Pavement Materials

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Lecture No. 22

Chemistry of Bitumen

Welcome back friends, today we are going to discuss about the chemistry of bitumen. If you remember in the last class, we have just introduced the bitumen as a binding agent and we briefly discussed about the production process of the bitumen.

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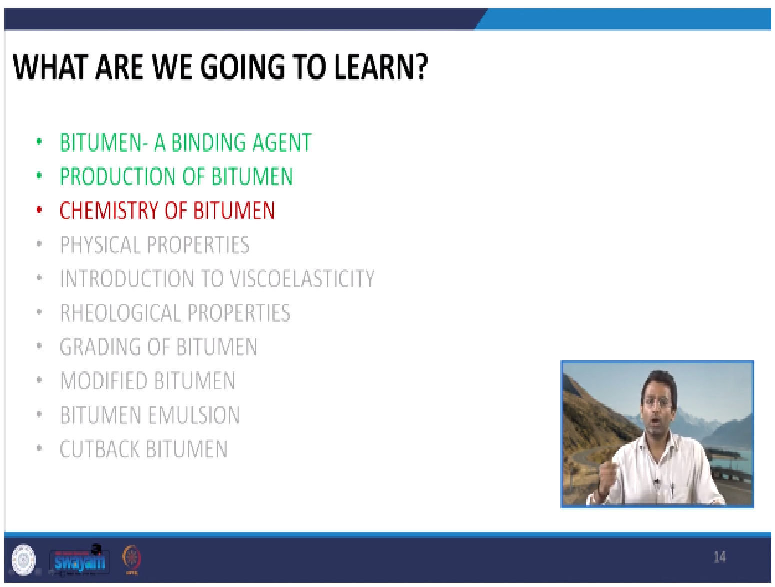

Talking about the chemistry of bitumen if you are in civil engineering or you are trying to do more of an experimental work or you are trying to learn the more of physical and mechanical properties of bituminous mixtures and extensive understanding of the chemistry of bitumen may not be of much importance for you. However, many a times to understand how the change in physical properties have taken place in the bitumen, it becomes critical to understand the chemistry of bitumen and to relate that change which has taken place with the chemical components of the bitumen.

So, in this particular lecture we will very broadly discuss about the chemical components of the bitumen, the different types of molecules which are typically found in bitumen and how these molecules talks about the properties or the behavior of the bitumen as an engineering material.

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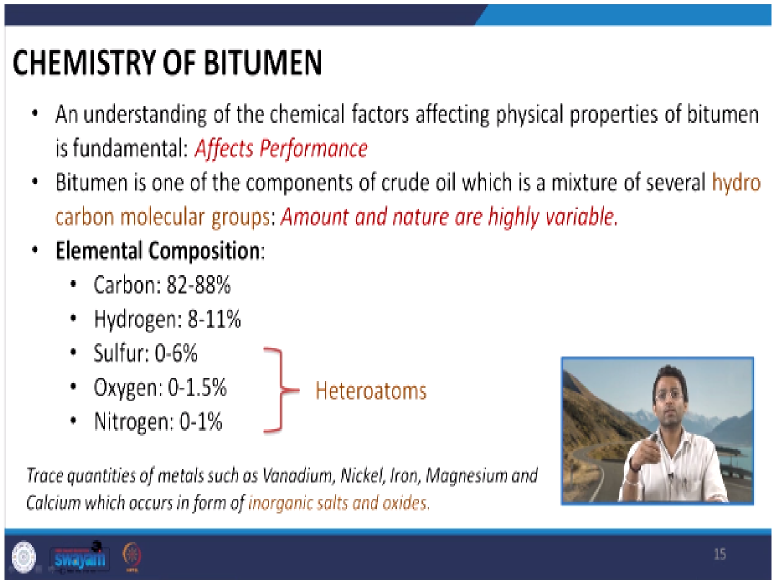

The understanding of the chemical factors which will be discussing today it definitely affects the physical properties, however it is not very straightforward to explain the chemistry of bitumen in simple terms. If you remember bitumen is a crude oil product and how is a crude oil produced, it is produced through a very complicated process over a period of millions of years from the remains of varied, from the remains of plants and animals which can be variable from place to place.

