Concrete Engineering and Technology
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Lecture - 27
Chloride penetration in concrete

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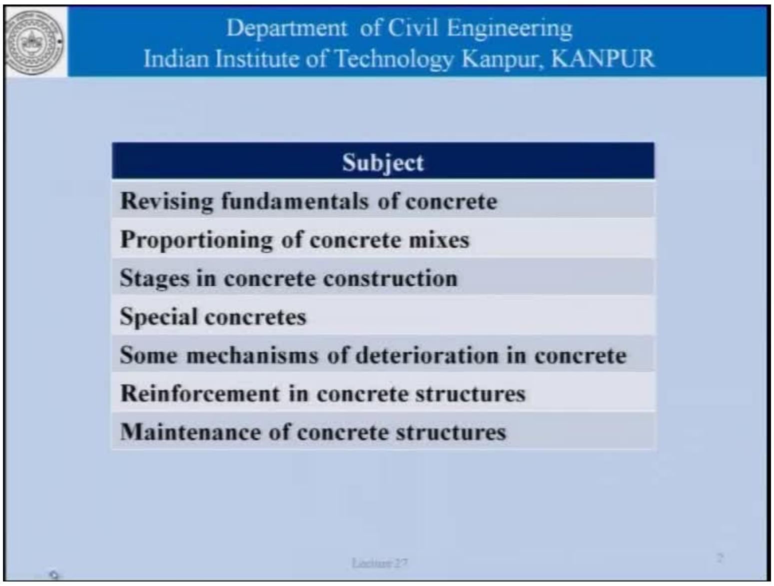

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Subject
Revising fundamentals of concrete
Proportioning of concrete mixes
Stages in concrete construction
Special concretes
Some mechanisms of deterioration in concrete
Reinforcement in concrete structures
Maintenance of concrete structures

[FL] and welcome back to concrete engineering and technology where we are talking of different aspects of the subject which are acquired importance in recent years, we were talking about some mechanisms of deterioration in concrete. And we had identified or decided that our discussion will be confined to reinforcement corrosion in concrete alkali aggregate reaction freezing and thawing a treatment of chloride penetration in concrete and carbonation. Within the subject of reinforcement corrosion and concrete chloride penetration plays a very important part.

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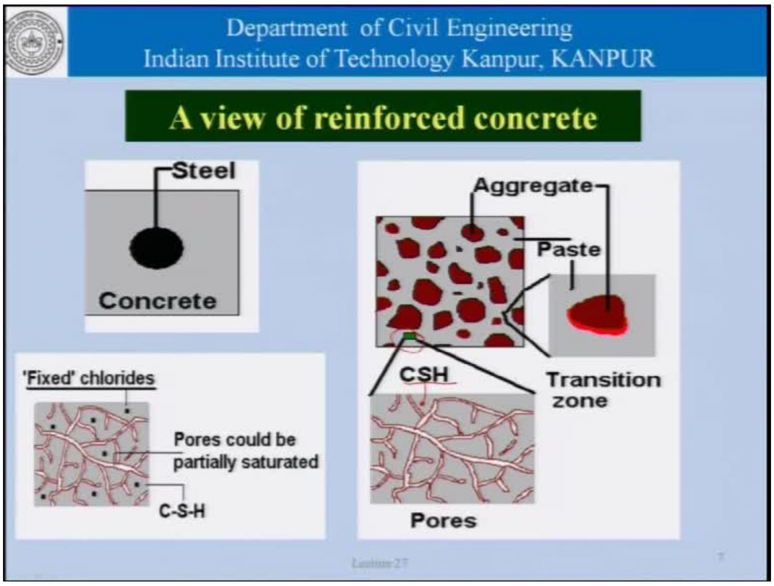
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A view of reinforced concrete

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And let us review what we did in the last lecture. We said that we will look at reinforced concrete as steel bars embedded in concrete and concrete itself would be basically considered a conglomerate of coarse aggregate embedded in mortar. And the cement paste would be the integral part of the mortar as shown here and would comprise of solid C S H and pore spaces. So, as far as chlorides are concerned they will be sitting either in the pore spaces or in the cement or in the chemical compounds of the solid hydration products. These are the things that we will talk about today, but this is a recap of what we did last time.

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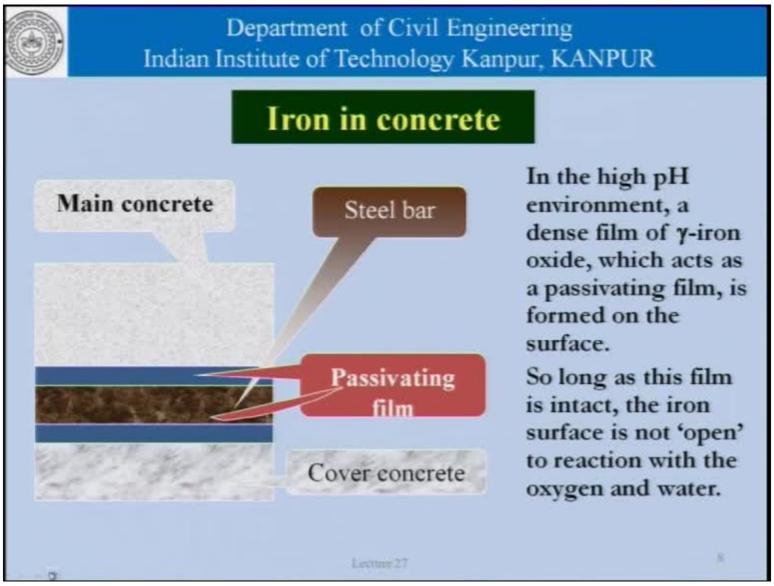
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Iron in concrete

In the high pH environment, a dense film of γ-iron oxide, which acts as a passivating film, is formed on the surface.

So long as this film is intact, the iron surface is not 'open' to reaction with the oxygen and water.

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We had also discussed why iron in normal conditions embedded in concrete does not corrode. And that is because there is a dense film of gamma iron oxide which is formed on account of the high p H in the concrete or the environment immediately surrounding the reinforcing bars. And this high p H is the result of the formation of large amounts of calcium hydroxide in the hydration of the constants of cement, that is C 2 S C 3 S C 3 and so on.

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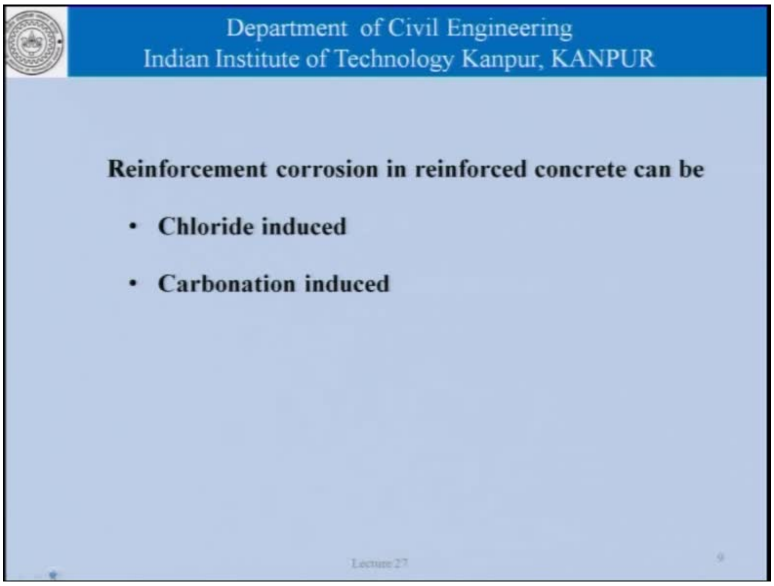

Reinforcement corrosion in reinforced concrete can be

- **Chloride induced**
- **Carbonation induced**

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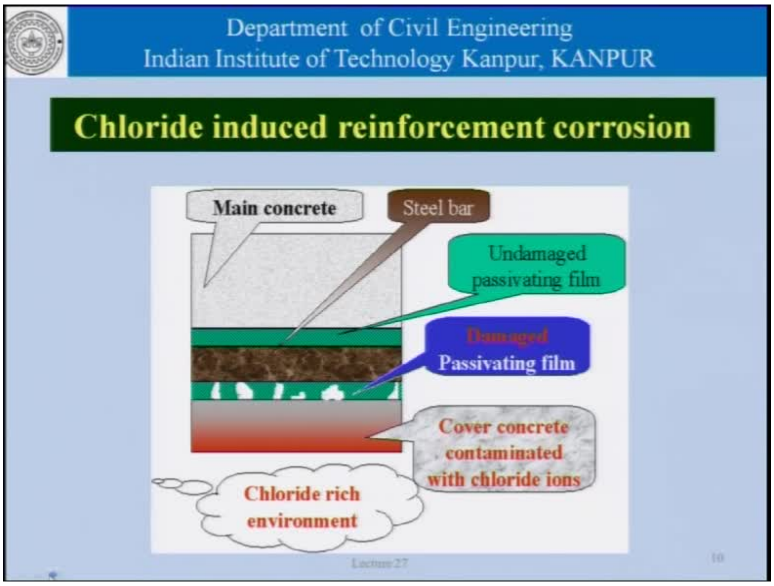

Chloride induced reinforcement corrosion

We had also talked about the fact that basically reinforcement corrosion in concrete is either chloride induced or carbonation induced. And in the case of chloride induced reinforcement corrosion, the passivating film is damaged even though electrochemically the environment itself does not change, that is the passivating film can theoretically thermodynamically still remain stable.

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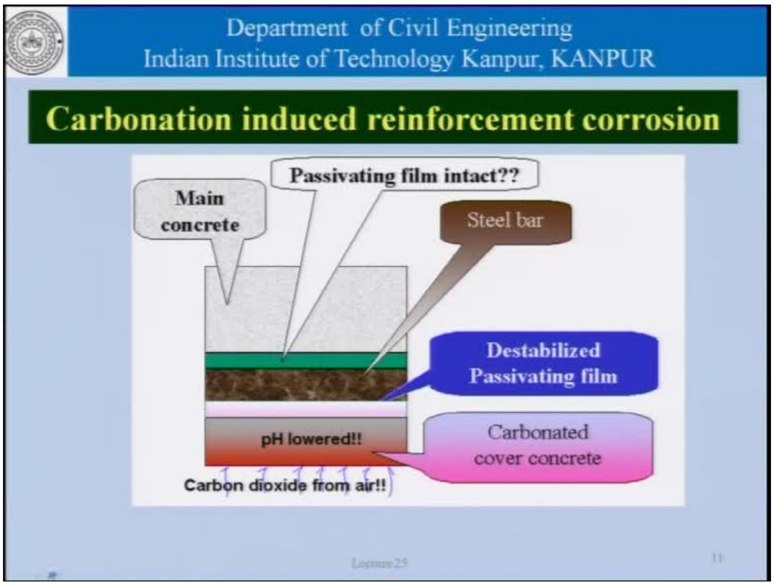

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Carbonation induced reinforcement corrosion

Main concrete

Passivating film intact??

