Mechanical Characterization of Bituminous Materials
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Module No # 05
Lecture No # 23
Aging of Bituminous Binders and Mixtures – Part II

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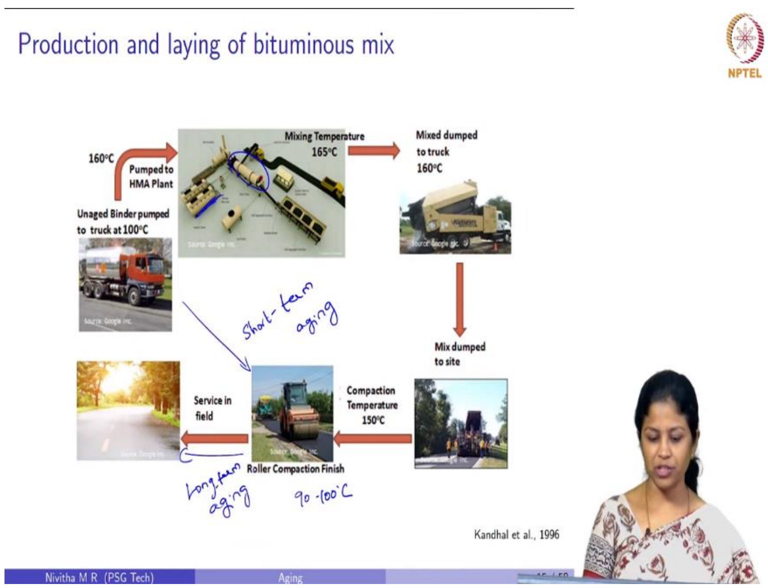

Now let see how bitumen is produced, how it is mixed and how it is laid on the pavement and what is the effect of temperature in each of these steps. So the first step is that we have bitumen which is supplied by a refinery. So in refinery it is stored in their storage tanks. So they heat this bitumen, pump it into this containers and bitumen is transported. And bitumen is now unloaded at the construction site and again it is stored in storage tanks here.

So every time to load and unload bitumen we need to heat it to flowing temperature so that it can be easily pumped in or pumped out. So the temperatures here range from 100 to 160 degree Celsius. So then it is stored in the storage yard at the batching plant. So in the batching plant when bitumen is mixed with the aggregates again it is heated and it is transferred to the batching plant here.

So this is the mixing drum where the aggregates and the bitumen are mixed together. So it is again heated from this storage tanks and transferred to this mixing drum. So mixing happens at a temperature of 165 degree for unmodified bitumen and even higher temperatures for modified bitumen. And now this mix is dumped on to these trucks. These trunks transfer bitumen from the batching plant to the specific point of construction.

And in the field this mix is spread on the granular layer and it is compacted. So when we finish compaction the temperature should be roughly between 90 to 100 degree Celsius. After it is compacted, it is now subjected to environmental conditions right. So in this process from the point when bitumen leaves the refinery to the point when the compaction has finished and the pavement construction is now completed, it experiences a number of heating and cooling cycles right.

So we said temperature act as a catalyst. So we can see the temperatures here range from 100 to 165 degree Celsius in this entire process. Then after we subject this mix to the environmental conditions the temperatures are different. They experience pavement temperatures and there is cyclic variation of temperatures on a daily basis and on an annual basis. So this is, this process from the point when bitumen leaves refinery to the end of compaction is called as short term aging.

The aging that happens in this material and the change in stiffness in this period is called as short term aging. Similarly we have long term aging which is nothing but from the point the mix is compacted on the field to the period in which it serves in field. So this is called as long term aging.

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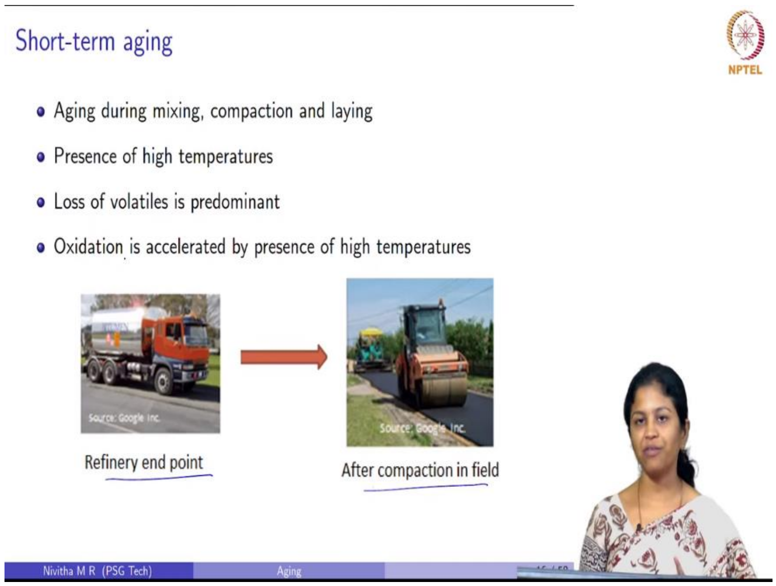

Let us look about each of these phenomena in detail. So short term aging is the aging during mixing, compaction and laying. So it is from refinery end point to the point after it is compacted in field. So what are the additional factors that influence this aging? One is the presence of high temperatures like we have discussed before the temperatures range from 100 to 165 degree Celsius. So there is presence of high temperatures in this case. So because of this presence of high temperatures the loss of volatiles are predominant. And this oxidation here which happens here is accelerated due to the presence of high temperatures.