Therefore, the chemistry of crude oil itself becomes very complicated and is a function of the way it was produced or way the phenomena would have taken place, it is dependent on the location where the phenomena took place where the crude oil was produced. So, each crude oil from different sources they are unique in themselves and is composed of a complicated mixture of hydrocarbon and there can be hundreds and thousands of such hydrocarbon species inside the crude oil and therefore in the bitumen.

Therefore, the amount and nature of the hydrocarbon which we expect or we are which we are trying to analyze it is highly variable in bitumen and probably this is one of the reason that researchers especially who are trying to understand the chemistry of bitumen in a more explicit manner still struggle to clearly explain the chemical composition of the bitumen. However, we can definitely understand the chemistry of bitumen in a broader aspect.

Let us first look at the different elements of which bitumen is composed. Bitumen is essentially an hydrocarbon, so carbon and hydrogen are definitely a part of bitumen, where carbon can be in the range of around 82 to 88 percent whereas hydrogen can be in the range of 8 to 11 percent typically. We also have presence of certain heteroatoms and these heteroatoms are sulfur, oxygen and nitrogen and the highest of these heteroatoms comprises of sulfur which is from 0 to 6 percent, whereas oxygen and nitrogen they typically are less than 2 percent.

In addition to these elements, a bitumen can also have trace quantities of different metals such as vanadium, nickel, iron, magnesium and calcium and they basically exist as inorganic salts and oxides in different forms of course.

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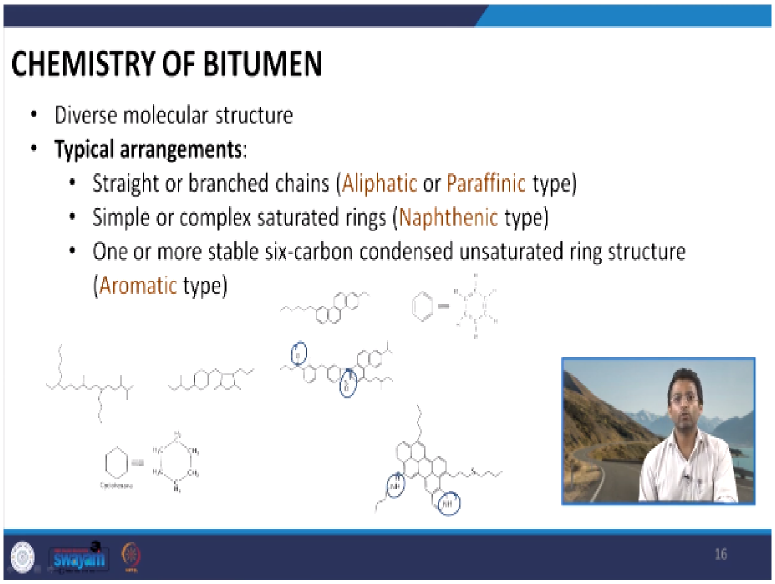

Now bitumen has a very diverse molecular structure, so if someone ask that what are the different molecules present in bitumen it would not be really possible to explain the exact molecular orientations but typically there are few arrangements which are commonly seen inside the bitumen, these are straight or branched chains and they are basically aliphatic or paraffinic type.

We can have complex saturated rings and these bitumen's are naphthenic type if they have more of complex saturated rings, it can also have one or more stable 6 carbon condensed unsaturated ring structure and this type of bitumen is said to be aromatic type. So, for example, the first picture which you see on the screen now it explains the aliphatic or paraffinic type where you have straight or branch chains and also it shows the naphthenic type where you have saturated rings whereas, in the aromatic type you will have unsaturated rings and you will also have the presence of heteroatoms here which you can see for example, sulfur and oxygen, nitrogen in different forms.

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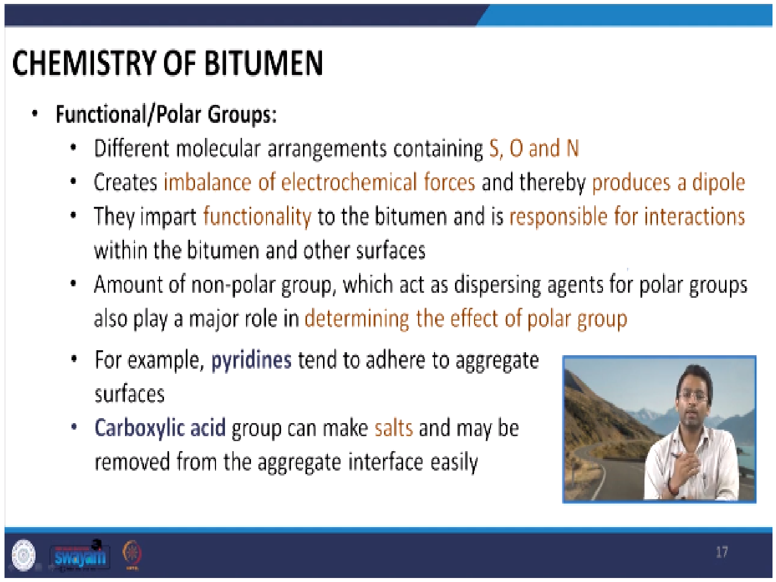