Steel bar

Destabilized Passivating film

pH lowered!!

Carbonated cover concrete

Carbon dioxide from air!!

Whereas in the case of carbonation induced reinforcement corrosion, penetration of carbon dioxide leads to the consumption of calcium hydroxide which lowers the p H of the pore solution. And therefore, the passivating film around the reinforcing bars which is stable at high p H becomes unstable. And therefore, we have a destabilized passivating film and with the passivating film gone the surface of the iron is open to attack from oxygen and water which is present in the concrete.

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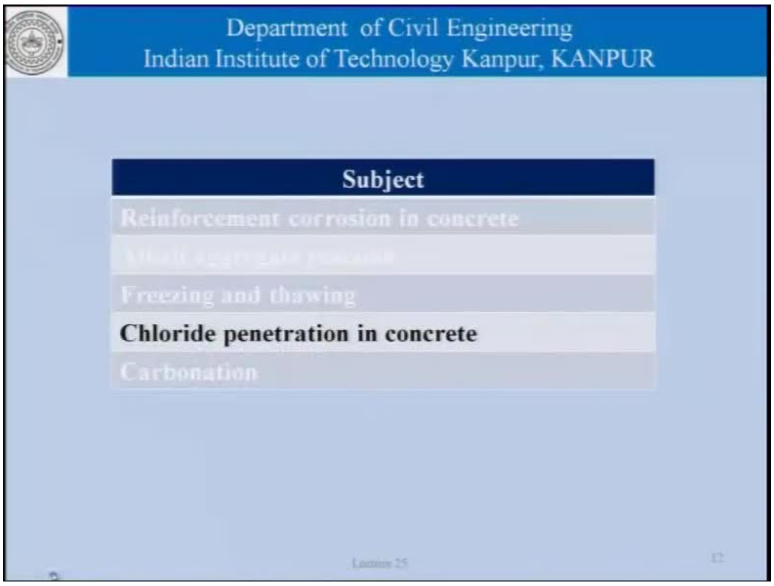

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Subject
Reinforcement corrosion in concrete
Alkali aggregate reaction
Freezing and thawing
Chloride penetration in concrete
Carbonation

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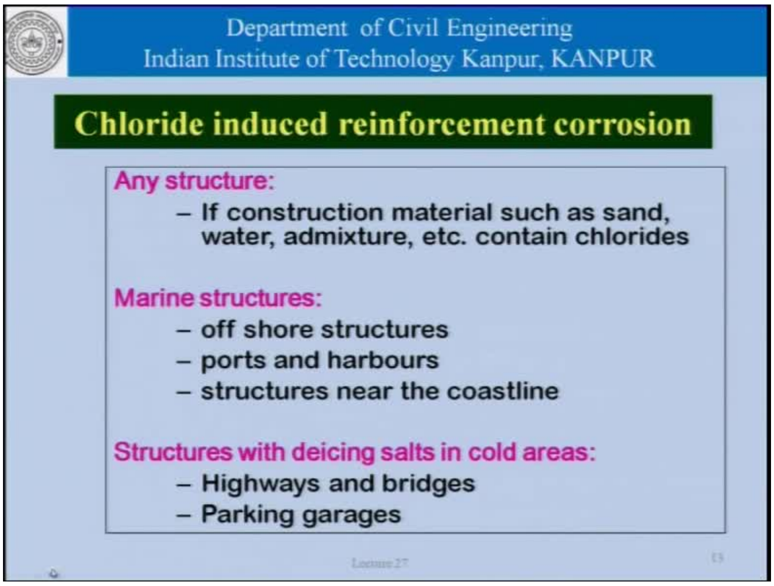

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Chloride induced reinforcement corrosion

Any structure:
- If construction material such as sand, water, admixture, etc. contain chlorides

Marine structures:
- off shore structures
- ports and harbours
- structures near the coastline

Structures with deicing salts in cold areas:
- Highways and bridges
- Parking garages

Now in the class today, we will confine our discussion to different aspects of chloride penetration in concrete, how the chlorides move into concrete and how are those processes modeled? What are the parameters involved and so on? So, getting started of the discussion, let us recall that chloride induced reinforcement corrosion can occur in any structure if the construction material such as sand water or admixture contained chlorides. And that is why our codes and standards lay down specific limits on what is the maximum permissible chloride content as far as sand is concerned or water is concerned admixture is concerned and so on.

Marine structures such as offshore structures ports and harbors structures near the coastline they are all susceptible to chloride induced reinforcement corrosion, because of the presence of sea or salt in the sea water. Similarly, structures with deicing salt applications in cold areas are susceptible to reinforcement corrosion, because there the chloride ions come in the form of deicing salts. And the structures in that category would be highways and bridges in cold areas, parking garages which are themselves covered. But cars coming from highways and bridges with the deicing salt in their tires and the underbelly that is deposited on the slabs of the parking garages. And that reinforcement the reinforcement there is rendered susceptible to corrosion.

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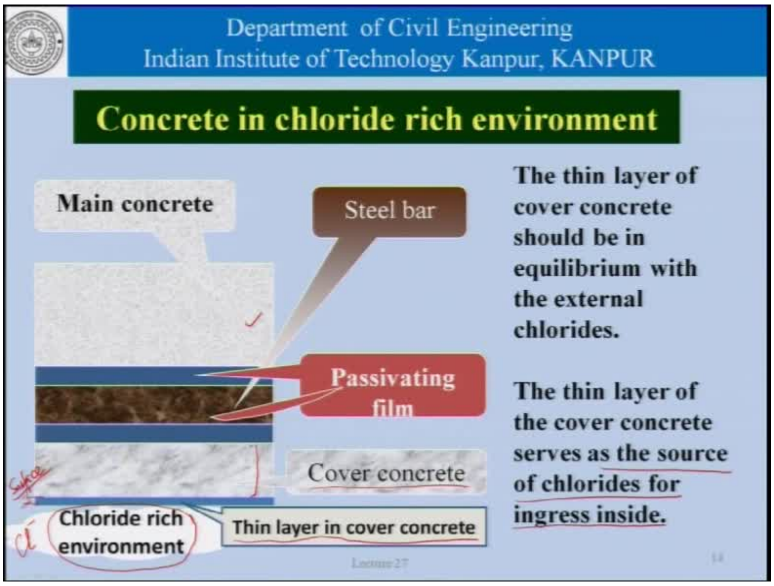

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Concrete in chloride rich environment

The thin layer of cover concrete should be in equilibrium with the external chlorides.

The thin layer of the cover concrete serves as the source of chlorides for ingress inside.

Now, let us take a look at the concrete in chloride rich environment a little more closely. We have a cover concrete and we have chloride rich environment outside. There has to be equilibrium a physical equilibrium between the chloride content in the atmosphere and the chloride content in a thin layer of cover concrete just outside here which is near the surface. The chloride in the environment has to be in equilibrium with the chloride present in the pore solution in a very small thin layer which is closed to the surface. So, we are further dividing the cover concrete into a thin layer of cover concrete which is in contact with the atmosphere and the normal cover concrete which is somewhere here.

And of course, that is different from the main body concrete shown beyond the reinforcing bars and the passivating film of course is as shown. It should be remembered that this thin layer and whatever chlorides it contains serves as the source of chlorides for ingress inside. So, what really happens or at least the way the models are constructed are so what really happens or the way the models are constructed? They assume that the chloride rich environment is in equilibrium with the surface layer of concrete and that surface layer of concrete serves as the source of chlorides for the penetration of chlorides further into the cover concrete. So, once that distinction is clearly understood we can proceed further and understand this as a diffusion process.

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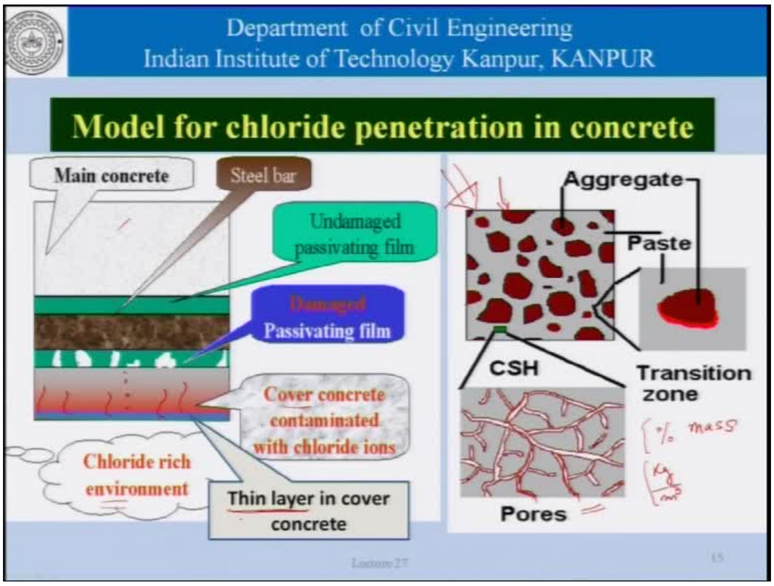

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Model for chloride penetration in concrete

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What we are looking at is something like this. That there is a thin layer of cover concrete, then as time goes on more and more chlorides penetrate from this surface layer inside the concrete. And what we have is a cover concrete contaminated with chloride ions. The concentration of these chloride ions could be different at different points in the cover concrete and it stands to reason to believe that as we go deeper into the concrete. The extent of penetration of chloride ions will be lesser that is the concentration will be lower. The concentration of chloride ions in concrete is generally expressed as a percentage by mass that is kilograms of chlorides to a kilogram of concrete powder or sometimes expressed as kilograms of chlorides per cubic meter of concrete. Different units are used depending on what is our convenient.

So, we can convert one from the other, because we know the density of concrete and all these other constants. So, we can proceed with that having said all these we must also remember where does the chloride ions establish themselves? Where do they physically occur? If we look at this picture which shows the pore spaces and the solid hydration products, and this picture which shows coarse aggregate or fine aggregate depending on whether you are looking at mortar or concrete. Whether it is this thin layer or it is the cover concrete at large or it is the main body concrete, all these concretes have essentially this structure. And therefore, the chlorides form the atmosphere that is this environment here they have to move into concrete through these pore spaces and some of these pores need not be connected and therefore, they will not contribute to the ingress of chloride ions into the concrete, but basically the chloride ions move through these pore spaces and move inside and this thin layer has a similar structure.

