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## **Lecture – 42 Natural gas Processing- hydrate removal**

Welcome, now we shall learn about another processing of the Natural gas related to the removal of the gas hydrates from the natural gas.

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As we learnt earlier, that the gas hydrate was also talked about when we were looking into the production of the natural gas from the natural gas hydrate, now, here we see the various ways that how the gas hydrates inhibit the natural gas processing and why they have to be removed. So, in this lecture we shall be learning more about the gas hydrates the need for their removal how these gas hydrates are formed the different ways of inhibiting the formation of these hydrates then we shall look into some of the estimation methods to find out the formation temperature of the hydrate and the amount of inhibitor required to inhibit their formation.

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So, first let us look into what gas hydrates are.

Now, gas hydrates are a class of solid ice like nonstoichiometric compounds. Now in this case we have to see this ice like so, if I look at this particular picture we find that this is a gas hydrate and it looks exactly like ice. But the difference is this we cannot make out the difference between ice and this gas hydrate by our naked eye, we have to do some analysis, and we find that this particular piece of apparently solid ice is burning.

These burning characteristic tells us this is not water ice, but this is gas hydrate and this is burning because of the presence of the methane.

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So, these hydrates are different from the salt hydrates which we are more accustomed within our fundamentals of chemistry. So, in this the salt hydrates are not the these kind of hydrates, because the salt hydrates are stoichiometric compounds where is the hydrate hydrates are non stoichiometric compounds. And we have some examples of these salt hydrates like magnesium chloride with 6 water of crystallization copper sulfate with 5 water of crystallization.

Similarly, magnesium sulfate with 7 water of crystallizations so and so forth. And these hydrates are formed when watems water forms a cage structures, and how this cage is formed this cage is formed by hydrogen bonding among the water molecules. And in this particular cage any guest molecule like this methane, ethane H 2 S CO 2 etcetera are trapped there are many gases with can form gas hydrates.

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And here we see in this particular pictorial representation, how we get different type of structures here, here we find for the methane for example, has been trapped in a cage of water, in this particular diagram these black bits are representing the hydrogen molecule hydrogen atom whereas, these red ones are representing oxygen.

And here depending on the type of this particularcage, we have different types of hydrate structures, and here we do have s 1 structure s 2 s structure and structure one structure 2 and structure 8. And we find that different gases form different types of these hydrate structures. And these hydrate structures dictate the amount of the gas that can be captured in the particular water cage.

Now, understand this all the water cages in the structure may not be completely filled up some of them may remain partially filled so, but we have to understand that the depending on the type of the gas molecule the, this structure will be differing.

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Now, why these hydrates are not wanted in natural gas system the reasons are this firstly, slow assurance. What is meant by flow assurance? By this we mean that we want to ensure that there is an unrestricted flow of the hydrocarbons from the well to the processing point.

And the hydrocarbon flow get hindered by the deposition of the wax and asphaltene solids, the scaling by some inorganic salt deposition and by the gas hydrates.

So, all these causes the slow inhibition of the natural gas or the petroleum. So, they are unwanted in the system and gas hydrates are most feared, because they can form without any warning and then they will block the flow quickly unlike the other depositions because other depositions take time, but this gas hydrate can form anytime all of a sudden if they are the conditions in with respect to the pressure temperatures and other impurities are favorable.

And then if we are using some kind of chemical inhibitors to prevent the gas hydrate formation, even then we find that due to some operational failure of the pumps or the separators, we find that the inhibitors may not be injected properly into the system so that it will it may lead to the formation of the gas hydrates in the line.

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Now, what are the conditions which favor the formation of the gas hydrates? Favoring does not mean that the formation is guaranteed, but the conditions are such that it will main lead to the formation of the gas hydrates. Generally, it is at high pressure and low temperatures dictated by the thermodynamics.

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And we can find this a typical figure which is showing the pressure versus temperature diagram of some hydrocarbon with water. And we find here that this is the zone here within which we find these hydrates are formed in this zone we find the hydrate and free water is there, in this zone we have hydrate and ice water.

That means, if we lower the pressure which if it comes to this particular region this hydrate will dissociate into the hydrocarbon gas, and the ice and if we are lowering the pressure over here we will find we will get water and hydrocarbon gas, and in this case we shall get liquid water hydrocarbon and the water.

So, there is a particular zone in which we shall be getting the hydro hydrates.