Bitumen ideally is inert and does not have much tendency to interact with others, however due to the presence of heteroatoms in different molecular arrangement bitumen gets the ability to interact with others and this groups, this molecular arrangements having sulfur, oxygen and nitrogen they are called as functional or polar groups in the bitumen.

These polar groups they create an imbalance of electrochemical forces and finally create a dipole and this dipole has a tendency to interact within the bitumen with other molecules and also with other surfaces such as aggregates and later we will see that this is the presence of these functional groups which describes the adhesion between the bitumen and the aggregate particles. So, these polar groups they impart functionality to the bitumen.

The amount of non polar group in relative to the amount of polar group is very important because the amount of non polar group they will determine, because these non polar group they act as dispersing agent for the polar groups, so they will determine how the polar group is finally going to affect the properties of the bitumen. For example, we have pyridines, this particular functional group they have a tendency to make strong contact with the aggregate surface, so a bitumen which has more pyridines can be expected to have better adhesion with the aggregate surface.

We also have carboxylic acid groups, the problem with carboxylic acid group is that they can create salts and this salts can be removed or can be dissolved easily in the presence of water, so though the carboxylic acid group is interacting with the aggregate but the interaction results in formation of salt which can be washed away by the water and the adhesion between the bitumen and the aggregates can be broken easily.

However, if this salts are of divalent in nature for example, let us say we have calcium salts, this salts cannot be broken easily in the presence of water which can further impart better adhesion between the bitumen and the aggregate particle. So, you see that there are various chemical aspects which can be linked to the behavior or the interaction of the bitumen within the bituminous mixture.

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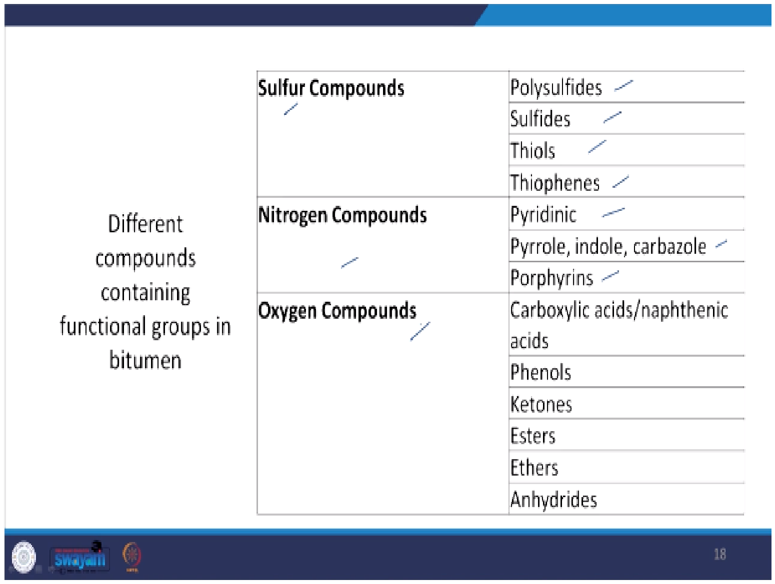

As I said in the previous slide that various functional groups can be present, the typical groups which are found is shown in this particular table. For example, if you see sulfur compounds we have polysulfide, sulfides, thiols, thiophenes. If you talk about nitrogen compounds we have pyridinic form of molecules, we have pyrrole, carbazole, we have porphyrins etcetera.

We also have oxygen based compounds for example, we can have carboxylic acids, we have naphthenic acids, we can have phenols, ketones, esters, ethers, anhydrides and these compounds they can be present in different forms and they can affect the physical and rheological properties of bitumen, the aging characteristic of the bitumen to different degrees.

