agingMechanical Characterization of Bituminous Materials

Prof. Dr.M.R. Nivitha
Department of Civil Engineering
PSG Collage of Technology, Coimbatore

Module No # 05
Lecture No # 22
Aging of Bituminous Binders and Mixtures – Part 1

Today we are going to talk about aging of bitumen and bituminous mixtures. So what is this aging? Aging on a very general note can be defined as the process of getting older right. So we tend to get old as human beings and all living beings in this world tend to get older. Similarly is the infrastructure which is present; the physical infrastructure which is present outside. So we construct buildings we construct roads.

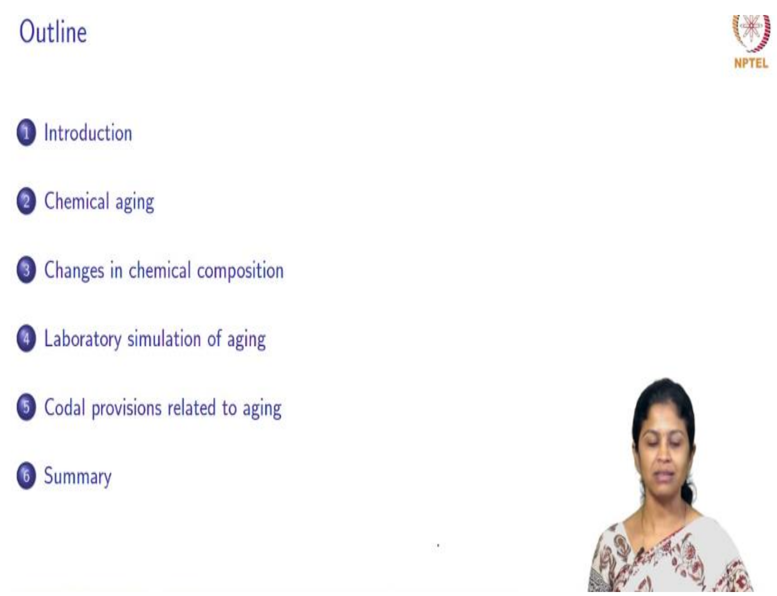
So we leave them out in the open to atmospheric conditions. So these infrastructures tend to get old. Now we construct a building and we do not use it at all right? we leave it there and we do not use that building at all. Do you think there will not be any distress on those building? we will take the example of a road. Let us construct a road and then just leave it there; not even a single vehicle has traversed that road over a period of 10 years.

Now do you think the pavement will remain fresh and new as in when it was constructed? no right, we all know. So this pavement is going to age because it is subjected to environmental conditions. So whether the pavement is used or it is not used, it is going to have the impact of the environmental factors. So when we construct a pavement and then leave it, there is an effect of sunshine right.

So we have these radiations falling on this pavement; it is open to atmospheric conditions. So there is some oxidation that is going to happen in this material; it is also subjected to the effect of moisture. We have rainfall and we have heat freeze and thaw periods in very colder climate so all of them is going to have an effect on the pavement. So this aging is an inevitable phenomena whether we desire or not our infrastructure facility is going to face this aging.

So in addition to effect of aging is what the impact of the vehicles that is going to be on the pavement. So in addition to the effect of aging the number of repetitions, the speed of the vehicles and lot of other factors are going to cause distresses on the pavement.

(Refer Slide Time: 02:28)