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So, these zones have to be avoided whenever we are making any kind of operation. Now the hydrates are also formed that even if there is in the requisite temperature and pressure, but unless there is sufficient amount of water the hydrate cannot be formed. So, it needs the presence of water free water and then the gas should be at or below the dew point of the water so that the water can form liquid, it cannot be the vapor phase, but it should be in the liquid phase.

So, it should be the temperature of the gas should be at or below the dew point of the water, and if you are agitating the system then what happens by agitation, we are able to mix up the gas and the water properly. So, this mixing up will be inducing the gas hydrate formation. And then we have some presence of some seed crystals if there is some concede crystals are imputed are there, these seeds are effecting and they will favor

the formation of the hydrates, because this hydrate formation is primarily a crystallization process.

So, if crystallization is favored by the presence of some kind of seed particles.

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Now, we find that in case of natural gas the gas hydrates may form at temperatures will above the freezing point of water. And methane forms the hydrate at the lowest temperature among all the hydrocarbons, because it has the least molecular weight among all the hydrocarbons. And the heavier hydrocarbons cannot form hydrates because they cannot be accommodated in the water cage.

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So, it is on the lower hydrocarbons which are prone to forming the hydrates. And here in this particular graph we show that how the various types of gases are forming hydro hydrates, here we have pure methane and here we have pure ethane and here we have pure propane.

Whereas, if he mix them up we find their hydro hydrate formation is happening somewhere in between and in this particular figure, suppose we take any particular component methane. So, we find this particular line demarcates this hydrate region, and this is the non-hydrate region.

So, the any pressure for a given temperature any pressure above this pressure will be favorable for hydrate formation. Similarly, for a given pressure any temperature below this temperature will be favorable for hydrate formation. So, this region above any of these lines is the hydrate formation region, and below the line is the non-hydrate region.

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Now, here we see that the addition of some of the impurities hydro higher hydrocarbons carbon dioxide or H 2 S, these may raise the hydrate formation temperature; that means, the formation may get delayed.

The addition of nitrogen has been found to decrease the hydrate formation temperature.

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So, that means, if we add hydrogen then maybe it is good for us to have the delayed hydrate formation whereas, in the carbon ducts destroyers, they will what they will raise the formation temperature. Now there are various ways of predicting the gas hydrate formation condition. First we find that we find that gas hydrate formation we basically we want to know the pressure and temperature or for a given pressure what would be the temperature or the vice versa.

Now, gas hydrate may not form as I was telling you that even if we have the thermodynamically favorable condition, why? Because this hydrate formation is a very complex process which involves crystal formation and this crystal formation where we know that is not an easy task. So, it even if we have the right temperature pressure, we may find that the hydrate is not getting formed, but still the operating conditions have to be maintained outside the hydrate formation region to see to it that there is no chance any of any hydrate formation.

Now, there are various methods proposed to the literature to predict the hydrate formation temperature, I shall be talking about only one of the methods and this is the method in which we find that this t is a formation temperature for a given pressure p and this is based on the gas gravity.

So, in this particular equation T is in degree centigrade and P is in bar absolute. And this can also be given graphically from this particular figure, also we can find out that for a given temperature and for a given gas gravity, and you know that gas gravity represents is or is a equivalent to denoting any particular component.



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So, even if into the gas gravity I can find for a given temperature what would be the formation pressure or for a given pressure what would be the formation temperature of the gas hydrate. So, any temperature below this temperature or any pressure higher than this, higher than this pressure will be conducive to the formation of the gas hydrate.

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Now, there are various ways of inhibiting this hydrate formation. One thing is this we can operate on the all the whole system outside the hydrate formation region, but this main always not be possible for the demand of the particular operation. So, we may have to go to those conditions which are conducive to the formation of the hydrate.

Now we can what we can do we can? Thermally heat the line by heating the line we are trying to keep the temperature above the formation temperature, but in this case what happens is this is more convenient for short lines, because heaters operate with minimum attention and there also we need for heating of we need some kind of fuel. So, the we energy expended for this inhibition of the hydrate formation. And generally for long lines, about say more than a mile or so the gas approaches ambient temperature. And in that case chemical injection is preferred.

We can also dehydrate the system as we learnt in the chapter the dehydration ; that means, if we take out the water and the water level comes down comes down so much so, that even if there is the right pressural right temperature the gas will not be able to find enough water to form hydrates.