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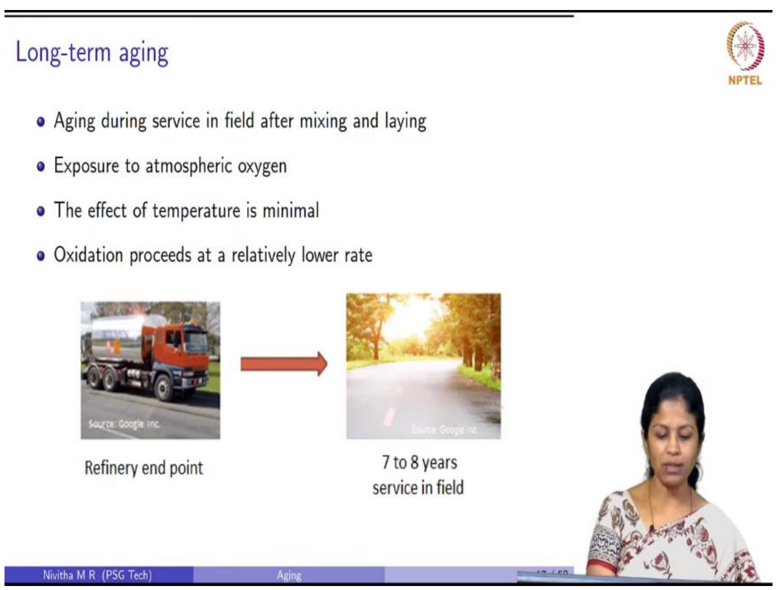

Whereas when we come to long term aging it is the aging that happens during service in field. So we do not have high temperatures. In India the pavement temperatures may not exceed 70 degrees in most of the locations for most of the time duration. So in that case the temperatures are limited here. So it is exposed to atmospheric oxygen in this case also. And the oxidation will proceed at a relatively lower rate.

When we look into the kinetics of oxidation the kinetics are completely different in short term aging and long-term aging because of the effect of temperature and the availability of oxygen in both of these cases.

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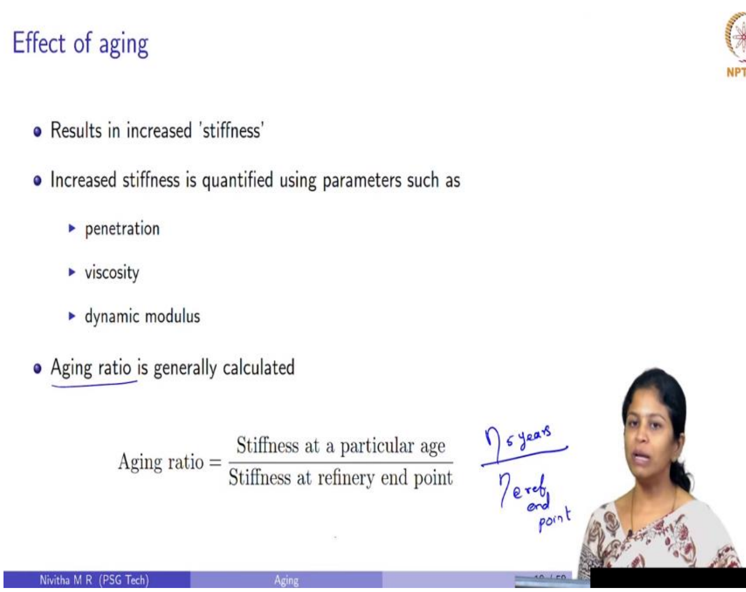

Now let see what is this effect of aging? So why are we interested in this aging phenomena? It is because aging causes an increase in stiffness, like we have defined before, aging causes hardening of this material. So this increase in stiffness is quantified using different parameters. We can either measure a penetration before aging, after aging, see what is the effect of aging on penetration value. Similarly we can measure viscosity, dynamic modulus, any parameter; we can measure before aging and after it has aged and quantify what is the effect of aging.

So to quantify the effect of aging people generally calculate something called as an aging ratio. So aging ratio means stiffness at the particular age, say for example I want to find out what is the increase in stiffness after the binder has been subjected to 5 years of aging in field. So what I do here is I take out a core from the pavement after 5 years; I extract bitumen from that, measure its viscosity. So then this is the viscosity at 5 years by the viscosity at refinery end point. This will tell me the aging ratio of this material. So this aging ratio is used in specifications to limit the amount of aging that the material undergoes either after short term aging or after long term aging.

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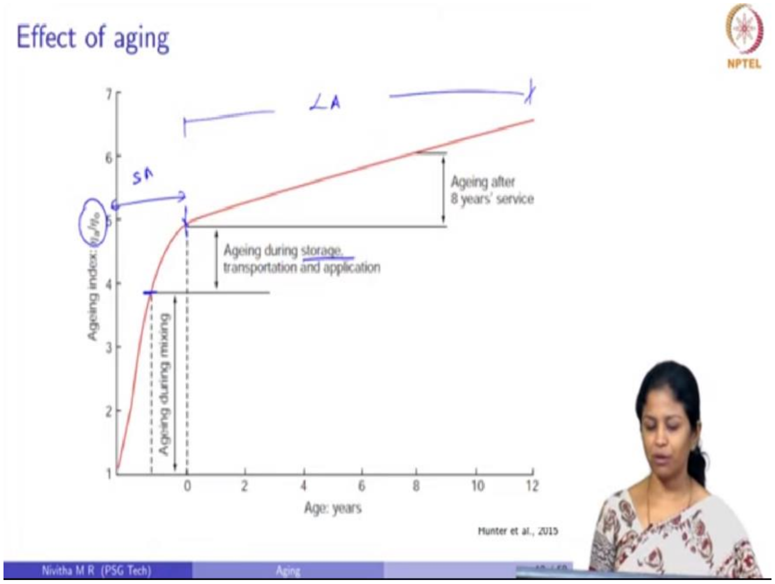

So this is a very nice figure which is given in the shell bitumen handbook by Hunter et al. So we can see they have calculated something as an aging index on the y axis. You can see it is viscosity at a particular age divided by the viscosity, the initial viscosity, which is represented by eta naught. And the x axis shows the age in years. They have also shown it in three different stages. The first stage is aging during mixing.

So this the time when bitumen has been mixed in the batching plant. So this point right corresponds to the time period till the end of mixing after that it is the aging during storage transportation and application. So then it is transported. So this storage here is, in western countries what they do is, they prepare bituminous, mix store it in hot silos and then take it for construction. But in India we do not have that practice; we prepare bituminous mixes and straight away transport it.

So this is mixing and then this is further transporting and till the end of compaction process and this is after service in field. So this is the short term aging period. They have divided into 2 mixing and during storage transportation and application. And this entire thing corresponds to long term aging. So now you can see what is this aging index in different stages. So initially during mixing there is a four times increase in viscosity of this material.

So that you can see here and there is further a increase during storage transportation and application. So at the end of this short term aging you can see there is about a 5 times increase in viscosity. This is again a generic figure it can vary depending upon a number of factors. Then after this it is subjected to environmental conditions. So after 8 years you can see what is the increase. So there is only a very small increase in the aging index.

So from 5 it has gone to 6 right. So most of the aging happens in the short term aging condition which is the initial phase where the material is mixed, compacted and laid on the pavement. So after that the amount of aging the material undergoes has been observed to be relatively lower.