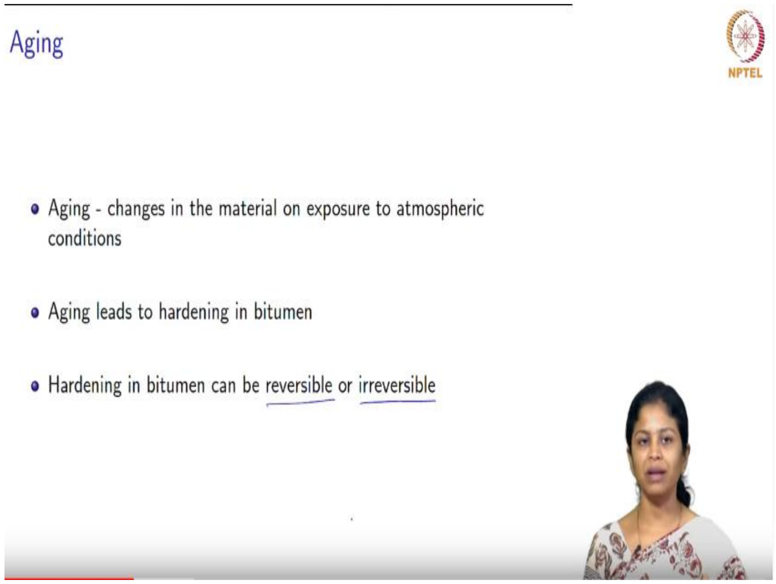


So in this lecture this is your outline of this presentation. So first we will introduce what is aging? There are 2 types of aging here reversible and irreversible, actually we should call it as hardening rather than aging. So we will introduce what are these two types of hardening, then we will move on to chemical aging which is specifically an irreversible type of aging. And then we look into what are the changes in chemical composition because of this aging phenomena.

Then we will see how is this aging simulated in laboratory because we said aging occurs over a period of time. So we cannot wait till the period of time the material ages to evaluate its performance. So we need to do some kind of accelerated testing in the laboratory to see how this material ages. So that we are going to look into what are the techniques available for aging of bitumen and bituminous mixtures.

And finally what are the codal provisions related to aging; so this is the outline of the contents for this topic on aging; we will be covering this in 2 lectures. So in the first lecture, in today's class, I am planning to cover the introduction part, the chemical aging and the changes in chemical composition on aging.

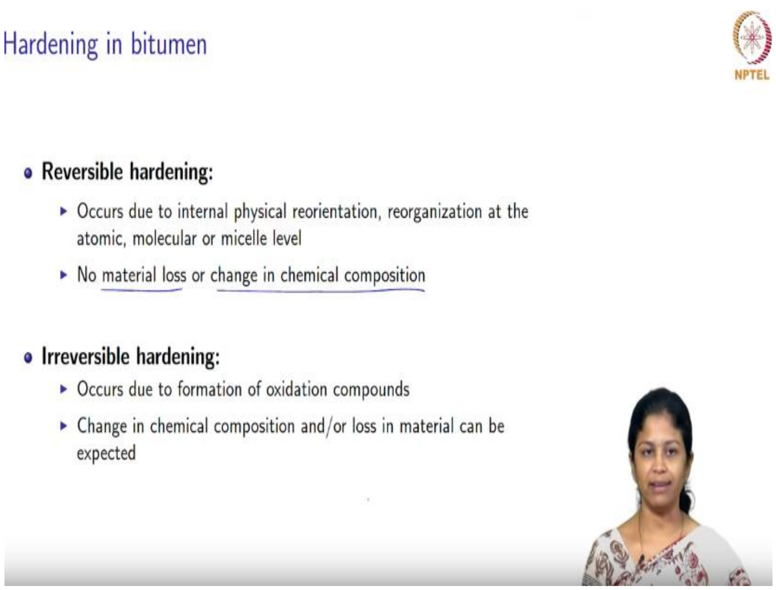
(Refer Slide Time: 03:38)



So what is aging? It is change in the material on exposure to atmospheric conditions. We do not do anything on this material just subjecting it to atmospheric conditions, what are the changes that the material experiences. So aging leads to hardening in bitumen. So that is the general perception right. So as an effect of aging the material tries to harden but not every time the material hardens it is because of aging; there are lot of other things also that can happen in the material which can lead to hardening in this material.

So we will generally first call it as hardening then we will move on to in specific to aging. So this hardening in bitumen can be reversible or irreversible. This irreversible hardening in bitumen is what we call it as aging in general but that is actually chemical aging in this material. We will see about this in detail. There is also some amount of hardening that happens in the material which is reversible in this nature. So we will first look into the reversible aging, when it happens in bitumen and then we will move on to the irreversible aging.