The chloride concentration in thin layer should be equilibrium with the chloride concentration in the chloride rich environment. We must also remember that this whole process of chlorides moving into concrete occurs when the concrete is wet. Most of this diffusion process, most of this ionic movement in fact all of these ionic movement to some extent takes place only through aqueous medium, there is no movement of ions if the concrete was perfectly dry. And the same argument holds if the environment had perfectly dry sodium chloride or any other chloride it will not be able to move into the concrete.

As far as engineering is concerned in all cases whether it is marine structures or it is deicing salts or it is a swimming pool where chloride or it is a swimming pool where chlorine has been used for keeping the water clean in all cases there is water involved. And therefore, what we are really asserting is that the water in the environment which is chloride rich and the pore solution they have to be in equilibrium. As far as chloride concentrations are concerned. That does not mean that the chloride concentration in the concrete will be the same as the chloride concentration outside.

Please remember that chloride concentration outside that is in the chloride rich environment that we are talking about is in terms of percentage of chloride ions in water. Whereas, chloride ion concentration in concrete is not given in terms of chloride concentration in the pore solution, because it is virtually impossible to extract pore solution, and then try to measure the chloride concentration there. We will come to that discussion a little later, but it must be clearly understood that chloride concentration in concrete is expressed generally as a percentage or in terms of kgs of chloride per cubic meter of concrete. As we talk before and therefore, to equate and therefore, to establish in equilibrium between chloride concentration in the chloride rich environment. And the chloride concentration in concrete is only a conceptual construct and not necessarily a very simple numerical issue.

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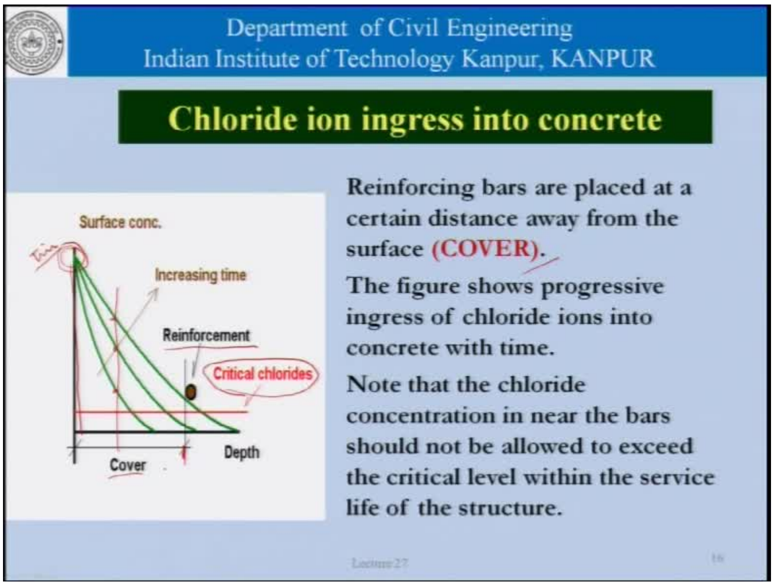

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Chloride ion ingress into concrete

Reinforcing bars are placed at a certain distance away from the surface (COVER).

The figure shows progressive ingress of chloride ions into concrete with time.

Note that the chloride concentration in near the bars should not be allowed to exceed the critical level within the service life of the structure.

Now, let us look at chloride ion ingress into concrete. What we are seeing is that this is the surface layer or the thin surface layer that we are talking about in that thin surface layer. We are assuming that the chloride concentration remains the same is virtually constant and the reinforcing bars are placed at a certain distance away from the surface and that is called the cover. And what this figure is showing is the progressive ingress of chloride ions into concrete with time that is to begin with maybe there was no chloride inside. And we could almost draw straight line like this, that there are no chlorides inside except that the thin surface layer has a certain amount of chloride.

With passage of time more and more chlorides went to the concrete with the surface layer acting as the reservoir. With the passage of time what we find is that at a given location from the surface the chloride concentration keeps increasing. And now as far as our previous model in terms of corrosion initiation is concerned, we should understand the chloride concentration in the neighborhood of the bar should not be allowed to exceed the critical level within the service life of the structure.

So, if we have a certain critical chloride concentration level that is that concentration level at which the passivating film is damaged. Then what we need to ensure is that at the location of the bar that is at the cover depth the chloride concentration should not be allowed to exceed this critical level in the service life of the structure. Soon on or later it will be exceeded that is no doubt true, but it should not be allowed to happen within the service life of the structure. And that is the principle of performance based durability design where we say that yes we understand that this structure is susceptible to corrosion. It is susceptible to chloride penetration chloride diffusion we have designed it such that the chloride concentration at the location of the reinforcing bar at the end of the service life will still be lower than critical chloride concentration.

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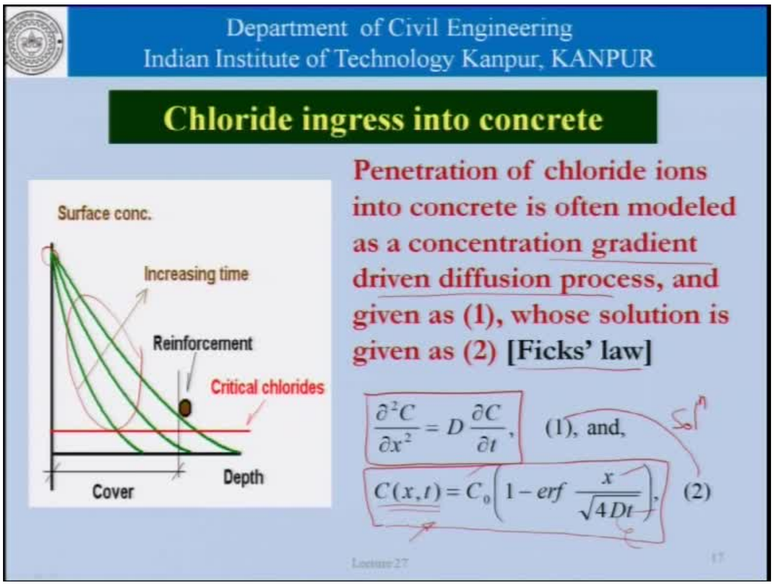

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Chloride ingress into concrete

Penetration of chloride ions into concrete is often modeled as a concentration gradient driven diffusion process, and given as (1), whose solution is given as (2) [Ficks' law]

$$\frac{\partial^2 C}{\partial x^2} = D\frac{\partial C}{\partial t}, \quad (1), \text{ and,}$$

Sol^n

$$C(x,t) = C_0\left(1 - erf\frac{x}{\sqrt{4Dt}}\right), \quad (2)$$

Now, this process of chloride ingress into concrete is often modeled as a concentration gradient driven diffusion process. And that in mathematical terms is given by referential equation which is given here. We are not going into the mathematics of deriving this equation and the solution of this equation is a form which is given here. So, the equation 2 is a solution of equation 1 and this is the so called well known Fick's law. What it says is that the chloride concentration at a given location is related to the depth time. The surface concentration and the diffusion coefficient and this build up from here that is with increasing time more and more chlorides get into the concrete. This phenomenon if it is represented as the concentration gradient driven diffusion process these curves can be represented through this kind of an equation. It stands to an argument.

We can discuss it whether or not chloride penetration in concrete is indeed at diffusion process or it is a concentration gradient diffusion process alone. For example in concrete, it is not only the chlorides which are moving in certain cases water also moves in the form of concrete. Consider the case of parking garages or deicing salt applications where the concrete surface is not really exposed to the same amount of chloride concentration. All the time it is not even exposed to water all the time only when it snows or when it the snow melts or it rains the surface becomes wet in other cases or at other times it remains dry. The same thing is true with many instructions where part of the structure which is submerged is always wet.

It is always under the action of it is always wet and submerged in the sea. It is a tidal zone, there is a splash zone and there is a zone in the concrete structure which remains clearly above the sea. And kind of chloride environment there is quite different. So, it stands to reason to say that all the chloride penetration does not occur through concentration gradient diffusion alone. Experts and researches in the area understand this and therefore, only model that is most easily available and can be applied is the diffusion model. And that is why it is common to use one is free to use another system another framework which replicates the natural situation better.

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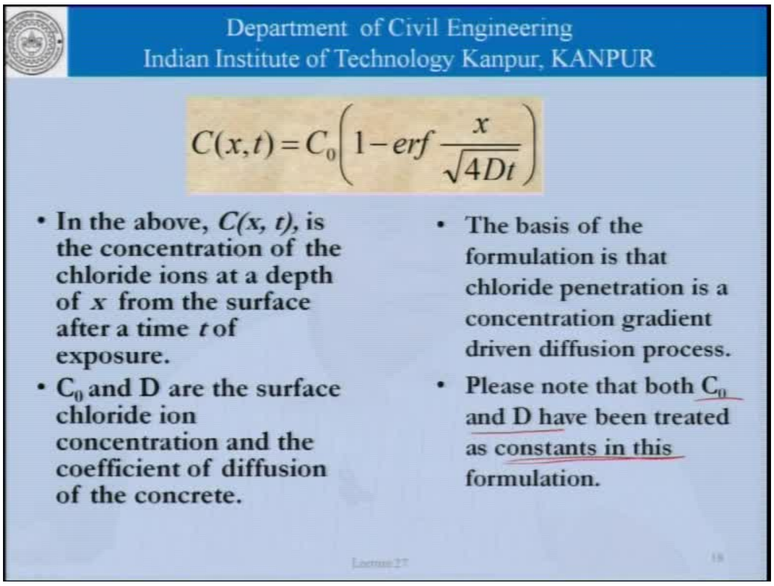

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$$C(x,t) = C_0\left(1 - erf\,\frac{x}{\sqrt{4Dt}}\right)$$

- In the above, *C(x, t)*, is the concentration of the chloride ions at a depth of *x* from the surface after a time *t* of exposure.
- C_0 and D are the surface chloride ion concentration and the coefficient of diffusion of the concrete.
- The basis of the formulation is that chloride penetration is a concentration gradient driven diffusion process.
- Please note that both C_0 and D have been treated as constants in this formulation.

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Looking at this equation little more closely C x t is the concentration of chloride ions at a depth of x from the surface after time t of exposure C 0 and t are the surface chloride and concentration and the coefficient of diffusion of concrete coefficient diffusion of chlorides in concrete. Now, we must remember that the basis of the formulation of this equation is the fact that the concentration gradient diffusion process governs and that C 0 and D are constants over time one and at different locations of the concrete structure for another. These assumptions are very fundamental in nature and have implications which an engineer must understand.