Now, since I said it is very, very difficult to actually quantify the exact chemical composition of the bitumen. So, researchers have proposed various models to explain the broad molecular distribution in the bitumen, so that this understanding of different composition can be linked with the physical and rheological properties of the bitumen.

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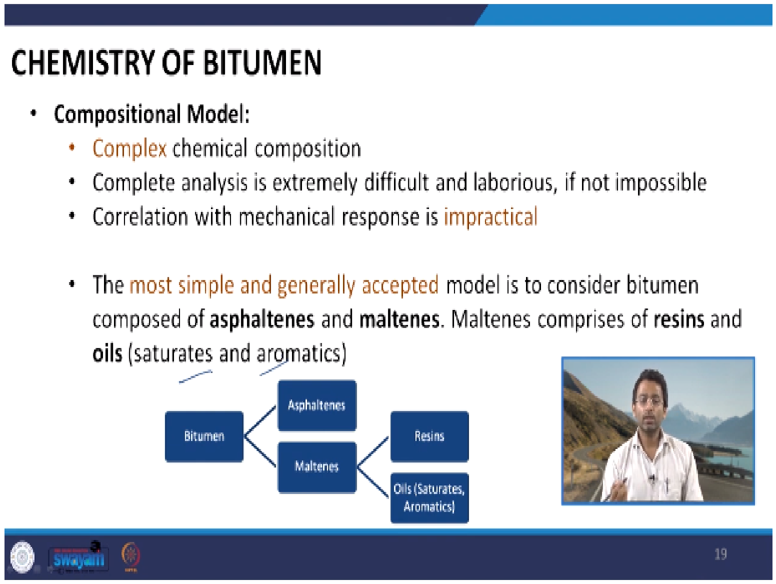

As I said in the previous slides that it is very, very difficult to exactly quantify the chemical composition of the bitumen, it is very difficult to exactly perform a complete analysis of the entire chemical system inside the bitumen and therefore the correlation of the chemistry of bitumen with the mechanical response is not very practical.

Over a period of time researchers have tried to propose different models to understand the broad categories of molecular system which are present inside the bitumen and they do this so that whenever they are trying to understand the physical properties of the bitumen or the response of the bitumen when it is subjected to different stresses and strains, they can come back to see how the chemistry of bitumen can be linked with this particular response.

One of this model it divides bitumen into two broad categories of molecular orientations. One is the asphaltenes and the other is the maltenes. The maltenes is further divided into resins and oils and within the oil we have saturates and aromatics. Now, let us try to understand about these compositions that is asphaltene and maltene fraction and how they affect the properties of the bitumen.

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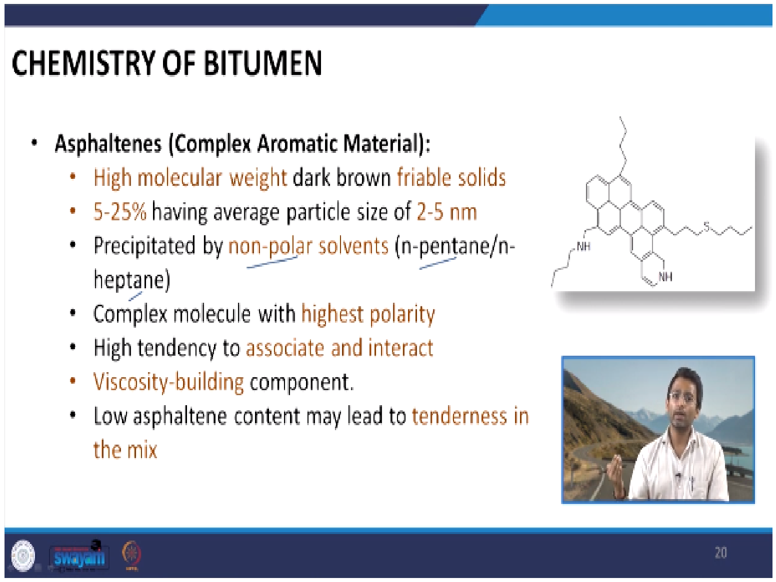

Asphaltenes they are basically complex aromatic material, they have high molecular weight and they are basically dark brown friable solids. If you see the percentage of asphaltenes present in the bitumen, it ranges in some bitumen it can be as low as 5 percent, whereas it can be as high as 25 percent, so it varies between 5 to 25 percent and the size of this asphalt in molecules it ranges from approximately 2 to 5 nanometers.