(Refer Slide Time: 04:45)

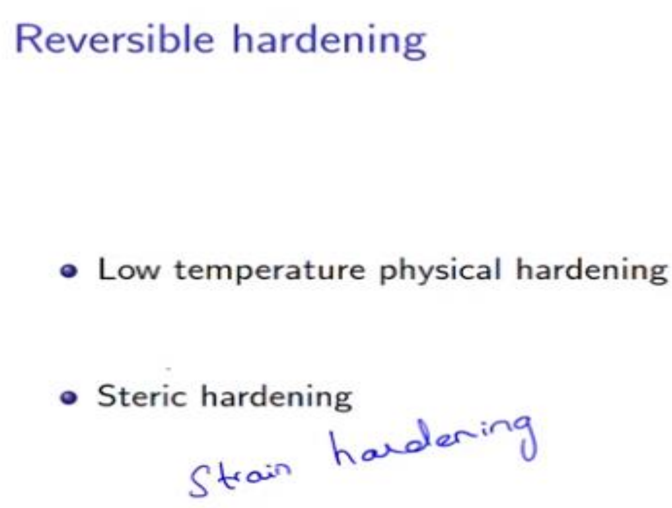


So this reversible hardening, we call it, occurs due to internal physical reorientation; so what happens is that we said we have different molecules that is present in bitumen. So these molecules try to internally reorient, they always try for an equilibrium state. So these molecules try to reorient themselves in the internal micro structure of this material. So this reorganization at the atomic level or a molecular level or at the micelle level is called as reversible hardening.

So we know right we have seen when we were talking about the chemical composition of bitumen we explained it in different stages. We talked about the atomic scale then we moved on to the molecular scale and then we also said about the micelle scale in the colloidal model of bitumen. So in any of these scales it can undergo some kind of a reorientation which is called as reversible hardening.

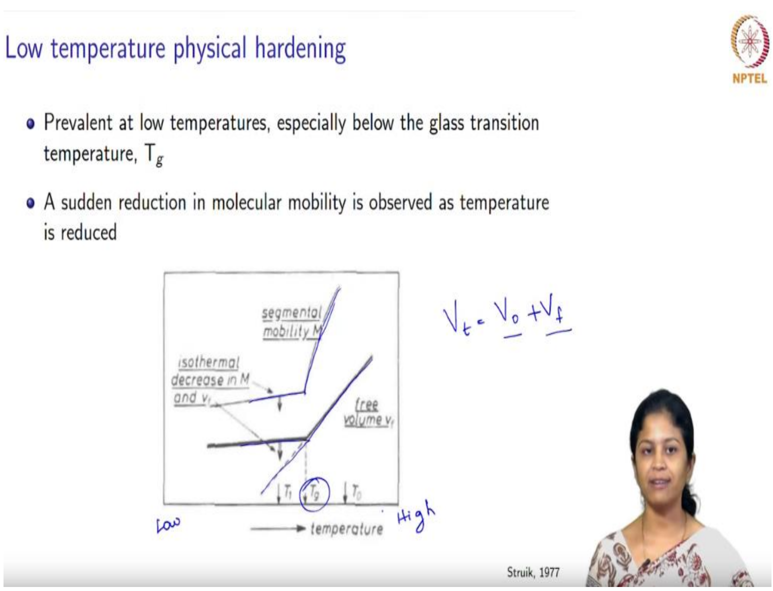
So we should note here that there is no change in material loss or there is no change in chemical composition because of its reversible hardening; it is only some reorientation of this molecule. In irreversible hardening this occurs due to the formation of oxidation compounds. So here we see there is some formation of new compounds that occurs here and there is change in chemical composition in addition to loss in material right? so this is irreversible hardening.

(Refer Slide Time: 06:14)



Now there are 2 types of reversible hardening which we can observe in bitumen; actually there are three types of hardening: low-temperature physical hardening, steric hardening and also strain hardening. In this lecture we will contain ourselves to low temperature physical hardening and steric hardening alone.

(Refer Slide Time: 06:37)



So what is this low-temperature physical hardening? So as the name suggests it occurs at low temperatures. So what happens is that when we reduce temperature from high temperatures with the reduction in temperature the molecules will try to reorganize themselves to form an equilibrium state or to attain an equilibrium state. So we can explain this in terms of a free volume concept. So what is this free volume? We have a space in which the molecules are present.

So let us say the volume can be composed of, the total volume can be composed of the occupied volume plus the free volume right. So it I take a unit space, it will have some points will have these molecules present and there will be some spaces because of these irregularities in these molecules. So we have an occupied space and a free space. So this is the occupied volume and free volume. So as this temperature reduces this free volume also keeps reducing and this is in accordance with the rate of reduction of temperature.