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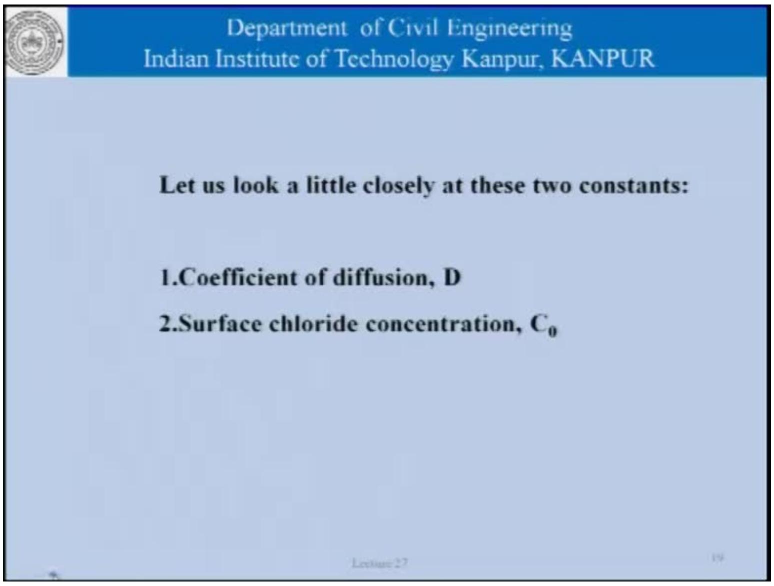

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Let us look a little closely at these two constants:

1. **Coefficient of diffusion, D**
2. **Surface chloride concentration, C_0**

So, for the time being we will leave at that we will proceed to take a closure look at the coefficient of diffusion D and the surface chloride concentration C 0 in this equation?

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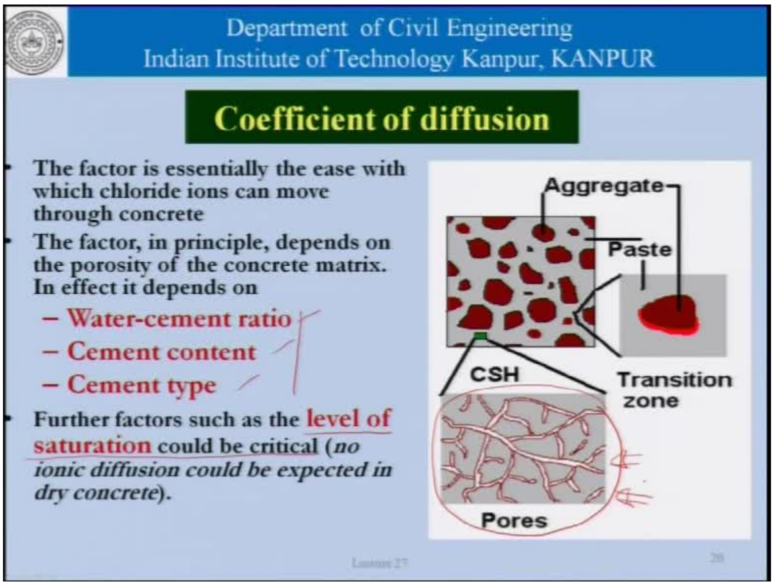

Coefficient of diffusion

- The factor is essentially the ease with which chloride ions can move through concrete
- The factor, in principle, depends on the porosity of the concrete matrix. In effect it depends on
  - Water-cement ratio
  - Cement content
  - Cement type
- Further factors such as the level of saturation could be critical (*no ionic diffusion could be expected in dry concrete*).

Now, as far as the coefficient of diffusion is concerned this factor is essentially the eves with which the chloride ions can move through the concrete that is if this pore structure here was very dense very tortuous, very fine. Then the ease of movement of the chloride ions will be low, it will be difficult for chloride ions to move in a structure which is very fine very long winded tortuous and so on. Compare to a structure which is open, large and so on and this is or this pore structure is related to the kind of factors given here; water cement ratio, the cement type, the cement content and so on. It is also the level of saturation that could be critical as I have said before there is no ionic diffusion expected in dry concrete.

So, depending on the water cement ratio the cement content and the cement type we will have different pore structures which will be formed as represented here. And if the pore structures are different, the ease with which the chlorides can move into concrete will be different. And that is why our pore in specifications tries to put down numbers on what is the maximum permissible water cement ratio or the minimum amount of cement content and so on. When we try to ensure durability of concrete indirectly what we are saying is that we are trying to control the diffusion coefficient of the concrete.

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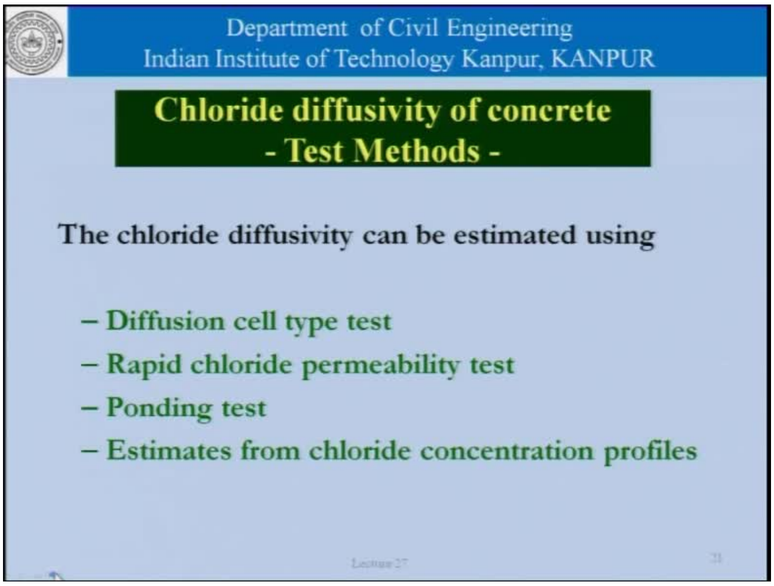

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Chloride diffusivity of concrete - Test Methods -

The chloride diffusivity can be estimated using

- Diffusion cell type test
- Rapid chloride permeability test
- Ponding test
- Estimates from chloride concentration profiles

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In practice the chloride diffusivity can be estimated using diffusion cell type test, it can be done through a rapid chloride permeability test, it could be done through a ponding test or it could be a estimated from the chloride concentration profiles of different concretes.

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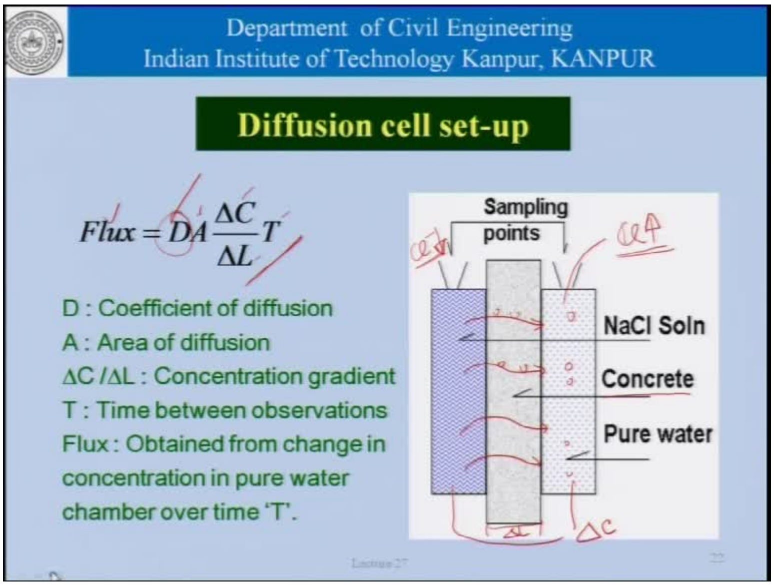

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Diffusion cell set-up

$$Flux = DA\frac{\Delta C}{\Delta L}T$$

D : Coefficient of diffusion
A : Area of diffusion
ΔC /ΔL : Concentration gradient
T : Time between observations
Flux : Obtained from change in concentration in pure water chamber over time 'T'.

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We will take a look at them one by one. let us talk at the diffusion self set up. This is a classical diffusion cell where we have a concrete block one side is N a C l, the other side is pure water it could be calcium hydroxide containing no chlorides to begin with. And over a passage of time what we except is chloride ions to move through the concrete and start appearing here.

And if we are able to sample the water here over a period of time, what we will find is that the chloride ion concentration will rise. And as far as mass balance is concerned s if this chloride concentration raises the kind of chloride concentration here will fall except that in most cases concentration here is so high that the decrease here is rather small. Also we must understand that when the chlorides move through the concrete, some of the chlorides are also in transient. And they are occurring within the concrete and they have to be accounted for if you really want to do the mass balance.

This is the flux that is the amount of chlorides or the chloride ions that are moving in a certain time. So, there is an area which is involved as a diffusion coefficient involved there is a concentration gradient in terms of delta C by delta L where delta L is this length here and delta C is the differential concentration of chloride ions at 2 ends, t is the time between observations. And flux is obtained from the change in the concentration in pure water in the pure water chamber over time the time t.

So, once we understand all these numbers then we know the flux as the how much chloride has moved in. We know the area of the concrete specimens that we have, we know delta C we know, we know delta L, we know t and we can actually estimate D. So, this is one method of estimating the diffusion coefficient directly, it is a very tedious process, it could take several months depending on what is the size of the specimen that we take what is the nature of the concrete that we take and so on and so forth.

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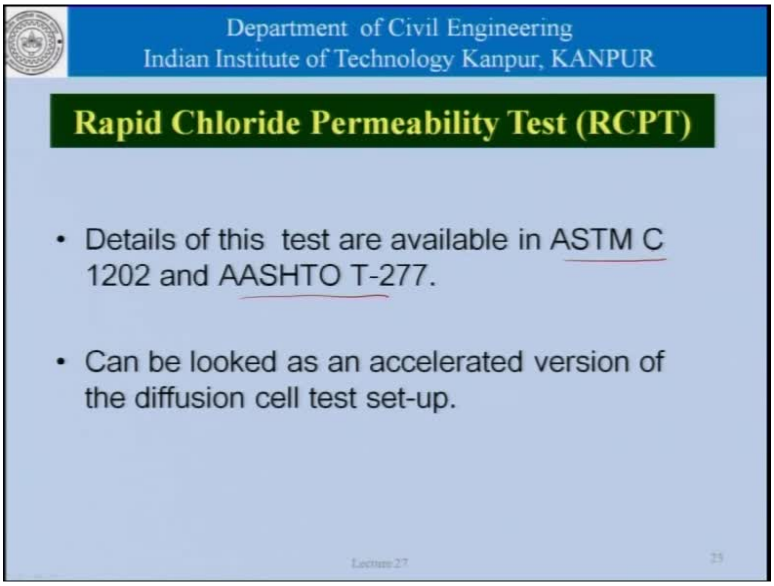

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Rapid Chloride Permeability Test (RCPT)

- Details of this test are available in ASTM C 1202 and AASHTO T-277.
- Can be looked as an accelerated version of the diffusion cell test set-up.