So, dehydration is another way of reducing the chances of hydrate formation, and it is generally done for the offshore and if it is economically feasible. And then we have the using some hydrate inhibitors, and this is these inhibitors are done only if we find that dehydration is not possible. And generally the inhibitors are added at the wellhead or the booster stations.

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Now, we have different types of chemical inhibitors, there are 3 types first is the antiagglomerates, how the work that these chemicals prevent the agglomeration of the hydrate so, that was the agglomeration is prevented they cannot from the crystal. So, these kind of chemicals act by preventing the agglomerate formation of the hydrates.

And then we have the kinetic hydrate inhibitors by this we mean, that they reduce or the retard the rate of formation of the hydrate that is what kinetic means. And, but in this particular type of inhibitor we find that if the amount of the inhibitor is large it may lead to the formation of the hydrates.

And lastly we have thermodynamic inhibitors what they do? There basically some antifreeze agent and they do they lower the temperature of the hydrate formation so that the hydrate formation gets delayed for a given pressure. And under these thermodynamic inhibitors, we have most common ones are methanol ethylene glycol and diethylene glycol we shall be calling them EG and DEG respectively.

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The disadvantages of this chemical inhibitors are that these inhibitors themselves can cause plugging, and they are costly and methanol is lost due to evaporation and glycol is lost not due to evaporation, but also by entrainment by the gas stream by decomposition or the dissolution in the hydrocarbons.

So, these are the disadvantages of the chemical inhibitors, and then we have the unreliability because if because these chemical inhibitors have to be injected into the system by some pumping mechanism, if we will find that there the pump has failed, or we find that, wherever we are storing the inhibitors that the depletion of these inhibitors has happened then we will find that that we may not be able to know it, and this is especially true if these either from this we have operated remote site.

So, if we are not able to monitor the process properly, we find that this particular operation by use of the chemical inhibitors may not be proving reliable. And these inhibitors may react with other chemical additives and thereby it will reduce the efficacy of the inhibitor.

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Now, let us see that how these different thermodynamic inhibitors are working, like we are talking about the operating temperature in this case we find that methanol can operate generally at any temperature, the EG generally works better for minus 90 degree centigrade or so because of it is lower viscosity and easier separation from the liquid hydrocarbons whereas, DEG is used generally above minus 6 degree centigrade, because it has lower vaporization losses than EG.

Now, as far as the depression of the hydrate formation temperature is concerned, methanol is found to be most effective followed by EG and then DEG. The mixing methods are also important, because how we mix up this particular inhibitors with the natural gas. And unless they get mixed properly they would not be effective in preventing the hydrate formation. And in this, we find that the glycols that is EG and DEG are generally spread as fine droplets in the natural gas stream to cause intimate mixing.

Whereas, methanol mixes very easily with the gas as it can itself vaporize. Then we have the freezing effect of glycol which is not found in case of methanol. That this glycol concentration should be between 60 and 80-bit percent, because what happens at this higher side if you go at for higher concentrations and at low temperature the glucose may become mushy, which inhibits the proper flow. Mushy means there will be kind of a semi solid gel like solid they will form and that will also prevent the flow and the separation of these glycols some the hydrocarbons.

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Next about the regeneration, we find that dry this diluted glycols are generally generated because they are quite costly. On the other hand, methanol may not be regenerated because, methanol comes cheap and the cost of regeneration is quite high. And generally we use distillation for separating the methanol from water. So, the cost is high so, and this raw material is also cheap. So, generally regeneration is not done by when we are using methanol.

Economy wise we find that glycol proves more economical for large volumes and or for continuous operations. Whereas, methanol proves more economical for smaller volumes for infrequent or intermittent operation, and mild hydrate formation problem is there then we use methanol.

Cost wise we find that methanol injection has low investment cost, but high operating cost due to chemical consumption. Whereas, in case of EG DEG the initial cost is more than methanol, but they have lower operating cost because we are able to regenerate these glycols. And action by we find that how they are preventing, the how they are acting, that glycol are preventing the hydrate formation, but cannot dissolve the already present hydrates whereas, methanol can dissolve the existing hydrates to some extent.

So, we have to consider all these factors and lastly for long lines methanol is preferred to glycols. So, in choosing these inhibitors we have to consider all these points.