Asphaltenes are the molecules which contain the heteroatoms in it and therefore has high polarity, in fact it has the highest polarity in comparison to all the other fractions, chemical fractions in the bitumen and therefore asphaltenes have very high tendency to associate and interact within itself and with other surfaces. Being a molecule of higher molecular weight they are the main viscosity building component of the bitumen, if the amount of asphaltene in the bitumen is less, studies have shown that that particular bitumen will have a tendency to produce a tender bituminous mixture.

Asphaltenes they can be separated from the bitumen system using non-polar solvents, so they can be precipitated using non-polar solvent because they do not dissolve in the non-polar solvent and two popular non-polar solvents that are used are n-pentane and n-heptane.

Now, here it is very interesting to note even with these two different solvents for the same bitumen we can get different amount of asphaltenes, so more are the number of carbon atoms, less will be the precipitation. So, therefore if we compare the amount of asphaltene which we will get from n-pentane and n-heptane, we will see that n-pentane will give higher yield of asphaltene from the same bitumen in comparison to n-heptane.

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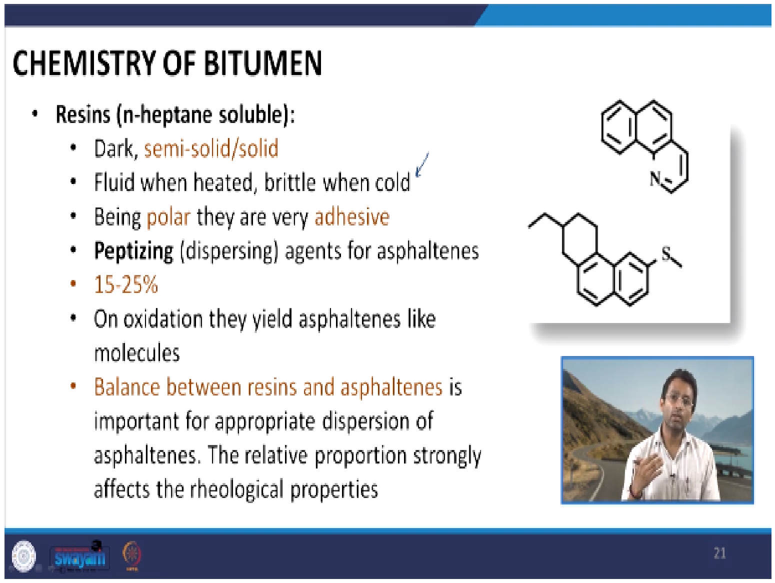

Resins which are a part of maltene, so if you remember we had asphaltenes and maltenes, in maltenes we had resins, saturates and aromatics and the saturate and aromatic are the part of the oil. So, now we are talking about resins, resins are n-heptane soluble, so asphaltenes are not soluble but and resins are soluble in n-heptane, the physical properties more like semi solid to solid, they become fluid when they are heated and then they become brittle when they are cold, this also indicates that the presence of resins it imparts the viscoelastic characteristic to the bitumen, that it becomes fluid when heated and it becomes brittle when it is cold.

Resins are also polar in nature and therefore they also have a strong adhesive property. If we look at the function of resins within the bitumen molecular system, resins acts as peptizing agents for asphaltenes, so they help the asphaltenes to stay dispersed within the oily medium.

Resins are approximately present in the range of somewhere between 15 to 25 percent and it is very important that there is a good balance between the amount of resins and the amount of asphaltenes and this relative proportion strongly affects the rheological property of bitumen. Once we subject the resin to high temperature, once we subject the resin to oxidation, it will yield asphaltenes like molecules.