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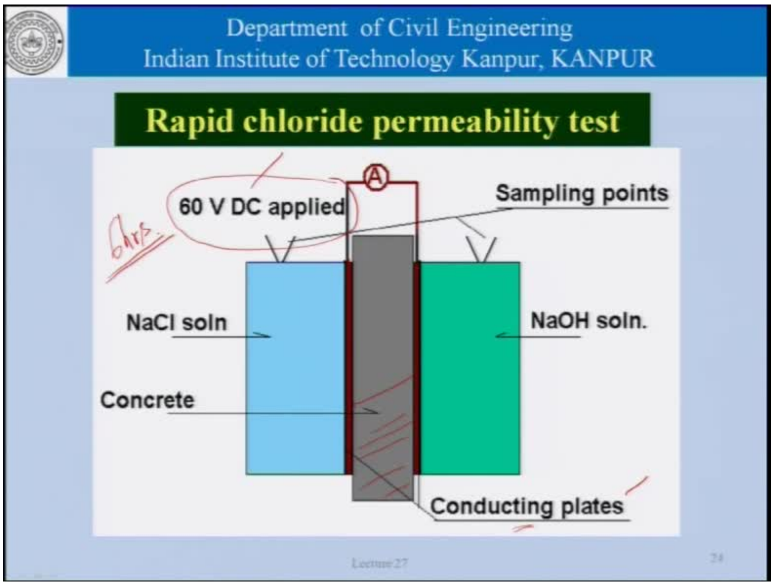

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Rapid chloride permeability test

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Coming to the next test which is the rapid chloride permeability test the RCPT, the details of this test are available in ASTMC 1 2 0 2 and AASHTO T 2 7 7. I am leaving out the exact test methods given in these 2 documents and what we can look at we can look at this test as an accelerated version of the diffusion cell setup. The RCPT test looks something like this where we have N a C l solution and an N a O H solution on 2 sides of a concrete disk. And on both sides of the concrete test we have these conducting plates and wed apply 60 volts of D C across these 2o conducting plates.

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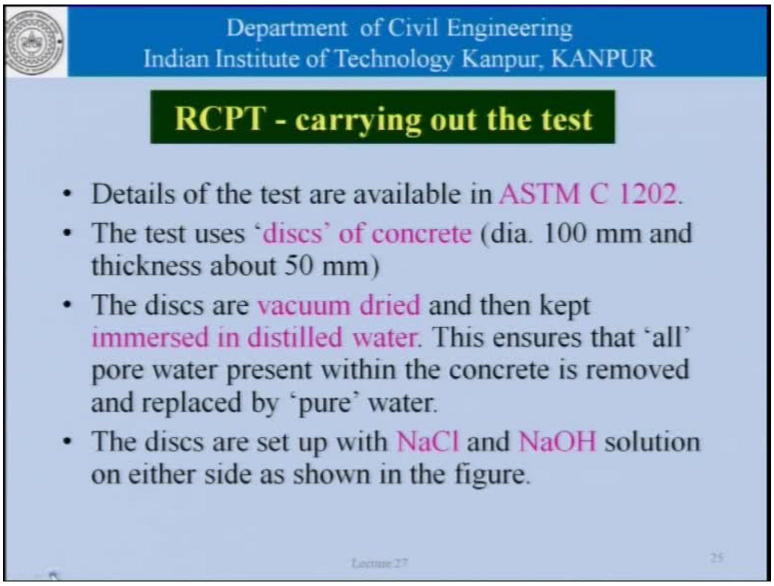

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RCPT - carrying out the test

- Details of the test are available in ASTM C 1202.
- The test uses 'discs' of concrete (dia. 100 mm and thickness about 50 mm)
- The discs are vacuum dried and then kept immersed in distilled water. This ensures that 'all' pore water present within the concrete is removed and replaced by 'pure' water.
- The discs are set up with NaCl and NaOH solution on either side as shown in the figure.

So, it is basically the diffusion sell setup with the addition of the conducting plates and the application of 60 volts of D C for a period of 6 powers and what we do as I said the details are available in STMC 1 2 0 2. The disk that we use of concrete in this case is known to be a 100 m m diameter and has a thickness of about 50 m m the disk need to be vacuum dried and then kept immerged in distill water.

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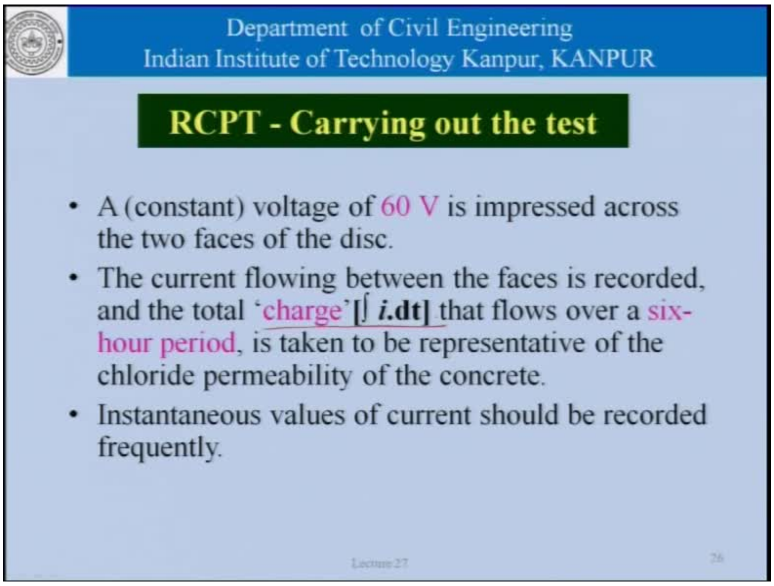

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RCPT - Carrying out the test

- A (constant) voltage of 60 V is impressed across the two faces of the disc.
- The current flowing between the faces is recorded, and the total 'charge' $[\int i.dt]$ that flows over a six-hour period, is taken to be representative of the chloride permeability of the concrete.
- Instantaneous values of current should be recorded frequently.

This ensures that all pour water present within the concrete is removed and is replaced by pure water. The disc are set up with N a C l and N a O H on either side as shown and 60 volt are applied across the 2 phases of discs. And the current flowing between the phases is recorded and the total charge that is i and t that flows over a 6 hour period is taken to be representative of the chloride permeability of the concrete.

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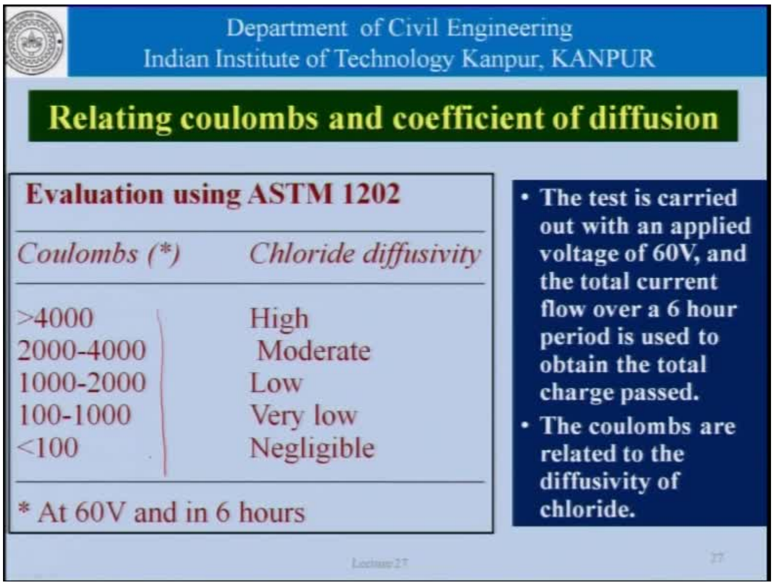

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Relating coulombs and coefficient of diffusion

Evaluation using ASTM 1202

Coulombs (*)	*Chloride diffusivity*
>4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very low
<100	Negligible

* At 60V and in 6 hours

- **The test is carried out with an applied voltage of 60V, and the total current flow over a 6 hour period is used to obtain the total charge passed.**
- **The coulombs are related to the diffusivity of chloride.**

Lecture 27

Instantaneous values of current need to be recorded frequently and what we get at the end is something like this; that we have with us a certain amount of charge that has passed for a particular disc a disc of 100 m m diameter 50 m m thickness across which 60 volts was applied for a period of 6 hours. And the current that is going through is recorded frequently and it is integrated over time to give the charge passed that is in coulombs. And what we have is a certain number of coulombs and the interpretation is to be made in terms of how much of coulombs do we get. And ASTM 1 2 0 2 suggests that the chloride diffusivity will be taken as high moderate low, very low or negligible depending on what the coulomb values are.

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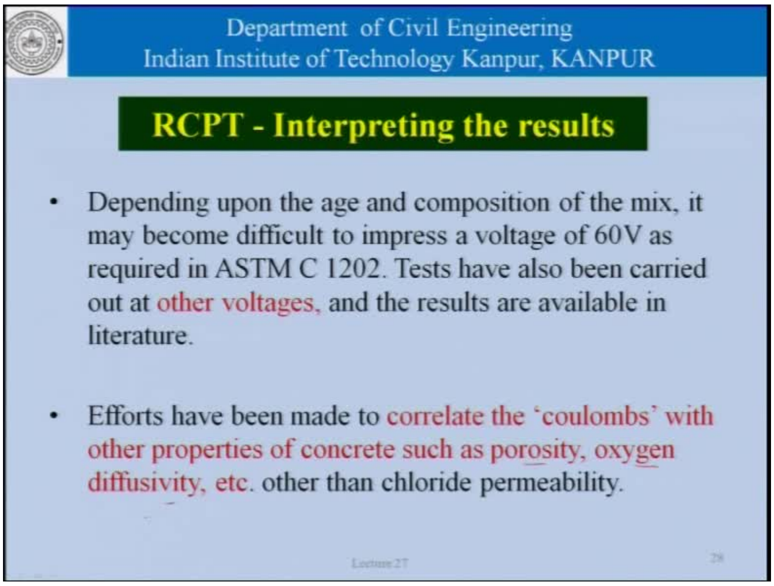

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RCPT - Interpreting the results

- Depending upon the age and composition of the mix, it may become difficult to impress a voltage of 60V as required in ASTM C 1202. Tests have also been carried out at other voltages, and the results are available in literature.
- Efforts have been made to correlate the 'coulombs' with other properties of concrete such as porosity, oxygen diffusivity, etc. other than chloride permeability.

