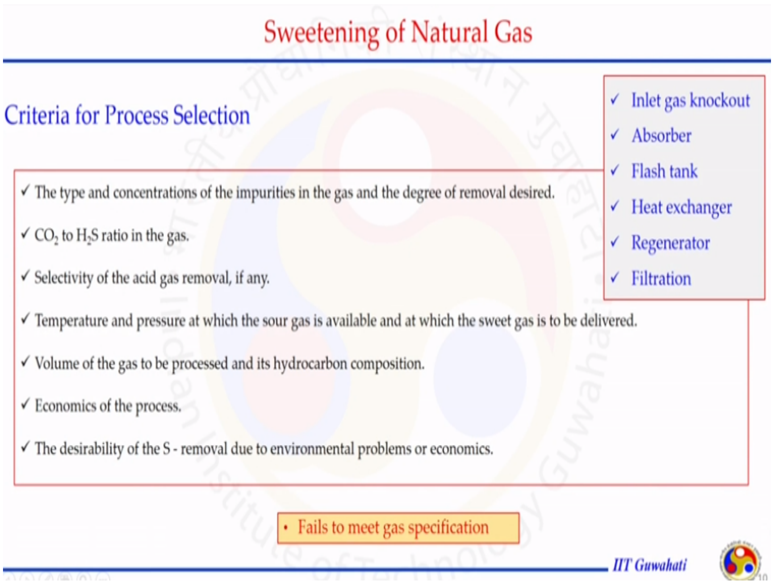

So after discussing some selective processes, those falls under the solid bed packing like the irony sponge process, amine solvent process, glycol amine again the combination of two solvents process. The selexol process which is having the more affinity for CO2 removal compare to H2S and the sulfinol process that should be used when we are targeting the H2S removal as primarily consult.

We can see there are several other processes and the selection of a process depends on several criteria. The foremost criteria is what are the composition of natural gas that is going to be treated in this sweetening process. How much percent of H2S and CO2 is present in the natural gas other than H_2S, CO_2 and the water vapor, how much percent of the other sulfur compound like COS, CAS, Mercaptans are present in the natural gas.

So the type and the concentration of these impurities or the sour gases or the acid gases which makes the natural gas as the sour gas are present and at what level they should be removed. The selectivity of the acid gas removal is also very important. The target is removing the H_2S or CO_2 the temperature and pressure at which the gas is going to be treated or going to enter in the sweetening process is also one of the criteria to choose the sweetening process.

Important one is also the volume of the gas that should be treated and other than considering amount of the gas, the composition of the gas and the temperature and pressure, it is going to be treated the economics of the overall process should also be considered because each process includes certain type of the equipment those should be installed to remove the acid gases.

The equipment list could be the inlet knockout drum depends on the impurities present in the natural gas or at other places when we are using the different solvent before it is going to the regeneration process, knockout drum may be required, absorber tower, flush tank, heat exchanger network to exchange the heat or to reduce the temperature of the solvent when before it is going to the absorber tower back and the filtration, if this solid particles are present or if the solid based processes used.

The desirability of the sulfur removal due to environmental problems or economics should also be considered. So the selection of a process based on the composition, based on the economics, based on the several criteria should always be judged or controlled based on the gases specification required before it is going to send to end consumer.

So if we chose a particular process is going to fail in meeting the guidelines of the transportation system, the process is not going to be useful. We have to choose a process that is going to meet the gas specification that is decided by the regulatory authority. So with this, I would like to end my topic on the sweetening process.

In this lecture we discuss briefly about some of the sweetening process those are use at the industrialist scale to make the sweet gas from the sour gas and meeting the specification of the pipeline thank you very much for watching the video we will meet in the next lecture thank you.