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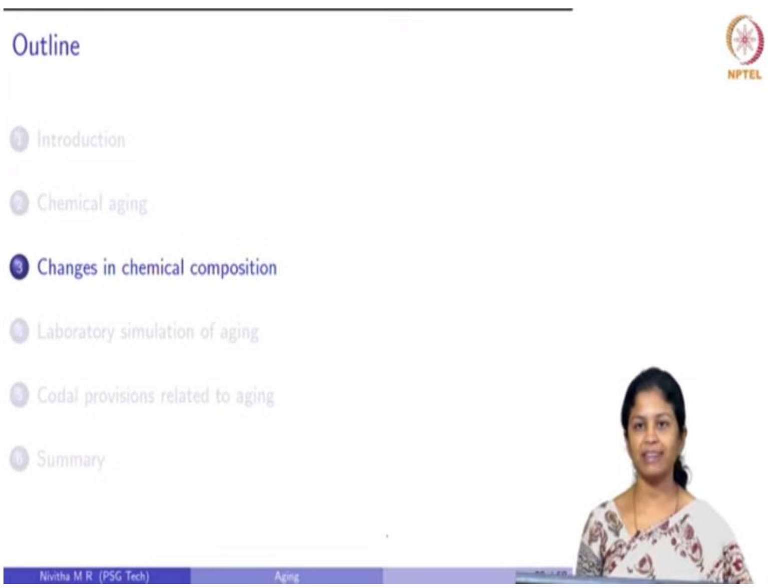

Next we move on to what are the changes in this chemical composition of this material at different stages.

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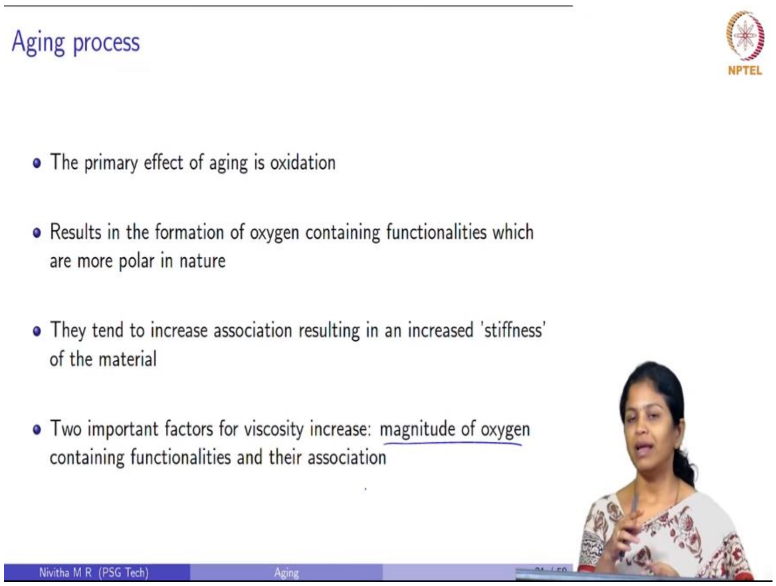

So we said the primary effect of aging is oxidation; uptake of oxygen molecules and formation of oxides. So this in bitumen, there are number of functionalities which we have defined earlier. So these functionalities absorb these oxygen molecules and they are more polar in nature. So these polar points act as points for association of these molecules. So they have strong interactive forces. So because of this association the molecules tend to agglomerate and increase the viscosity of the system.

So there are two important factors responsible for viscosity increase. The first one is the magnitude of oxygen containing functionalities and the second one is association. It is not sufficient that we have some x increase in carbonyl compounds or formation of oxides in bitumen. They should also be able to form interaction points and associate the bitumen molecules. So both of them together lead to an increase in viscosity of the system.

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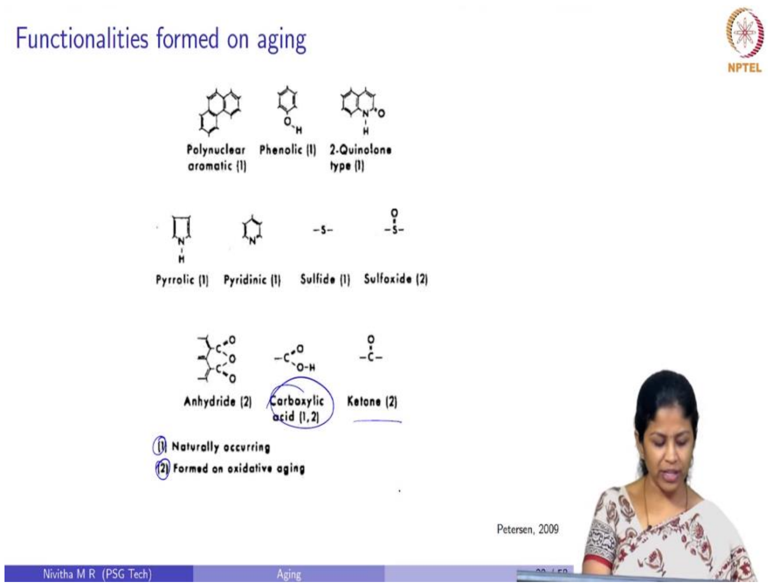

So we can see here this is a figure by Petersen where he has listed the functionalities in the bitumen which are naturally available and which are formed on aging. You can see here there is a legend 1 and 2. 1 shows materials which are naturally occurring in bitumen, 2 shows the material which are formed on oxidative aging. So you can see poly nuclear aromatics, phenolics, 2 quinolone type, pyrrolic, pyridinic, sulfide are all present in bitumen.

Whereas sulfoxide, anhydride and ketones are formed on aging. This carboxylic acid can be naturally available in bitumen, can also be formed on oxidative aging. So these are some of the commonly observed functionalities as a result of aging in bitumen.