So, basically what the test has done is that the chloride diffusivity or the chloride permeability has been taken as related to the passage of current through the concrete of course. As far as interpretation of these results is concerned depending upon the age and composition of the mix it may become difficult to impress 60 volts of electricity as required in ASTM 1 2 0 2. And there are papers in literature where test have been carried out at other voltages and the results need to be referred to. Effort has also been made in literature to correlate the coulombs with other properties of concrete such as porosity or oxygen diffusivity strength and so on.

Because at the end of it what we are trying to measure is related to the porosity, it is not porosity itself porosity itself is measured in terms of volume of pores in a given volume of concrete or in a given mass of concrete, but the diffusivity is also related to the porosity. So, we are making an indirect assessment of porosity through this process and we are trying to determine that using the passage of current. And those coulombs will have some kind of an indirect relationship with the other parameters such as strength, oxygen, diffusivity, porosity and so on. And efforts have been made in literature to relate these parameters also.

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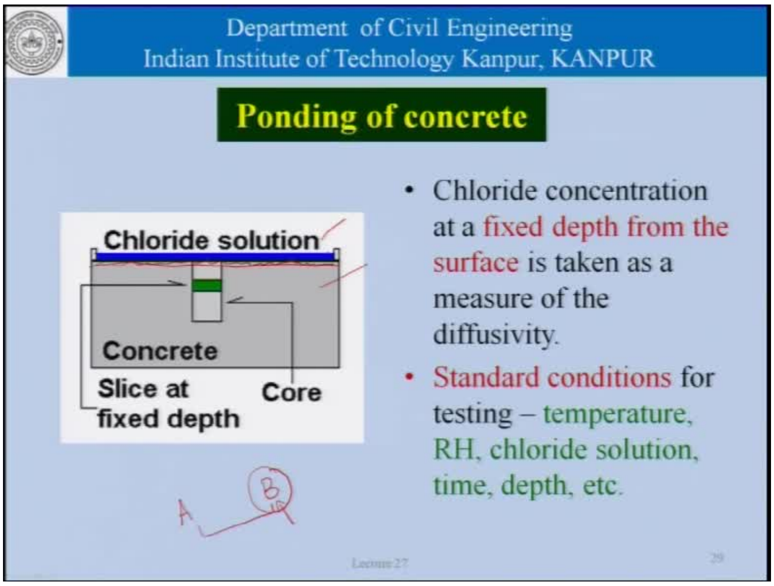

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Ponding of concrete

- Chloride concentration at a fixed depth from the surface is taken as a measure of the diffusivity.
- Standard conditions for testing – temperature, RH, chloride solution, time, depth, etc.

Coming to the third method that may be used to estimate the chloride permeability we have ponding of concrete in this case or concrete specimen is prepared. And a chloride solution is just allowed to stand on the concrete surface and after a passage of time the chloride concentration at a fixed depth from the surface is taken as a measure of the diffusivity. So, we take a slice as shown here at a certain depth from the concrete surface we need to take a core, first take a slice at a certain depth and find out the chloride concentration. In that concrete when we compare the chloride concentration at the same location for a concrete a with that in a concrete b if the chloride concentration and concrete be is higher than it stands to reason that that concrete b has a higher chloride diffusivity, what this method does is not give you a quantitative number in terms of the diffusion coefficient.

But helps us rank different concretes in the order of chloride diffusivity this method can also be used to study the effectiveness of a coating. If there is a system or some method by which we want to coat the concrete here and say this coating is such that it will prevent the ingress of chlorides into concrete. So, this kind of a method will become very handy in determining how effective is the coating which has been applied in the surface?

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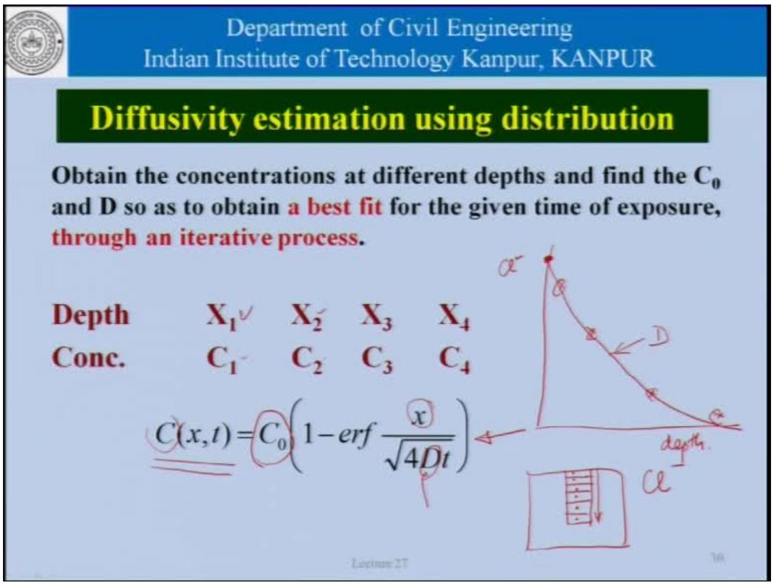

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Diffusivity estimation using distribution

Obtain the concentrations at different depths and find the C_0 and D so as to obtain a best fit for the given time of exposure, through an iterative process.

Depth	X_1	X_2	X_3	X_4
Conc.	C_1	C_2	C_3	C_4

$$C(x,t)=C_0\left(1-erf\frac{x}{\sqrt{4Dt}}\right)$$

Coming to another method where diffusivity can be estimated that is using the chloride profiles that are distributions. We need to obtain the concentration at different depths and find the C 0 and D. So as to obtain the best fit for a given time of exposure through an iterative process, what this method really says is that we know or we somehow are able to obtain the different chloride concentrations at different depth from a concrete structure or a concrete specimen whatever we are dealing with. If we have a concrete specimen like this which has been exposed to chloride environment for a certain amount of time and so on and after that we take a sample out of this make a core make slices and determine the chloride concentration at different depths.

So, as we come deeper into the concrete the concentration will go down. And once we have those numbers and we plot chloride concentration versus depth. And we assume that the concentration profile should follow this equation, that is C of x t should be C 0 times 1 minus error function x upon 4 root of 4 D t. Then for the different excess we know different c’s and that is what indicated here at x 1 it is c one at x 2 it is c 2 and so on. And since we have several of these points through an iterative process a numerical process we can try to estimate the values of C 0 and b. So, we can get the theoretical value of the surface chloride and concentration and also the diffusion coefficient for this concrete based on the values that we had.

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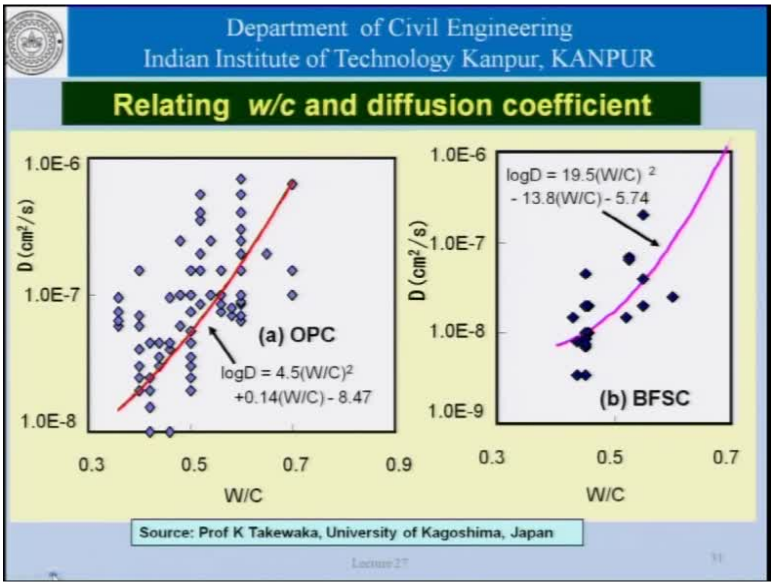

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Relating *w/c* and diffusion coefficient

Source: Prof K Takewaka, University of Kagoshima, Japan

Lecture 27

Efforts have been made in literature to relate water cement ratio which is known to be the most important parameter as far as porosity is concerned or for that matter the cement type and we will find that if we collate the information about the diffusion coefficient from different sources we will get a scatter which is of the nature shown here. It is not a very promising site it does not occur very well to student who sees that there is virtually no relationship between the water cement ratio and the diffusion coefficient. But then this is only to start what we must understand is that this data has been taken from diverse sources experiments carried out under diverse conditions and so on. And we need to work a lot more and get better information about diffusion coefficient and its relationship with parameters such as the water cement ratio or the cement type and so on.

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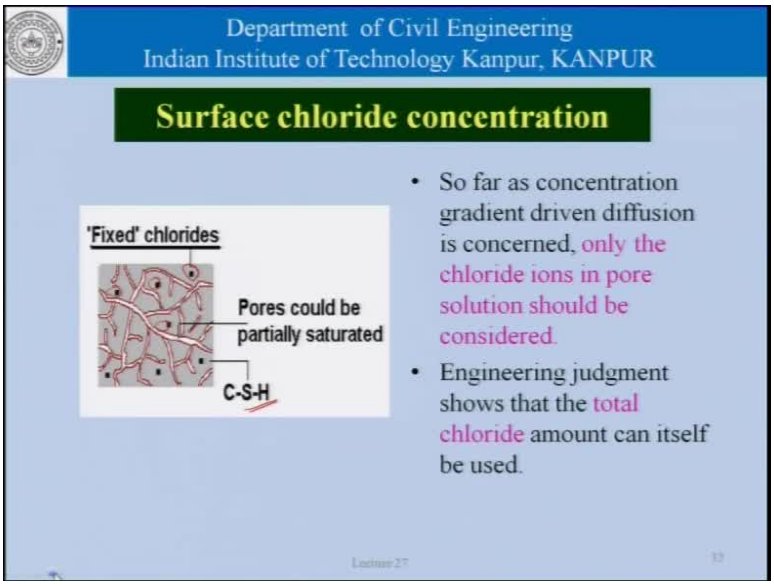

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Surface chloride concentration

- So far as concentration gradient driven diffusion is concerned, only the chloride ions in pore solution should be considered.
- Engineering judgment shows that the total chloride amount can itself be used.