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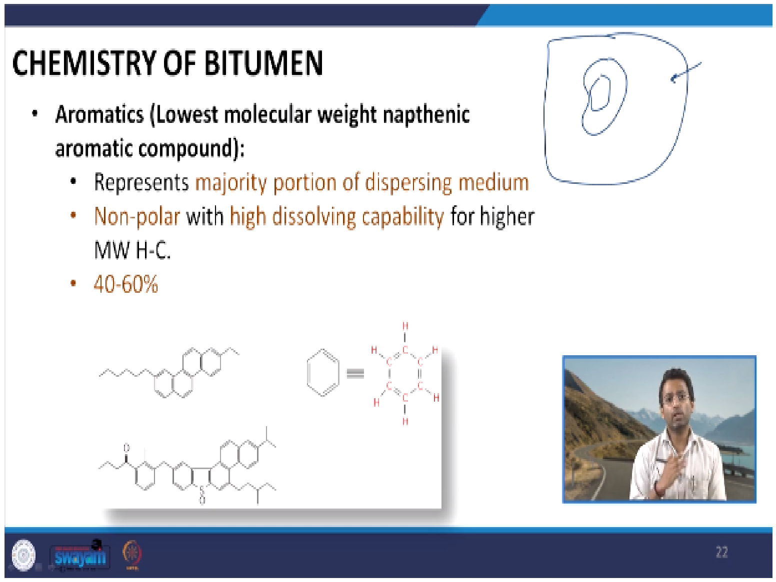

The next fraction are the aromatic molecules, they are the lowest molecular weight naphthenic aromatic compound and they represents the major portion of the dispersing medium, which means the asphaltenes which are peptized by the resins they are basically dispersed in this aromatic system, they are mostly non polar in nature and they have high dissolving capability for higher molecular weight hydrocarbon. The amount ranges from approximately 40 to 60 percent.

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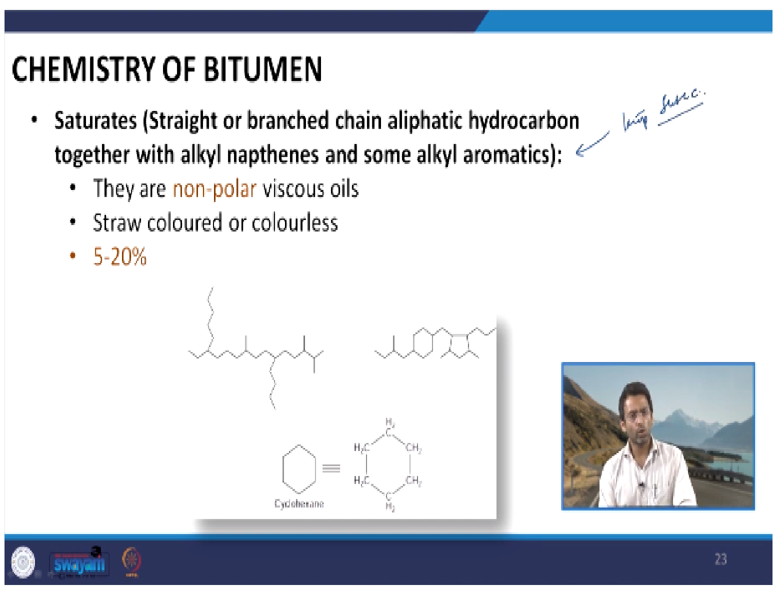

Finally we have saturates which are straight or branched chain aliphatic hydrocarbon, together with alkyl naphthene's and some alkyl aromatics, they basically are not very desirable in the bitumen because they negatively affect the temperatures acceptability. They are non-polar viscous oils and they are present in small quantity approximately 5 to 20 percent and they are mostly colorless.

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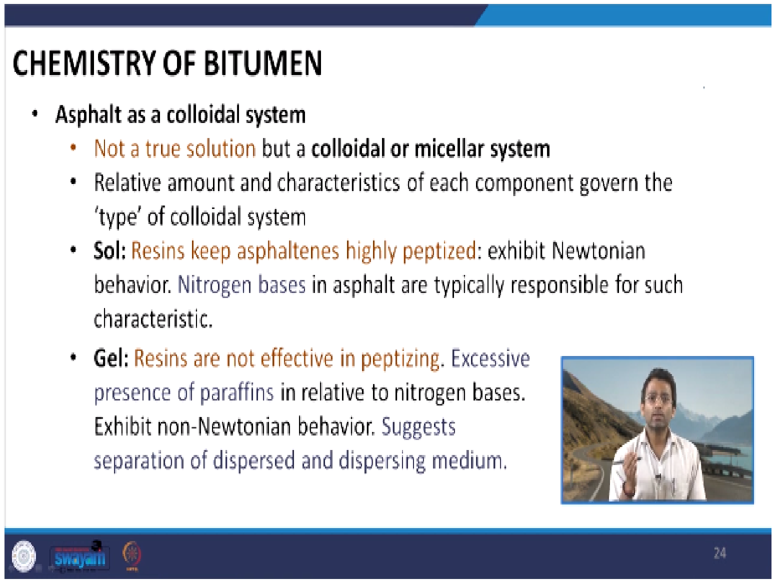

Having discussed about these broad categories, that is we have discussed about the asphaltenes, resins, saturates and aromatics and have tried to understand the properties of these individual components. Now, let us understand asphalt as a colloidal system, that how these different components interact and are present within the bitumen system. So, this particular model is one of the many models which are used to describe the distribution of the fractions within the bitumen.