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Now, if we compare the inhibited injection with the line heating we find that line heating cost may depend on the cost of the fuel. And so, the cost of investment will be between methane and glycol.

Next we come to the removal of existing hydrate, now when if we have already hydrate present in the system, generally what is done? The pressure is lowered below the hydrate formation pressure at the given temperature. And the pressure must be reduced on both the upstream and downstream side. It is not that we do not reduce the pressure on the downstream side; what if we reduce the pressure the, if we do the downstream pressure, without reducing the upstream pressure what will happen?

There will be large pressure difference and large pressure difference what will it will lead it will lead to this high velocity of the hydrate which break loose from the flow, and this high velocity of the hydrates what will happen ? They will they can heat the pipeline wall so, hard that it may lead to the breakage of the pipeline or even for the underground pipeline, the pipeline may come out of the earth.

So, you can see the severity with which these hydrates can act in the pipelines. So, whenever we are trying to reduce the pressure we have to make sure that both on the

upstream side and the downstream side we are reducing the pressure to prevent this kind of occurrence.

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Next we come to the design of the hydrate inhibition system. In this we shall be just looking to fundamentals without going to detail, the basis is that the hydrate inhibition means that we are transferring the water from the natural gas to the liquid inhibitor.

So, what happens, that determine we are in this design we try to determine the minimum amount of the injection rate of the inhibitors, and that is generally given in terms of the volumetric flow rate of the dry gas. And this is a based on the volumetric dry gas, we find that we are giving terms of the mass of the inhibitor needed per unit volumetric flow rate of the dry gas, that means, without the water.

Now, there are 2 basically 2 approaches for this semi empirical correlation, and one are computer simulation , and the basis for the steady state operation is that the incoming mass flow rate of the gas water and the inhibitor is equal to the outgoing mass flow rates of the corresponding components.

So, with this we find that hammarschimdt give this particular equation to find out the weight percentage of pure inhibited liquid phase water liquid water phase.

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And in this we find this mw represents the molecular weight of the inhibitor I is the subscript denoting the inhibitor. This is the temperature depression that occurs during the hydrate formation, and this is the hammer street constant, and in this particular table we find for the various these inhibitors EG DEG and methanol, this cage value and the molecular weight have been listed.

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And this method has been developed for typical natural gases and for dilute solutions with less than point 2 mole fraction of the inhibitor. And the glycol initial system generally meet this condition at below minus 23 degree centigrade. And it generally works for points up to 0.4 mole percent of EG in between these 2 temperatures.

And for methanol system with if we consider xw to be the mole fraction of water, between and this is the water mole fraction between 20 and 50 mole percent, at a temperature of about minus 100 degrees 106 degree centigrade, we find this is the particular equation is given to find out the depression in the temperature. And in this case the value of the A is given in terms of either the Fahrenheit or in terms of the degree centigrade.

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Now, in this particular equation, we find out the minimum amount of pure inhibitor required and this is what this I 100 represents the mass of the pure inhibited required per unit volumetric flow rate of the gas, and WG is the mass of water removed per unit volumetric flow rate of gas, and WI out and W in are the weight percentage of the inhibitor per unit mass of outlet and inlet stream respectively. In this we considered the outlet seem to be water and the inhibitor only and inlet also water inhibitor.

And with this particular equation, we find that these are the basic dc mass balance, that how much water has been removed by the inhibitor. So, by this mass balance we find gate this equation, and in this equation, if we replace this W out from the hammer sheet equation we get this particular equation.

So now we find that we can find out the amount of the water removed per unit volumetric flow rate of the gas in terms of the molecular weight of the inhibitor the temperature depression, and the amount of the pure hydrate you may used and the use it concentration of the inhibitor.

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Now similarly we can also estimate the methanol, and this is the equation which has been given to estimate the amount of methanol, but unit mass flow rate a volumetric flow rate of the gas, and this is the weight percentage of the methanol water with this particular equation is used in this equation we have in this function of pressure temperature this is given by this particular equation.

In this equation, we find that this depends both on pressure and temperature, these a 0, a 1, a 2, a 3, a 4 and a 5, these coefficients are functions of temperature, and this particular table gives us the values of these coefficients as a function of the temperatures.

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So, these this way we are able to estimate the amount of methanol or the amount of the other inhibitors to remove some amount of the water.

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And these are the references which gives more it gives more detail of these methods.

Thank you.