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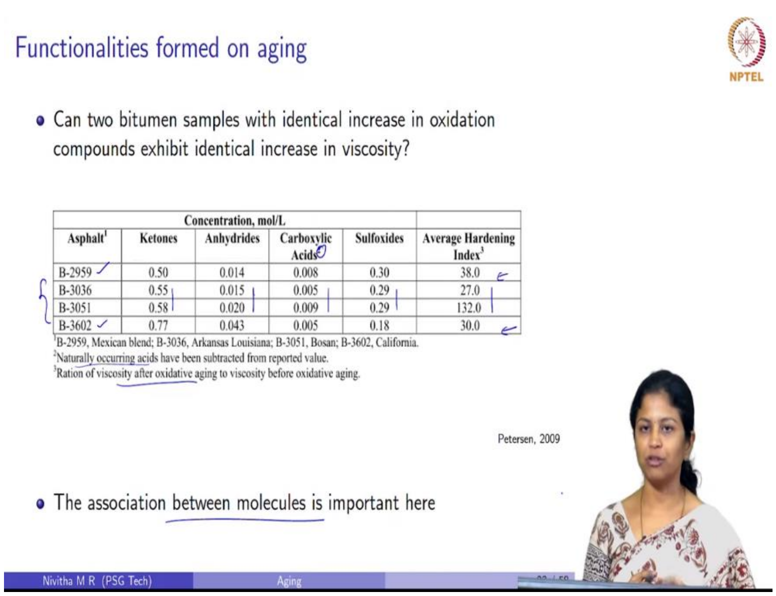

	Concentration, mol/L				
Asphalt[1]	Ketones	Anhydrides	Carboxylic Acids[2]	Sulfoxides	Average Hardening Index[3]
B-2959	0.50	0.014	0.008	0.30	38.0
B-3036	0.55	0.015	0.005	0.29	27.0
B-3051	0.58	0.020	0.009	0.29	132.0
B-3602	0.77	0.043	0.005	0.18	30.0

[1]B-2959, Mexican blend; B-3036, Arkansas Louisiana; B-3051, Bosan; B-3602, California.
[2]Naturally occurring acids have been subtracted from reported value.
[3]Ration of viscosity after oxidative aging to viscosity before oxidative aging.

Now like I previously said we said if there is increase in formation of these oxygen containing functionalities, we will have an increase in stiffness right. But that is not true because as I said the association between them is also important. So this was verified through a study and where they have considered 4 different types of bitumen. Let us now take these 2 types of bitumen here. B3036 and B3051; let us see what is the concentration of these functionalities.

One is ketone, anhydrides, carboxylic acid and sulfoxides. We saw that except for carboxylic acid, all the other 3 are formed only on aging; they are not naturally available in bitumen. These carboxylic acids can also be formed on aging and be naturally available in bitumen. So what they have done here is you can see the note here. The naturally available acids have been subtracted from the reported value. So what is reported here is only what is observed on aging.

Now we can see the ketone value for these 2 materials are almost identical. The anhydrides are almost close, carboxylic acids may be a small difference, sulfoxides are exactly the same. But we can see what is the average hardening index? So what is this hardening index here? The ratio of viscosity after oxidative aging to viscosity before oxidative aging. You can see 2 types of bitumen having similar oxidation products exhibit different increase in stiffness.

So here the association between the molecules is very important. We can take the other 2 bitumen B2959 and B3602. We can see that the ketones are relatively larger; the anhydrides are also relatively different, the carboxylic acids may be closer, sulfoxides are also higher. But we can see the hardening index is 38 in the case of B2959 and 30 in the case of B3602. So we need to understand that the formation of carbon I mean oxygen containing compounds is important. But their association is also important.

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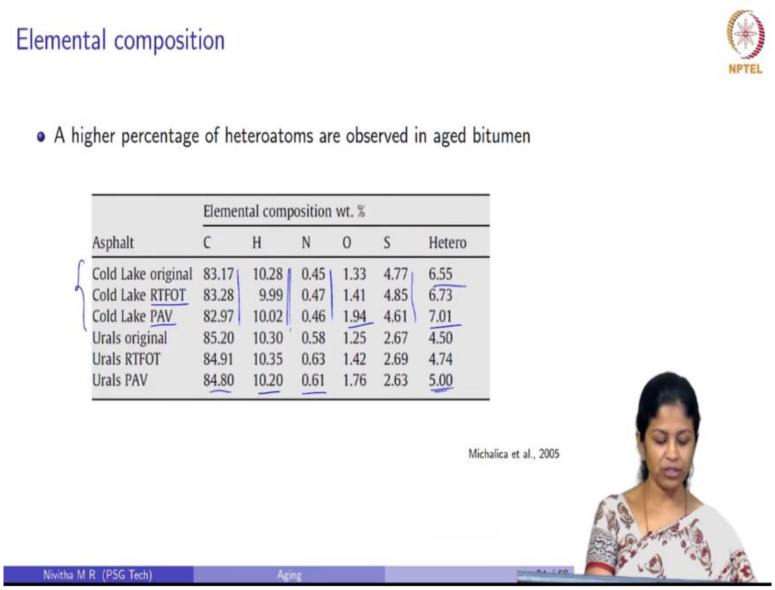

Asphalt	Elemental composition wt. % C	H	N	O	S	Hetero
Cold Lake original	83.17	10.28	0.45	1.33	4.77	6.55
Cold Lake RTFOT	83.28	9.99	0.47	1.41	4.85	6.73
Cold Lake PAV	82.97	10.02	0.46	1.94	4.61	7.01
Urals original	85.20	10.30	0.58	1.25	2.67	4.50
Urals RTFOT	84.91	10.35	0.63	1.42	2.69	4.74
Urals PAV	84.80	10.20	0.61	1.76	2.63	5.00

So next we will move on to what is this effect on aging on different levels of bitumen microstructure. We will talk about the elemental level, we will talk about the fractionation level and we will talk about the molecular level. So this is the study by Michalica et al. where they have considered 2 types of bitumen and aged them. So we can see there is a cold lake bitumen and there is a Ural bitumen.

So they are subjected to short term aging which is defined as RTFOT. I will tell you what this is in a while and we also have a long term aging which is defined as PAV. So we can see that in the case of cold lake bitumen the amount of carbon that is present is relatively similar in all the 3 cases. So because of aging we can say there is not much of a variation in the amount of carbon present in material.

There is also not much of a variation in the hydrogen because we said aging is because of oxidation. So there is only absorption of oxygen containing functionalities. Nitrogen also not much of a variation, oxygen we can see from 1.33 it has increased to 1.94. Similarly, sulphur also you can see I mean sulphur there is again not much of a change because this is only sulphur not sulfoxide.

So the heteroatom content in this material has increased from 6.55 to 7.01. In the case of Ural bitumen we can see again similar cases for carbon, hydrogen, nitrogen, oxygen we can see an increase, sulphur not much variation and an increase in the heteroatom content. So the in the elemental composition oxygen only increases the heteroatom content, in specific, the amount of oxygen that is present.