So, it says that asphalt is a colloidal system, which means it is not a true solution but a micellar system and the proportion of the individual fractions that is the amount of asphaltenes and maltenes they basically will decide the type of this colloidal system. So, there are two types in which we can describe the colloidal system of bitumen, one is the sol type system and the other is the gel type system. So, what is a sol type system?

In the sol type system, we have sufficient aromatics and resins which disperse the asphalt in properly, which means we have appropriate amount of resins which will peptize the asphaltenes and we have appropriate amount of aromatics which will keep this peptize asphaltenes dispersed within the bitumen system, this type of bitumen they typically exhibit Newtonian behavior and studies say that nitrogen bases present in the bitumen are basically responsible for such characteristic.

In the gel type bitumen, we do not have sufficient amount of resins to peptides the asphaltenes, so these asphaltenes they get a tendency to agglomerate and come closer to each other within the bitumen system. Studies have shown that excessive presence of paraffins in relative to the nitrogen basis they contribute to such a gel system.

In fact, we will study when we discuss about aging in a later class, that once we subject the sol type system to oxidation the amount of lighter components start getting reduced and it can transform itself to a gel type system, this type of bitumen they exist non Newtonian behavior and this suggest that there is a separation of the dispersed phase and the dispersing medium.

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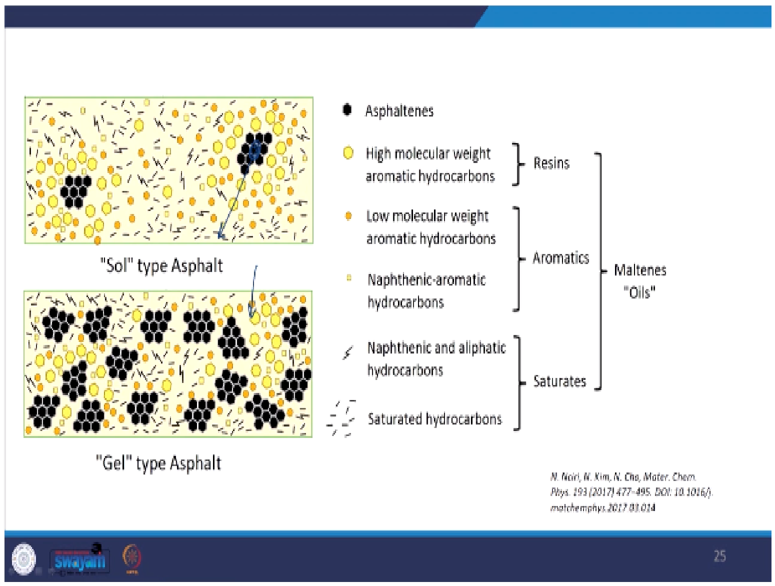

These two picture it shows the two colloidal system, the top one is shows a typical sol type bitumen, where you see that this dark components they are asphaltenes which are sufficiently peptized using the resins and this entire system they are well dispersed in the medium which contains aromatics and which contain saturates.

In fact, if we take the asphaltenes as the center, so as you move outward you will see that the molecular weight of the systems they get reduced, higher molecular weight present within the asphaltenes, as you go out we have resins relatively lower molecular weight, as you go out we have aromatics, as you go further out we have saturates.

Whereas, the next picture it shows a typical gel type structure, where you can see that lot of agglomeration of asphaltene molecules have taken place because we do not have sufficient dispersing medium within the bitumen system. Having talked about this let us finally talk about separating these fractions from the bitumen. If tomorrow I have to compare the properties of two or three different bitumen's it will be interesting to see how the response of these bitumen to any given loading condition is related to the inherent chemical fractions or inherent molecular fractions which are present in the bitumen.

So, we are interested to find out that in a bitumen what is the percentage of asphaltenes, what is the percentage of resins, what is the percentage of saturates and the percentage of aromatics. So, how do we separate this fractions if we have a sample of bitumen, so this can be done using a chromatographic technique, though there are other techniques but chromatographic technique is one of the most widely used and popular technique to separate these four fractions which we have talked about.