Now, let us come to the surface chloride concentration and try to understand that part a little bit better. So far as concentration gradient diffusion is concerned only the chloride in the pore solution need to be considered, because it is only the chlorides which are present in the pore solution that move because of concentration gradients. Engineering judgment shows that the total amount of chlorides in the cement paste or in a concrete is much different is higher than that is physically possible. If we consider the condition that the pore space and the pore solution have to be in equilibrium with the chloride solution outside amounts of chloride that we have in concrete is much higher. And therefore, we are forced to assume that a lot of chlorides are actually sitting crapped partially or fully in the hydration products that is in the C S H gel. And now once we understand or assume that the chlorides can be present in different forms fine we will say that the total chlorides is what we are trying to work with and what should be the number that we need use in the formulation of a problem.

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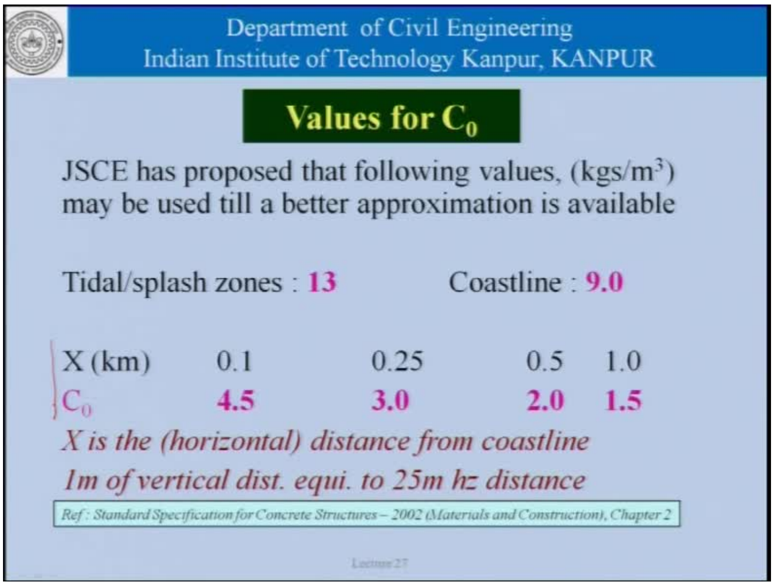

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Values for C_0

JSCE has proposed that following values, (kgs/m^3) may be used till a better approximation is available

Tidal/splash zones : **13**   Coastline : **9.0**

X (km)	0.1	0.25	0.5	1.0
C_0	**4.5**	**3.0**	**2.0**	**1.5**

X is the (horizontal) distance from coastline

1m of vertical dist. equi. to 25m hz distance

Ref : Standard Specification for Concrete Structures – 2002 (Materials and Construction), Chapter 2

The Japan society of civil engineers has suggested the following values in terms of kgs per cubic meter that may be used till such time as a better approximation becomes available. In tidal splash zones number may be taken as 13 in coastlines it can be taken as 9 and depending on what is the distance from the sea the number can be taken to be different as far as vertical as far as the height of the structure is concerned. It also suggests that a meter of vertical distance may be taken to be equivalent of 25 meters of horizontal distance. These numbers are engineering approximations based on observations and are now being worked out for greater accuracy. And the people across the world are trying to understand chloride concentrations and chloride penetration in concrete better and apply it for engineering decisions.

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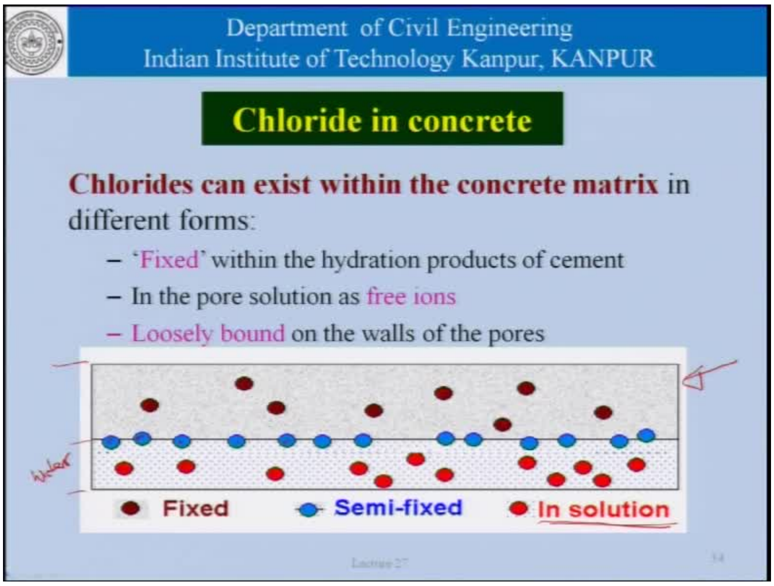

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Chloride in concrete

Chlorides can exist within the concrete matrix in different forms:

- 'Fixed' within the hydration products of cement
- In the pore solution as free ions
- Loosely bound on the walls of the pores

Lecture 27

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As far as the concrete now let us try to look at the different states in which the chlorides can exist within the concrete. One is fixed within the hydration products of the cement this is very likely to happen in cases when chlorides are present as part of the constituent materials at that time the hydration products are only being formed. And if there are chlorides those hydration products will be formed along with the chlorides in other words the chlorides will become a part of the hydration products. Then of course, there are chlorides in the pore solutions and they are basically free chlorides. And finally, there are loosely bound chlorides on the walls of the pores and this is what is diagrammatically represented here, where we have a pore and this is a large pore which is partially saturated with water.

So, we can say that this much is water and this is let us say sir and within the pore solution we have these chloride ions which are in solution and therefore, they are highly mobile. These are the chloride ions which are trapped chemically in the hydration products and these blue ones are chloride ions which are loosely bound or they are adhering to or they absorbed on the surface of the pore walls. And they can be called into solution or they can move into solution and go back to the absorbed state depending on whatever is going on inside the pore structure.

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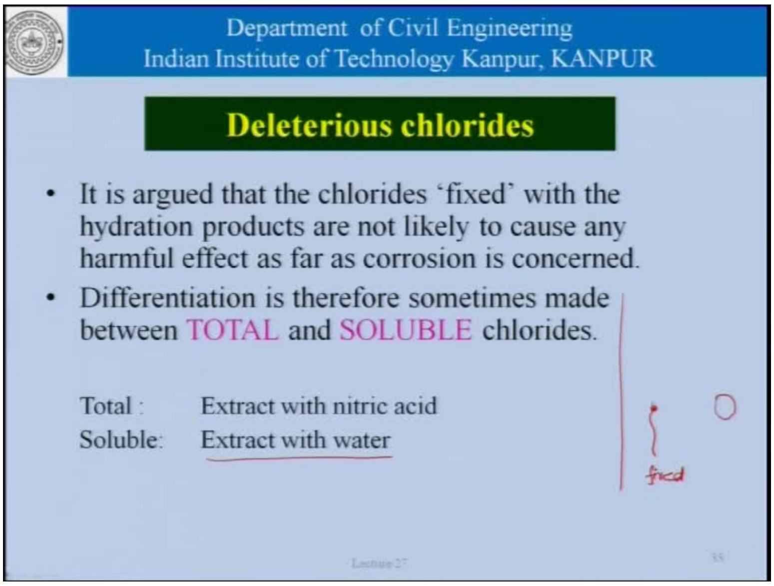

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Deleterious chlorides

- It is argued that the chlorides 'fixed' with the hydration products are not likely to cause any harmful effect as far as corrosion is concerned.
- Differentiation is therefore sometimes made between TOTAL and SOLUBLE chlorides.

Total : Extract with nitric acid
Soluble: Extract with water

As now, now the question is which of these chloride ions are really harmful from the point of view of reinforcement corrosion as first deleterious science are concerned it is argued that the chlorides fixed in the hydration products are not likely to cause any harmful effect as far as corrosion is concerned. The argument is as follows; that if we have a surface like this and a reinforcing bar here chlorides which are fixed in a location something here like here which is never which is not very close to the reinforcing bar these chlorides so long as they are fixed in the hydration products have no bearing on whether the bar will corrode or not. Therefore a differentiation is sometimes made in terms of total chlorides and soluble chlorides.

Total chlorides in concrete are determined by extracting the chlorides with something like nitric acid we take a powder of concrete boil it with nitric acid and all the chlorides which are there come out designs whether they are in hydration products whether in pore solution or adhering to the surface or water. In the case of soluble chlorides we do not want chlorides which are bound in hydration products to appear or come into solution. And therefore, the extraction is with water there methods to do it they are standardized in terms of for how long the water should be allowed to as to how long the process should be allowed to go on whether it there should be stirring boiling and so on. But the moral of the story is that at the end of it, it is difficult but the bottom line still remains that the total chlorides are the most important chlorides. And as far as engineering judgment is concerned they are the only parameter that can be used in terms of comparing with the critical chloride concentration.

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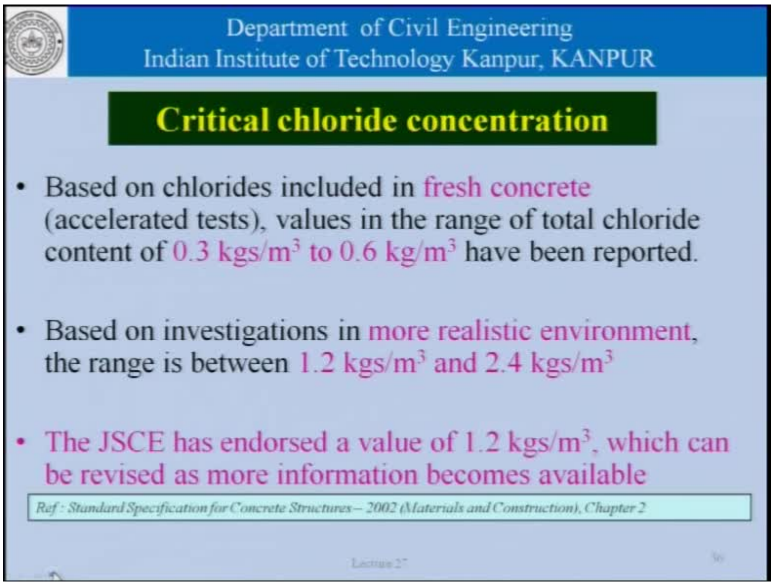

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Critical chloride concentration

- Based on chlorides included in fresh concrete (accelerated tests), values in the range of total chloride content of 0.3 kgs/m^3 to 0.6 kg/m^3 have been reported.
- Based on investigations in more realistic environment, the range is between 1.2 kgs/m^3 and 2.4 kgs/m^3
- The JSCE has endorsed a value of 1.2 kgs/m^3, which can be revised as more information becomes available

Ref : Standard Specification for Concrete Structures – 2002 (Materials and Construction), Chapter 2

Now, coming to another parameter which is the critical chloride concentration that causes the onset of reinforcement corrosion based on tests including fresh concrete accelerated test and so on values in the range of total chloride content of 0.3 to point 6 kgs per cubic meter have been reported. Investigations based on more realistic environment have suggested values in the neighborhood of 1.2 to 1 have suggested values between 1.2 and 2.4 k gs per cubic meter. And the JSCE has endorsed the value of 1.2 kgs per cubic meter in the hope that the number will be revised hence more information becomes available.