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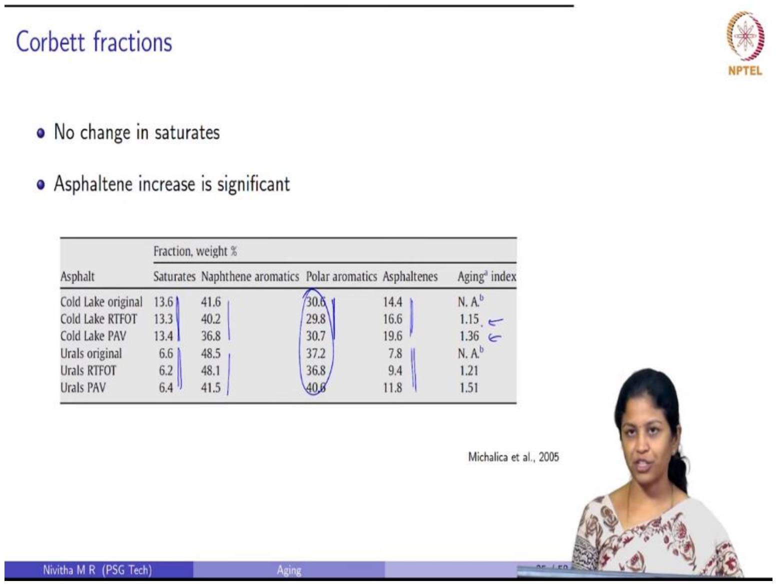

Now let us see what is the effect of aging on the Corbett fractions. So like I said earlier we define Corbett fractions in terms of saturates, naphthene aromatics, polar aromatics and asphaltenes. So when we look at these two types of bitumen we can see that there is no change in the saturates fraction for both of the bitumen. So these saturates are linear long chain aliphatic compounds. We have already seen what saturates are?

So they do not absorb any of these oxygen containing molecules. Next is the naphthene aromatics; there is a very small reduction in the naphthene aromatics fraction for both of these bitumen types. Then we will move on polar aromatics; again in the cold lake bitumen we do not see any variation in the polar aromatics fraction whereas in the case of Ural bitumen there is a slight increment in polar aromatics fraction.

But when we come to asphaltene fraction we can see there is a significant increase in the asphaltene fraction from 14.4 to 19.6. So people say that there is inter conversion of these fractions happening. So saturates nothing happens to saturates. Naphthene aromatics, some amount may be converted to polar aromatics or they might remain the same. Some amount of polar aromatics are converted to asphaltenes. So depending upon the conversion rate of naphthene aromatics to polar aromatics and polar aromatics to asphaltenes, this fraction of polar aromatics can remain constant, increase or decrease. Then we see that there is a significant increase in asphaltene fraction in both this type of bitumen and the aging index right. Similarly as defined earlier we can see the aging index in short term aging and in the case of long term aging. So we see that there is a small increment in viscosity in short term aging and also increment in long term aging right.

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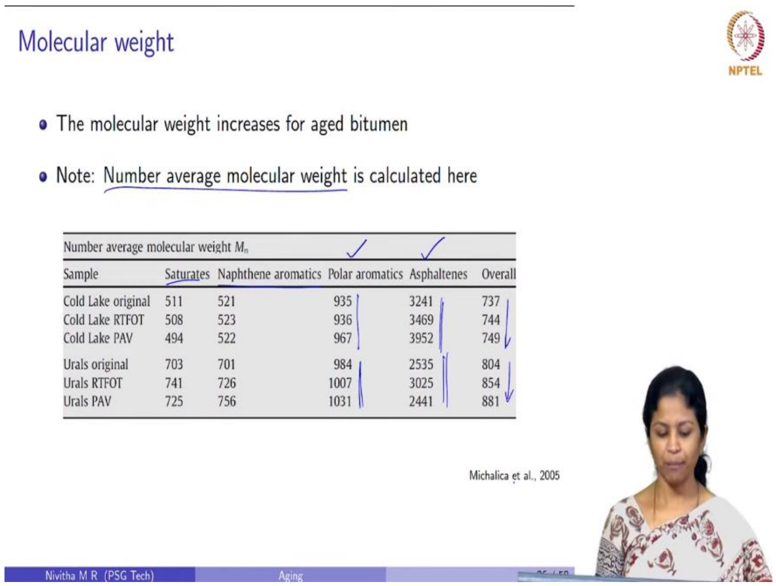

Number average molecular weight M_n					
Sample	Saturates	Naphthene aromatics	Polar aromatics	Asphaltenes	Overall
Cold Lake original	511	521	935	3241	737
Cold Lake RTFOT	508	523	936	3469	744
Cold Lake PAV	494	522	967	3952	749
Urals original	703	701	984	2535	804
Urals RTFOT	741	726	1007	3025	854
Urals PAV	725	756	1031	2441	881

We will see what is the effect of this aging on the molecular weight of each of these fractions. So it has been said that the molecular weight increases for aged bitumen because of all these associations which we were discussing. So the number average molecular weight is given here. So you know what a number average molecular weight is and what a weight average molecular weight is.

So here we need to remember that a number average molecular weight is what is calculated right. Now let us compare the increase in molecular weight as a result of aging for all those 4 bitumen fractions. So in this saturates fraction, there is a small reduction in the number average molecular weight we can see. In the naphthene aromatics there is not much of a change; in the polar aromatics there is a small increment in the molecular weight. In the asphaltenes we can see a good increment in the molecular weight.

So this is similar for these two types of bitumen. The cold lake bitumen and Ural bitumen. So we said the polar aromatics and asphaltenes are bigger molecules; they contain lot of sites where the polar compounds can attach themselves. So because of that these polar aromatics and asphaltenes form lot of oxidation products. So what people have seen is that the oxidation products are mostly formed in the polar aromatics and asphaltenes fraction of bitumen compared to saturates and naphthene aromatics.

So overall we see an increment in molecular weight in the case of both the bitumen types. So maybe when you consider the weight average molecular weight, the increase in molecular weight will be more predominant.