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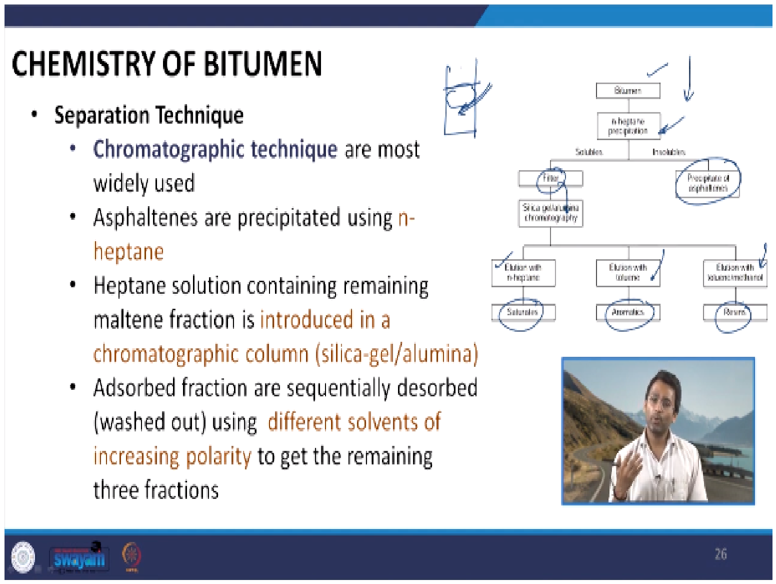

As we discussed that asphaltenes can be precipitated using non-polar solvents like n-heptane, so first we will take the bitumen, we will dissolve it in n-heptane and will precipitate the asphaltene out of it, so we can have a direct measure of the amount of asphaltene present in the bitumen. After that now we have a solution of n-heptane which contains all the other fractions, is not it, we have the maltene fraction which comprises of resins, saturates and aromatics.

So, this remaining heptane solution which we have after precipitating asphaltenes they are introduced into a chromatographic column which can be made up of a silica gel or an alumina gel and they get adsorbed in this particular column. This adsorb fraction they can be sequentially washed out from the system using different solvents of increasing polarity and when you use one particular solvent a particular fraction can be separated and the weight can be measured, then further elution is done, we further wash out the column using another solvent of different polarity, so we can separate out the next fraction and likewise the last fraction can be separated out using a particular solvent.

So, this particular flow chart it explains the process of doing the chromatographic separation. So, we take the bitumen, n-heptane precipitation, insoluble we have, so you get a direct measure of the amount of asphaltenes, the soluble they are filtered and introduced to the silica gel or alumina gel chromatographic column.

So, you can do an elution with n-heptane and this will give you saturate it will separate out saturate the remaining proportion you elute with toluene and it will separate out aromatics along with it and the remaining part in the chromatographic column, it can be eluted using a toluene and a combination of methanol and you get the measure of resins from it. So, this way you can approximately find out the percentages of different fractions within the bitumen system.

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The usual chromatographic which is done, in practice it is a tedious process, it is a costly process. So, researchers have been parallelly working on simplifying the method and one such method which can be of interest to the readers is this particular process where they have developed a Fast SARA method, where in comparison to the conventional method you can find out, you can know the amount of different fractions in the bitumen, the chemical fractions in the bitumen in less time and with a simple process.

So, if anyone is interested to explore more or to understand more on the separation technique you can visit this particular paper and read it. So, that is all in today's presentation. Just to recap that today we have talked very briefly about the basic chemistry of bitumen, we discussed about different elements which are present in the bitumen, we discussed about the functional groups which impart functionality to the bitumen so that it can interact within itself and with other surfaces, we saw the broad molecular composition of the bitumen by dividing it into asphaltenes and maltenes, where maltenes were further categorized as resins, aromatics and saturates.

We discussed about the properties of these different fractions and finally we talked about a method which can be used to separate these fractions from the bitumen and to know the relative proportions of these fractions in a bitumen sample. In the next class we will start discussing about the physical properties of the bitumen and as we move forward in this particular module, we will always try to come back to see that how the physical properties which we are discussing can be related to the basic chemistry or the basic chemical fractions which we have discussed today in the bitumen, thank you.