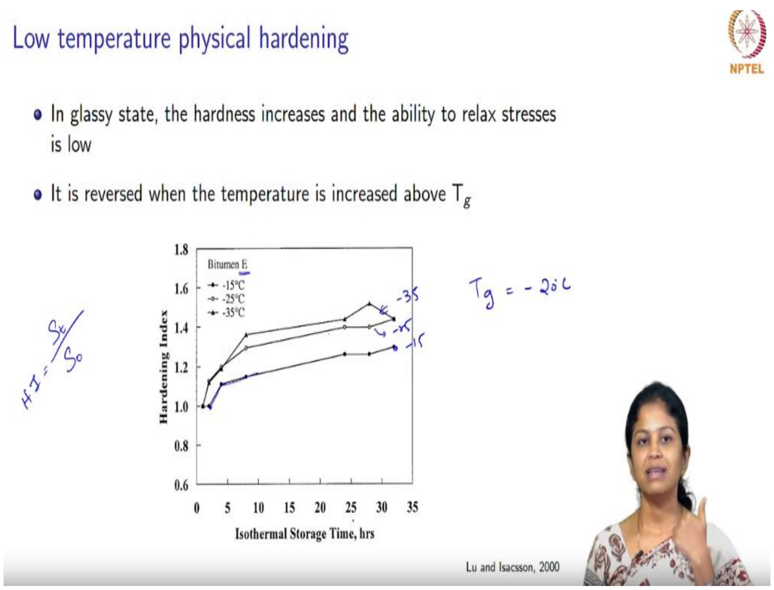
But at a point when the glass transition temperature is reached, suddenly there is a reduction in this molecular mobility; these molecules now no longer try to move or reorganize themselves as the same rate in reduction in temperature. So we see a lag in the reorganization of these molecules with reduction in temperature. So because of this lag, if we take the free volume from high temperatures this is low temperature and this is high temperature.

So when the temperature is reduced we can see this free volume keeps reducing up to a point so when this glass transition temperature is attained. So this is the equilibrium state and this free volume tries to follow the equilibrium state but after this particular case this is the equilibrium state but then this free volume is something higher right. The free volume does not reduce as rapidly as it was before the glass transition temperature.

So because of this reduction in free volume now what we do is say for example I store this material at a temperature which is lesser than the glass transition temperature. So we should remember that the materials have not still attained their equilibrium state. So when I store it at a particular temperature which is lesser than it is glass transition temperature, these molecules will now try to reorient themselves and try to attain equilibrium state. So at a given temperature there will be some internal activity which is happening between the molecules which will lead to an increase in stiffness of this material.

So this is the phenomena which leads to low temperature physical hardening in this material. We can see this graph here shows the molecular mobility. So this molecular mobility keeps decreasing and it is in accordance with this free volume reduction. So after this glass transition temperature this reduction in molecular mobility is observed and this leads to a lower rate of reduction in free volume. So now what is this consequence of low-temperature physical hardening and why are we interested in it in the case of bitumen.

(Refer Slide Time: 09:59)



So what happens is that in the glassy state the hardness of bitumen increases substantially and the ability to relax stresses reduces. So this is very very important for pavements when the temperature falls below the glass transition temperature, this may not be very common in India. But imagine countries like Canada where the pavement temperatures can easily reach up to -30 or -40C.

Generally the glass transition temperature of bitumen is roughly about -20 degree Celsius a general number. So when the pavement temperature falls below this glass transition temperature then there is some this low temperature physical hardening which happens. So the hardness in material keeps increasing though the temperature is maintained constant alright. So this is the impact of low temperature physical hardening and people have quantified this impact of low temperature physical hardening.