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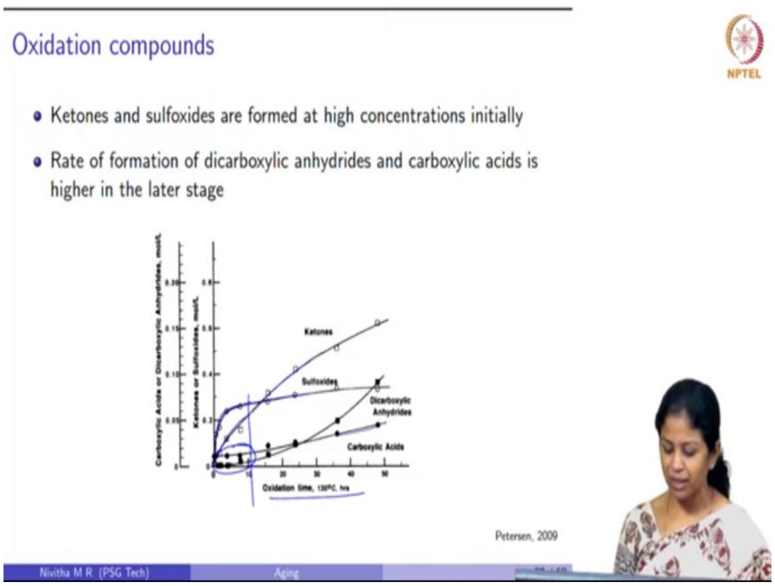

So now we will see what are these oxidation compounds they are formed and how are they formed in bitumen. So like we said earlier ketones and sulfoxides are formed only on aging. So these are the compounds which are formed initially at a higher rate. So this is a figure which shows the concentration of these functionalities as a function of oxidation time. So here oxidation is carried out at 130 degree Celsius.

We can see in the initial stage, say for example 10 hours of aging, there is a significant increase in these sulfoxides which is shown here and the ketones which are formed in bitumen. So these are the two functionalities which are formed at a higher rate in the initial stages of aging. Then further these sulfoxides tend to slow down but the formation of ketones occur on a close to a linear rate. Then we look at the other two functionalities which are dicarboxylic anhydrides and carboxylic acids.

So these two functionalities in the initial stage are formed on a lower percentage. But with subsequent aging you can see their concentration is higher. Now when we look into the short term aging and long term aging; we can see that more amount of ketone and sulfoxide formation is observed in the short term aging. Whereas more amount of dicarboxylic anhydrides and carboxylic acids are formed in the long term aging stage.

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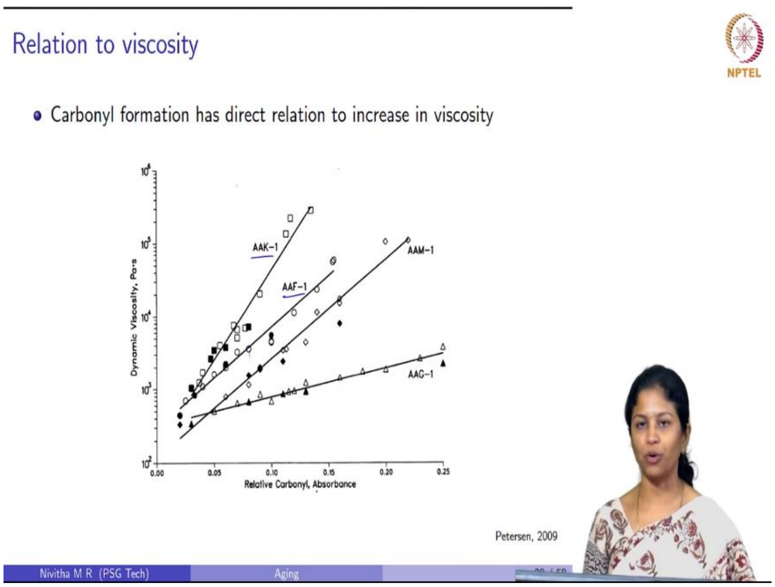

And what is this effect of formation of these functionalities on the rheological properties of bitumen. So there are many studies which have established positive correlations between the magnitude of carbonyl formation and the viscosity or any other rheological parameter to quantify the stiffness of the material. So in this study they have considered different types of bitumen. So this AAK, AAF are different types of bitumen which are labeled so in the SHRP library.

So we can see that they have measured the amount of carbonyl absorbed by these materials and the relative increment in viscosity. So for most of these bitumen, they were able to establish a linear correlation between the amount of carbonyl compounds absorbed and the increment in the viscosity. Like I said earlier the association is important. So they have measured this for few types of binders. There are few other studies which have also shown that they were not able to obtain a positive correlation. I have not shown that figure here but that cases were also reported.

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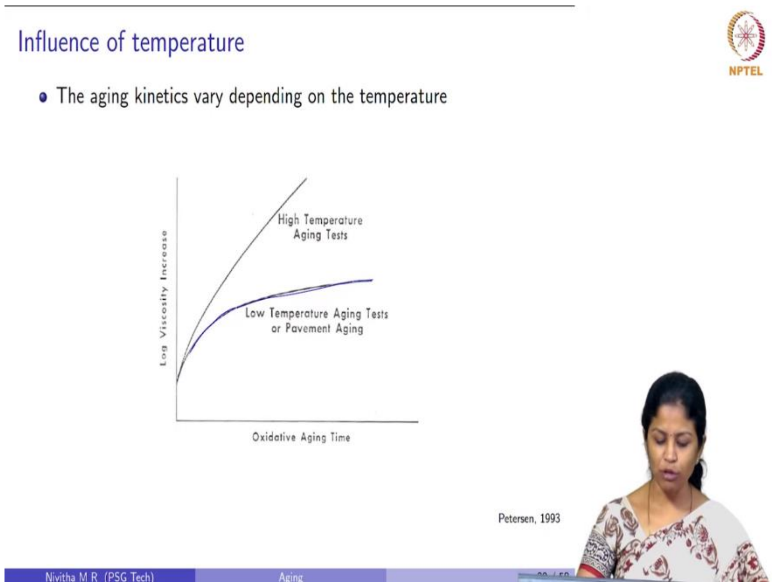

Next we will move on to the influence of temperature on the kinetics of aging. So this is a hypothetical figure which shows the influence of temperature on the viscosity increase. So we can see that at low temperature the viscosity increase is increasing initially and it kind of slows down after certain period of time; whereas in the case of high temperature aging it almost proceeds closer to a linear fashion.

So we will see let us see what is the influence of temperature on the oxidation process. So this is represented based on the colloidal model. So we know what a colloidal model is. We have the asphaltene fraction which is dispersed in the maltene phase, this maltene composes of polar aromatics, naphthene aromatics and saturates.

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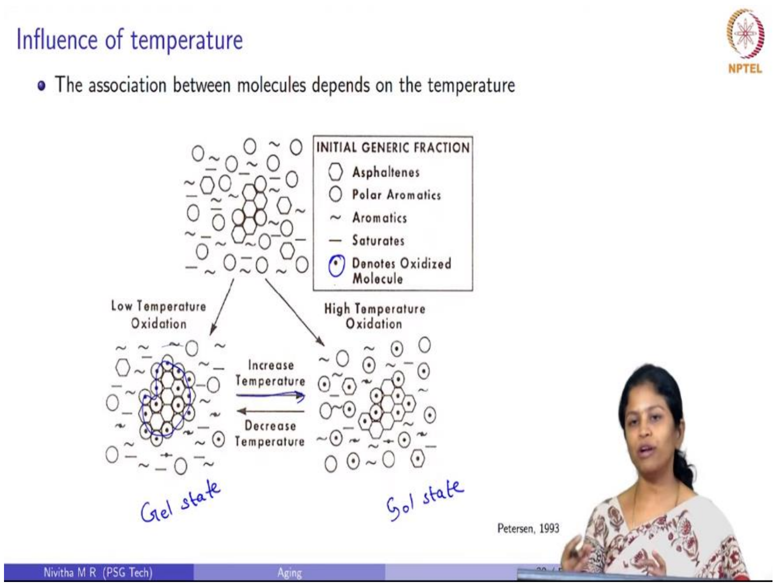

So this is a hypothetical case which is explained by Petersen for oxidation at different temperatures. Let us now look at low temperature oxidation. At low temperatures we said the material can exist in a sol or a gel state depending upon the temperature. We have already discussed when we were talking about the chemical composition of bitumen. Now at low temperatures the material is in a gel state.

So what do we mean by gel state? The molecules are associated with each other in a strong manner. And we can see the dot here denotes oxidized molecules. So when the material is in a gel state and when the oxidation occurs most of the molecules only in the periphery undergo oxidation. We can see that these molecules which are present in the inner core may undergo oxidation only at a later stage or in some cases they may not undergo oxidation at all.

But as temperature increases, when the temperature increases what happens is that the association is broken down and the material now moves from a gel state to a sol state. So here the association is broken down, the materials are now dispersed. So now there is more tendency for a lot of these molecules to get oxidized. So because of this, the oxidation is very rapid at high temperatures compared to that at low temperatures.

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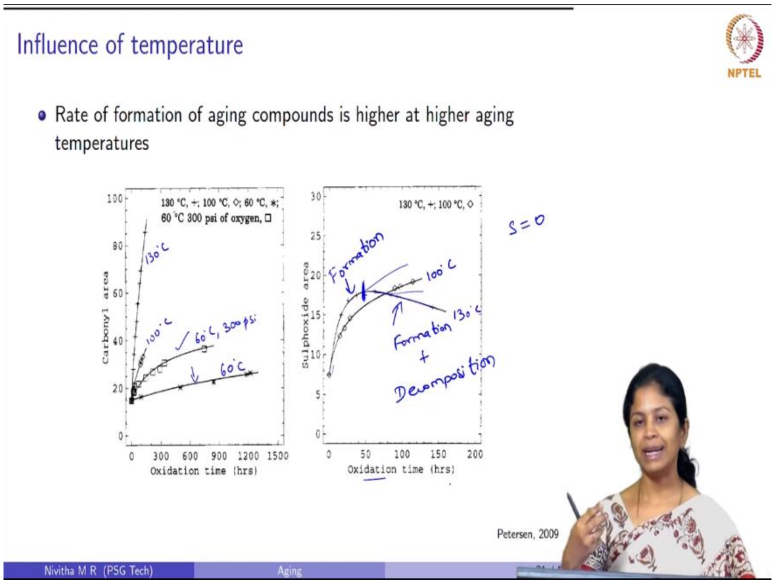

And this is verified experimentally also for bitumen. So in this study they have measured the formation of carbonyl and sulfoxide area at different temperatures. We see this corresponds to 130 degree Celsius, this one corresponds to 100 degree Celsius; this is 60 degree Celsius in the presence of 300 psi of oxygen and this is at 60 degree Celsius at normal conditions. So we can see at high temperatures the formation of carbonyl area is very rapid and it reduces with reduction in temperature.

And we can also see due to the availability of oxygen, the formation of carbonyl area is higher in this case compared to this case. In the sulfoxide area, there are two temperatures given here; this is 130 degree Celsius and this is 100 Celsius. So at 100 degree Celsius there is a formation of sulfoxide area and it keeps increasing. Whereas at 130 we can see it has increased substantially in 50 hours of oxidation itself and after that we can see a reduction in sulfoxide area.

What people of have seen is that beyond a particular point the decomposition of sulfoxide is initiated. So because of this decomposition of sulfoxide, the sulfoxide again breaks down into other compounds. So because of this decomposition there is reduction in the sulfoxide area because this area just corresponds to S double bond O. So there is formation beyond this particular up to this point there is only formation, beyond this point there is formation and decomposition.

Depending upon which phenomena dominates over the other, we will see an increase or a constant value or a reduction for the sulfoxide index. So if this formation dominates the decomposition we will see an increase here. But if this decomposition dominates then we will see a reduction in sulfoxide value which has been observed in this study. Again this formation and decomposition can be initiated at different temperatures and different time combinations.