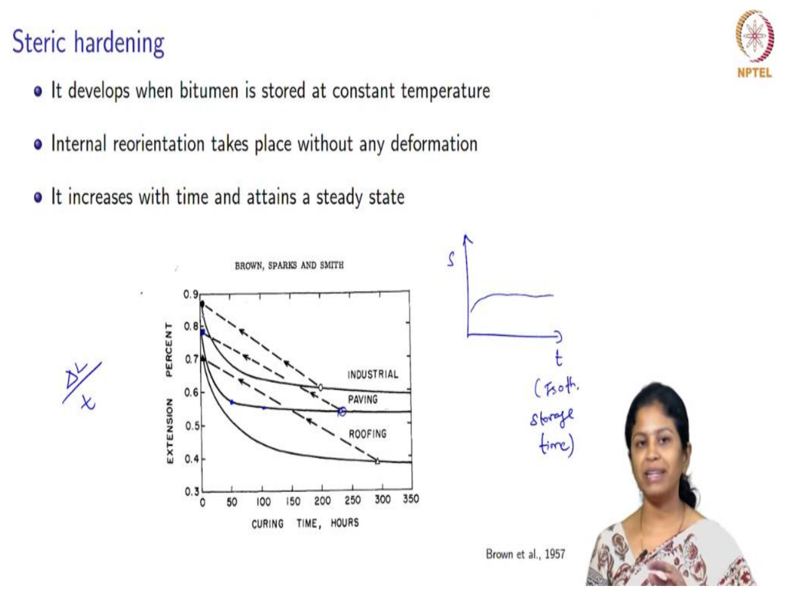
So this is the study by Lu and Isacsson. What they have done is, they have considered a bitumen of type E and they have tested it at 3 temperatures, -15 -25 and -35 degrees. So they have measured the hardening index. So what is this hardening index? This hardening index is nothing but the ratio of stiffness at sometime t divided by the ratio of stiffness at time 0. So let us take the temperature -15 degree Celsius. So they have maintained bitumen at -15 degree Celsius and then they have measured the increase in stiffness. So this is isothermal storage time isothermal means constant temperature, so when the material is stored at a constant temperature. So this line here right this corresponds to -15 degree Celsius.

So initially they have measured it; this is the starting point and then when it is measured after some 5 hours of storage close to 5 hours of storage they see an increase about 1.1 times increase in stiffness and with time you can see after 30 hours of storage it has reached more than 1.2 times increase in stiffness compared to when immediately the temperature was reduced to -15 degree Celsius right.

So this is for -15 degree Celsius; we can say similar behavior for -25 and -35 degree Celsius; we can also see as we go down lower and lower, the hardening index keeps increasing. So this is for -15, this one is for -25 and this one is for -35. So as the temperature increases the hardening index with time also increases. So this is the phenomena of low temperature physical hardening and this phenomena is reversed when the temperature is increased above the glass transition temperature.

So we have seen that the, the material has stiffened right? It has increased about 1.2 times, 20% increase is observed when it is stored for 30 hours. Now we take this material slightly heat it above its glass transition temperature. So then what people have seen is that they have seen that it reverts back to its original state. So this is completely reversible and to reverse it we need to take this material slightly above its glass transition temperature.

(Refer Slide Time: 13:22)



The next phenomena is steric hardening; people say that, steric hardening actually occurs at room temperature and people say that steric hardening occurs due to similar phenomena how low-temperature hardening is observed but there was no proof related to this; so we will just see what steric hardnening is. It is developed when bitumen is stored at constant temperature. So we said low temperature physical hardening occurs at constant temperature.

Similarly steric hardening also occurs at constant temperature; so this phenomena is also because of internal reorientation of molecules and there is no deformation. So this steric hardening also increases with time and it attains a steady state; it does not mean that if we keep storing this material over a long period of time it will keep increasing in it is stiffness; it does not happen that way. So if this is stiffness with respect to time, time means isothermal storage time alright.

So when if suppose this is the initial stiffness it might slightly increase and then it will try to remain constant right. So this is the effect of steric hardening so this was measured by an interesting experiment which was conducted by Brown, Sparks and Smith. So what they have done is that, they had taken bitumen in the form of a cylinder 25mm dia and 100 mm in length. So they had taken a cylinder and subjected it to extension test at different curing periods they had calculated the percentage extension.

So what is this percentage extension? it is change in length over the time period over which the stress was or the extension was applied. So they have taken 3 different types of bitumen; one is an industrial bitumen, second one is a paving grade bitumen, third one is a roofing grade bitumen. So each of them were subjected to different loads; this industrial and roofing bitumen were subjected to 1000 gram of load for 1000 seconds whereas this paving grade of bitumen was subjected to 500 gram of load for 500 seconds.