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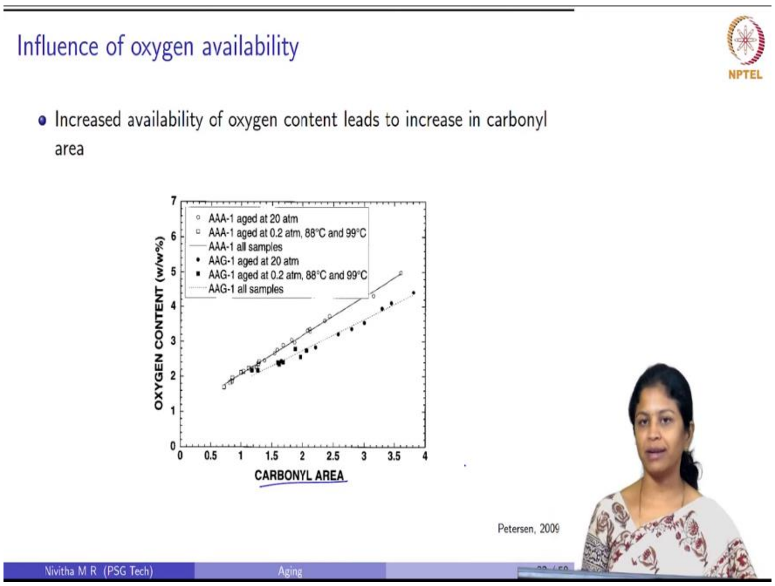

Now we will see that the amount of carbonyl area is directly proportional to the availability of oxygen. We have seen that if there are more oxygen molecules available for bitumen they tend to absorb these oxygen molecules and form carbonyl compounds. So this carbonyl area formation has a linear correlation with the oxygen content. If there is more oxygen content then there is more formation of carbonyl area.

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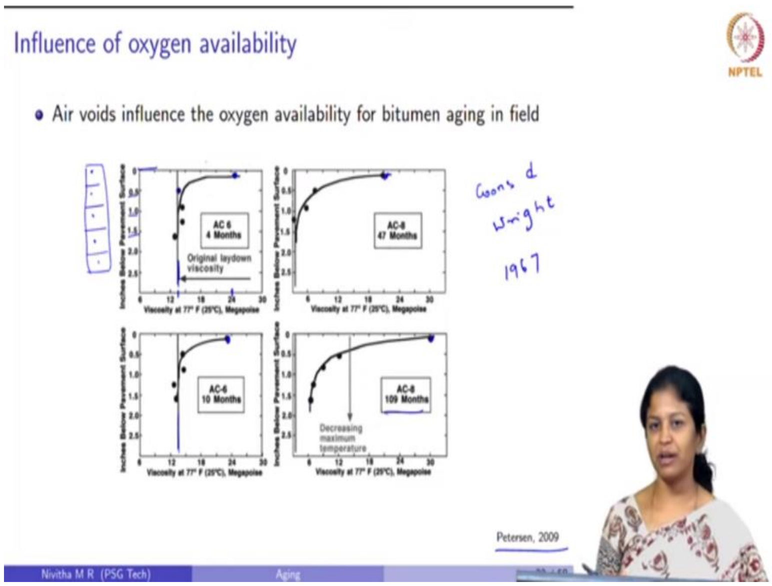

Now we will see what is this influence of oxygen availability on the aging that happens in field. So there was a study by Coons and Wright in the year 1967. So they had extracted core from the field, sectioned cores and extracted bitumen from each of these sections. So that data is represented by Petersen et al. in this figure. So they have taken two types of bitumen AC 6, so this AC is a kind of viscosity grading which is based on the American grading system.

So they have two types of bitumen AC 6 and AC 8. So we can take this particular figure here; on the Y axis is inches below the pavement surface. So this is the surface of the pavement; so they have taken something like a core here; sectioned it and taken bitumen from each of these points right. So this one corresponds to the surface. So what they have done is that for each of this section they have extracted bitumen, measured its viscosity.

So this point here corresponds to the viscosity in this particular section which represents the surface. And then this point is at 0.5 inches below the surface, again this is 1 inch below the surface something in between we have one more point for 1.5. And this point here, this line here right, which is the original laid down viscosity. So the viscosity of the bitumen after it has been laid on the pavement.

So we can see here that there is a substantial increase in viscosity we can see what is the viscosity in the initial case and what is the viscosity after 6 months of aging sorry after 4 months of aging in field. So we can see that at the surface there is almost a 2 times increase in viscosity from close to 12 it has gone to 24 right. There is an increase in viscosity on the surface whereas even at 0.5 inches from the surface we can see that there is not much of an increase in viscosity.

This is also again for AC 6 grade of bitumen which was taken after 10 months. Here also we can see the increase in viscosity on the surface and the closer value of this viscosity to laid down viscosity at different depths. Whereas if we take the AC 8 grade of bitumen, here we can see that at the surface again there is almost like 3 time increase in viscosity for this case on the surface and we can also see some amount of increment at different depths from the surface.

And they have also seen that at 109 months for this particular core. So they say that there is a decreasing effect of maximum temperature here and depending upon the air void distribution in each of this case, the availability of oxygen at lower layers is going to be different. Depending upon these two factors the amount of aging that happens in this material will be different. So we know that as temperature increases the amount of aging is higher.

So the amount of aging at the surface is relatively higher because of the higher temperatures and higher availability of oxygen. Whereas when we come down there is a reduction in temperature and there is also reduction in availability of oxygen. So because of these two factors the aging is going to be relatively lower at the lower layers.

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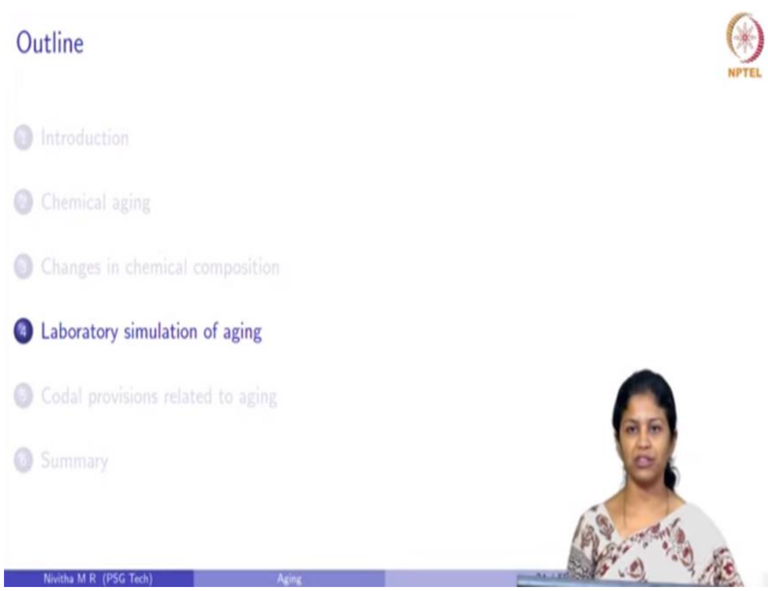

So now we will stop with this in today's class. In the next class we will discuss about the laboratory stimulation of aging and codal provisions related to aging. Thank you