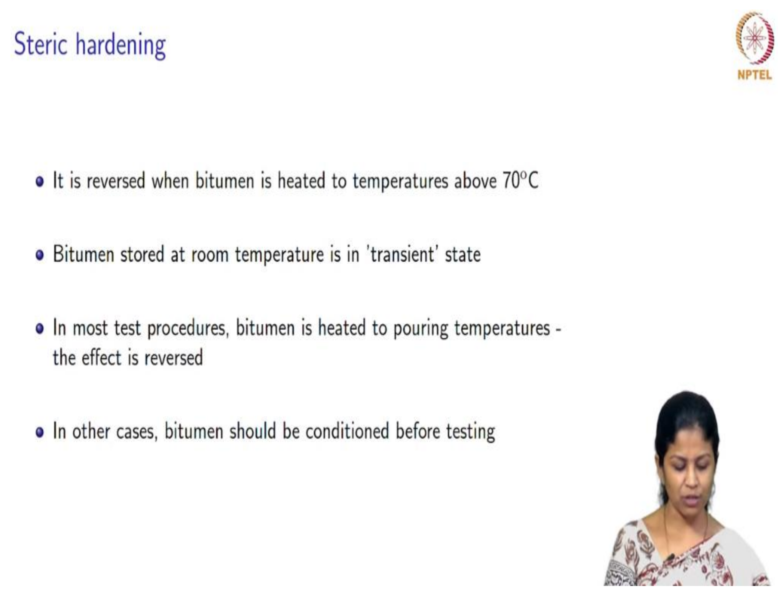
So to normalize the effect time applied they had calculated this Delta L / t. So that is this extension percentage and then this is the curing time. Curing time means the time period for which the material was stored at isothermal temperature. So what they have seen is you can see first the solid line which is given here. So this solid line shows that initially let us take paving grade bitumen initially the extension percentage is 0.8.

But after we cure it for some amount of time say for example for 50 hours we see that it has reduced less than 0.6% right; it is the same material we are not doing anything to this material except that we are storing it at constant temperature. So this storing has reduced the extension percentage which means that the material has become harder and after 100 hours there is a very small reduction and beyond 100 hours we can see there is very negligible reduction in extension percentage.

So from the zeroth time up to 52 some period between 60 or 70 hours it has reduced, the material has hardened drastically and beyond that point of time it has almost stabilized right. So this is in the case of paving grade bitumen. Now what they have done is that, after they have cured it for 220 hours so they had tried to heat the material right. So once this material was heated so this time is now reset to 0 at zeroth time they have again measured the extension percentage. You can see it has reverted back to this initial value; the same value was obtained after the material was heated.

So similar to the case of low-temperature physical hardening when we heat this material to a particular temperature this effect of steric hardening is removed and the material now completely reverts back to it is original state.

(Refer Slide Time: 17:38)



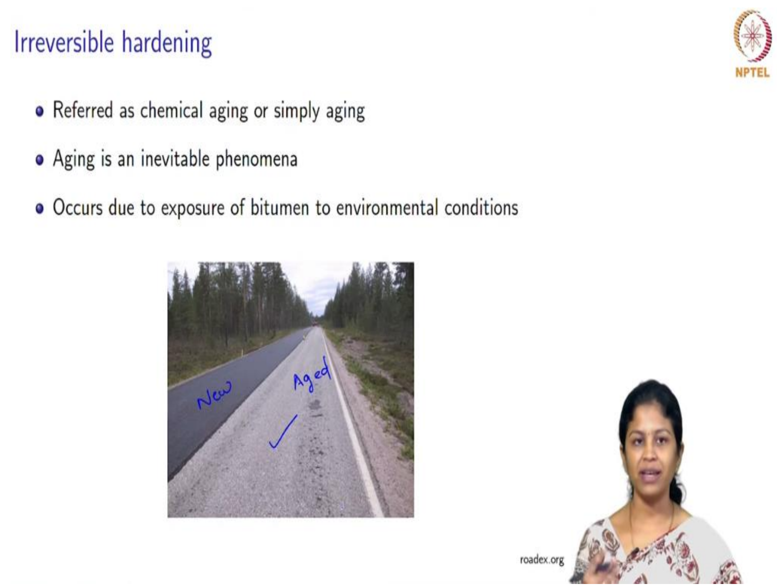
So that is what I said when bitumen is heated beyond temperatures greater than 70 degree Celsius it reverts back to its original state and the effect of steric hardening is removed. Now why is this important to us? We obtain bitumen from refinery we store it for considerable period of time and then we take this material do some tests on this material right. So in that state the material is considered to be in a transient state. So we have to revert back this effect of hardening.

So when it is stored at isothermal temperatures it is has a tendency to form steric hardening. So we need to revert back this effect of steric hardening only then the material is tested in its original state. So that is why it is required to condition sample before we do any tests on bitumen. So if we see some test like viscosity where we heat the bitumen to pouring consistency, we heat it to temperatures of 90 to 100 degree Celsius.

So at those temperatures the effect of steric hardening is automatically removed. So we actually heat it to pour it easily but we should remember that we are doing something else also in that process; we are removing the effect of steric hardening. Now if there are there is some test in which you do not have to condition the sample, you do not have to heat the sample to pouring consistency then in those cases we have to condition the sample before testing.

So how is this sample conditioned? you take some amount of sample; you keep it in a constant temperature water bath say roughly around temperatures of 60 degree Celsius. Keep it for half an hour then take that material and conduct any test that we want; so by this process we are removing this effect of steric hardening in bitumen. So it is very important to remember this when we are doing any test on bitumen

(Refer Slide Time: 19:32)



Next we move on to the irreversible hardening this irreversible hardening is referred to as chemical aging or simply aging right. So when people say aging they refer to this irreversible hardening or chemical aging that happens in bitumen. So this chemical aging is an inevitable phenomena and it is also an irreversible phenomena; like I said we subject the pavement to environmental conditions; it oxidizes, it undergoes lot of other processes, it ages.

We can say a pavement here the one on the right side right this one is an aged pavement and the one on the left side is a new pavement. We can see the appearance of an aged pavement; it is dull gray in color it has lost that shine, whereas a new pavement is fresh black in color it has that shine in it. So the effect of aging actually reduces the shine in material and you can actually distinguish a new and an old pavement by this color.

(Refer Slide Time: 20:40)

Causes of aging

Effects	Influenced by					Occurs	
	Time	Heat	Oxygen	Sun-light	B & G Rays	At Surface	In Mass
1. Oxidation (in dark)	x	x	x	-	-	x	-
2. Photooxidation (direct light)	x	x	x	x	-	x	-
3. Volatilization	x	x	-	-	-	x	x
4. Photooxidation (reflected light)	x	x	x	x	-	x	-
5. Photo chemical (direct light)	x	x	-	x	-	x	-
6. Photo chemical (reflected light)	x	x	-	x	-	x	x
7. Polymerization	x	x	-	-	-	x	x
8. Development of internal structure (aging) (Thixotropy)	x	-	-	-	-	x	x
9. Exudation of oil (Syneresis)	x	x	-	-	-	x	-
10. Changes by nuclear energy	x	x	-	-	x	x	x
11. Action of water	x	x	x	x	-	x	-
12. Absorption by solid	x	x	-	-	-	x	x
13. Adsorption of components at solid surface	x	x	-	-	-	x	-
14. Chemical reactions or catalytic effects at interface	x	x	-	-	-	x	x
15. Microbiological deterioration	x	x	x	-	-	x	x

Traxler, 1963

Now let us look in detail about chemical aging. So Traxler has listed a number of factors which are responsible for chemical aging in bitumen. So you can see this table here; there are about 15 factors which are listed here; he calls them as effects and each of these factors can be influenced by a number of parameters. So what are these parameters that are listed here? One is time, second one is heat, oxygen, availability of sunlight and beta and gamma rays.

And he has also said because of each of these effects where does the aging occur. Some factors will cause aging only on the surface of bitumen whereas some factors will cause aging in the entire mass. So that is also listed in this particular table. The first effect is oxidation. So what is this oxidation? This is a very common term which we would have heard in different perspectives. So oxidation is absorption of oxygen and formation of oxides, so that is the oxidation process.

So this oxidation is listed here as to occur in dark right in the absence of sunlight but with the availability of oxygen we can have an oxidation process. So this oxidation process is influenced by 5 parameters and here for this particular case there are only 3 parameters that influence; one is time. So if the material is subjected to the availability of oxygen for a longer period of time then there is more aging.

Similarly heat, when it is subjected to oxidation in the presence of elevated temperatures then the rate of oxidation is higher. Similarly availability of oxygen; if there is more amount of oxygen available to this material then there is more oxidation happening in this material and it is also shown here that this oxidation occurs only at the surface. So if I have a say 1 centimeter thickness of bitumen present on a plate only the surface will oxidize and it will kind of form a skin.

So that will prevent the availability of oxygen to the molecules which are present inside. So this phenomena occurs only at surface. Similarly there is something like photo oxidation where the oxidation occurs under the presence of direct light. So this is also very common because our pavement is subjected to environment conditions there is sunshine and radiation falling on the pavement so there is oxidation under direct light.

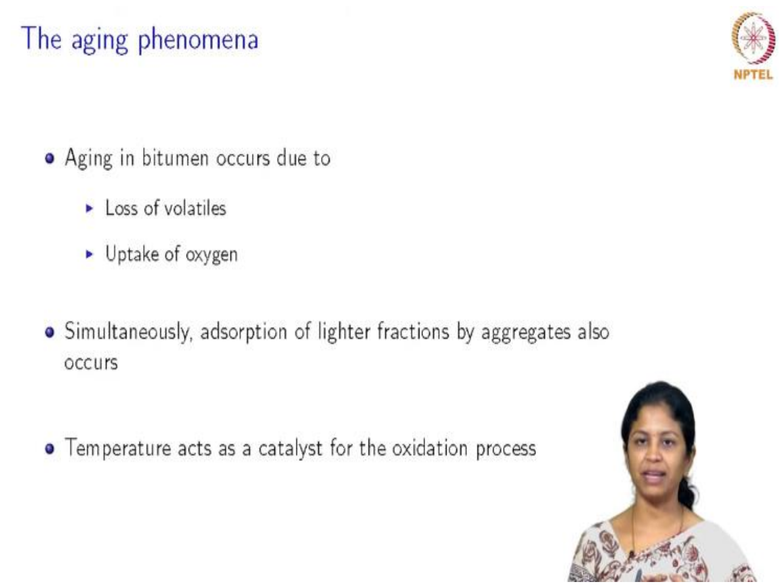
So this oxidation also occurs or is influenced by time, heat, availability of oxygen but in addition the amount of sunlight; this also occurs at surface. The next one is volatilization. This phenomena occurs because of the removal of lighter fractions which are present in bitumen. So when bitumen is heated we said there are a number of lighter fractions right; so these lighter fractions. So what are these lighter fractions? When we look in terms of Corbett fractions we define composition of bitumen in terms of saturates, naphthene aromatics, polar aromatics and asphaltenes.

So this saturates and naphthene aromatics fractions are called as lighter fractions. So these lighter fractions try to evaporate from bitumen and that is called as volatilization. So this occurs in the presence of time so more time it is subjected there is more amount of volatiles that is lost. Similarly heat also accelerates the process. This occurs at the surface and in the inner mass of this material. So if I have some 10 mm of material the loss of volatiles will occur uniformly across the entire thickness of this material.

So similarly there are number of other parameters; we have photo oxidation in the presence of reflected light. This is direct sunlight the second case is direct sunlight whereas the fourth case is reflected light and there are also photochemical reactions; these are chemical reactions induced by the presence of light. So this can also occur in the case of direct light or reflected light. There is also polymerization happening in the material, development of internal structure, removal of some oil fractions, there can also be changes because of nuclear energy, changes because of the action of water, adsorption of components at solid surface.

So this is what happens when bitumen is mixed with aggregates so it is hypothesized that some amount of lighter fractions which is present in bitumen is absorbed on the surface or I should call this adsorbed, adsorbed on the surface of aggregates. So this is also a surface phenomena and there can be chemical reactions or microbiological degradation. So these are some of the effects which will lead to aging in bitumen and it is influenced by various parameters; it can occur either at the surface or at the inner portion of this material.

(Refer Slide Time: 26:01)



But here for bitumen there are two predominant factors which people have observed and which has led to aging in this material; the first one is the loss of volatiles and the second one is the uptake of oxygen; that is nothing but the oxidation process. So people have said that these 2 are the predominant factors in the case of bitumen; in fact oxidation is even more predominant or highly predominant compared to this loss of volatiles.

We do not want more amount of volatiles to be removed from this material; we will see when we talk about the specifications; they have a limit on how much of volatiles should be removed from bitumen. So there is also adsorption of lighter fractions like I previously said on the surface of aggregates. So for all this process, temperature acts as a catalyst; so we have the influence of temperature at different degrees in different stages of a pavement.

During construction the effect of temperature is something else; during service in field the effect of temperature is something else. So in one way or the other temperature acts as a catalyst to this aging process.