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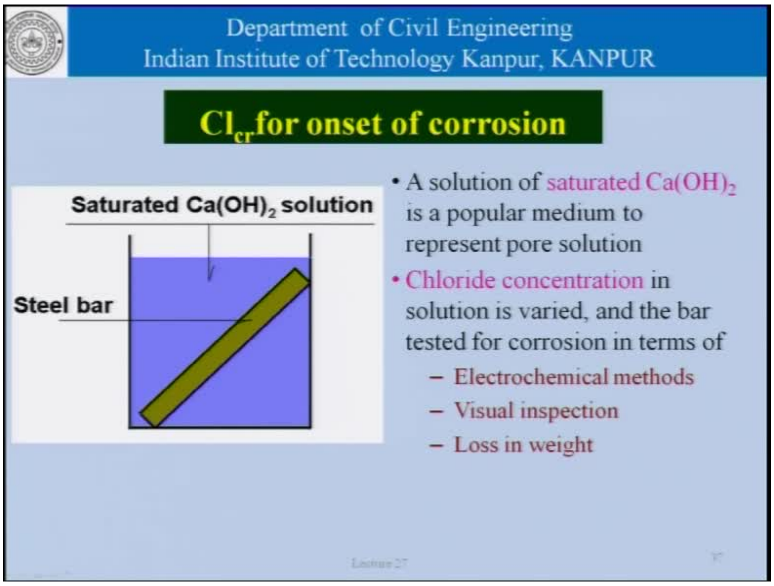

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Cl_{cr} for onset of corrosion

- A solution of saturated $Ca(OH)_2$ is a popular medium to represent pore solution
- Chloride concentration in solution is varied, and the bar tested for corrosion in terms of
  - Electrochemical methods
  - Visual inspection
  - Loss in weight

Now, how do we determine this value? We determine this value by test such as immersing a steel bar in a saturated calcium hydroxide saturated solution which is a popular medium to represent pore solution and vary amount of chlorides in that saturated solution and test the bar at the end of the test using electrochemical methods visual inspection or loss in weight and so on.

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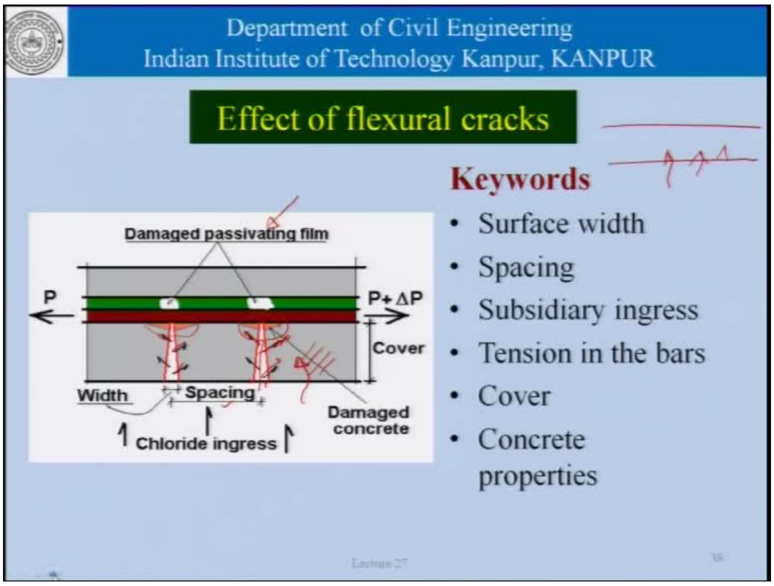

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Effect of flexural cracks

Keywords

- Surface width
- Spacing
- Subsidiary ingress
- Tension in the bars
- Cover
- Concrete properties

We must also try to look at the effect of flexural cracks when we have a concrete beam we also have sometimes some flexural cracks in the beam. And these flexural cracks promote faster chloride penetration into concrete, and whether or how this flexural cracks effect the chloride penetration is something which an engineer should be aware of and this, what we are looking at. We have a certain width of flexural cracks; we have a certain spacing of flexural cracks. This causes local damage around the reinforcing bar and it is likely to damage the passivating film again in the neighborhood of the cracks. So, the keywords in this kind of a study would be surface width that is the width of the cracks at the surface the spacing of the cracks subsidiary ingress. Subsidiary ingress means this is what primary ingress is because that is what is being controlled by the water cement ratio and the strength of concrete the porosity of concrete here.

But as far as penetration of chlorides in these parts is concerned is not occurring through the main body concrete it is first going through the crack and then from here onwards certain amount of penetration is taking place. Except that this cracks spacing in most cases is quite small. Most of our codes do not allow cracks higher than say 0.2 m m or 0.3 m m and that 2 if there are aggregates within the crack, the crack does not look all that open as I shown here. And therefore, this penetration from the cracks is indeed, what can be called subsidiary ingress. The amount of corrosion that takes place on account of all this is also related to the extent of tension in the bars that is, what is the tensile stress in the bars. So one of the methods of controlling the crack width and therefore, subsidiary ingress, and therefore chloride levels at the reinforcement location. And therefore, finally, the reinforcement corrosion is to control the allowable amount of tensile stress in the reinforcement. And of course, the cover thickness besides concrete properties that is water cement ratio strength and so on and so forth.

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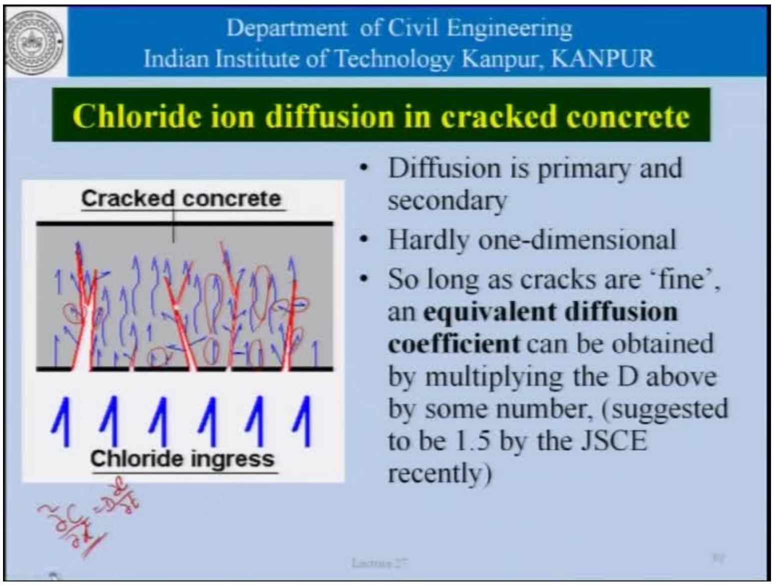

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Chloride ion diffusion in cracked concrete

- Diffusion is primary and secondary
- Hardly one-dimensional
- So long as cracks are 'fine', an **equivalent diffusion coefficient** can be obtained by multiplying the D above by some number, (suggested to be 1.5 by the JSCE recently)

$\frac{\partial^2 C}{\partial x^2} = D\frac{\partial c}{\partial t}$

Now, if we look at chloride ions diffusion in cracked concrete this is what really is happening. So, parts of this diffusion process here is through the main concrete part of this diffusion here is not main diffusion through the main concrete coming through the cracks and what we have is hardly a one dimensional diffusion. Normally we assume chloride penetration and concrete to be a one dimensional diffusion process. And that is why if you recall the, we saw the equation which look like del 2 c by del x square is equal to D times del c by del t. So, this del 2 c by del x square basically assumes a one dimensional definition process, which is hardly the case, if we look at a system like this where the diffusion is definitely not a one dimensional process. But then again it is a model so long as the cracks are fine they are very small in width an equivalent diffusion coefficient can be calculated by multiplying the diffusion coefficient D by some method may be 1.5 or 10.3 and so on.

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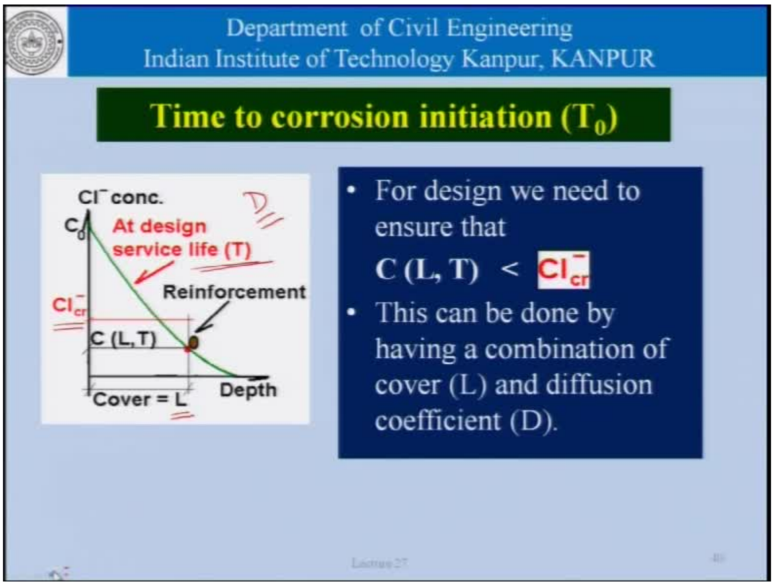

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Time to corrosion initiation (T_0)

- For design we need to ensure that

  $C(L, T) < Cl^-_{cr}$
- This can be done by having a combination of cover (L) and diffusion coefficient (D).

And finally, we want to find out the time to corrosion which can be the time to corrosion which will be determined by a graph like this which says that well at the end of service life t. The chloride concentration at the location of reinforcing bar that is at a depth l from the surface for a given concrete which has a diffusion coefficient D will reach either chloride concentration itself or just a fraction below that. And as far as design is concerned what we need to ensure is that the chloride concentration at l. At the end of the surface life t should be less than the c l c r that is the critical chloride concentration. And this can be done by having a combination of cover l and the diffusion coefficient D, either we can increase the cover or we can reduce the diffusion coefficient or a combination of these 2 methods so long as we do that we will be able to have a durable structure.

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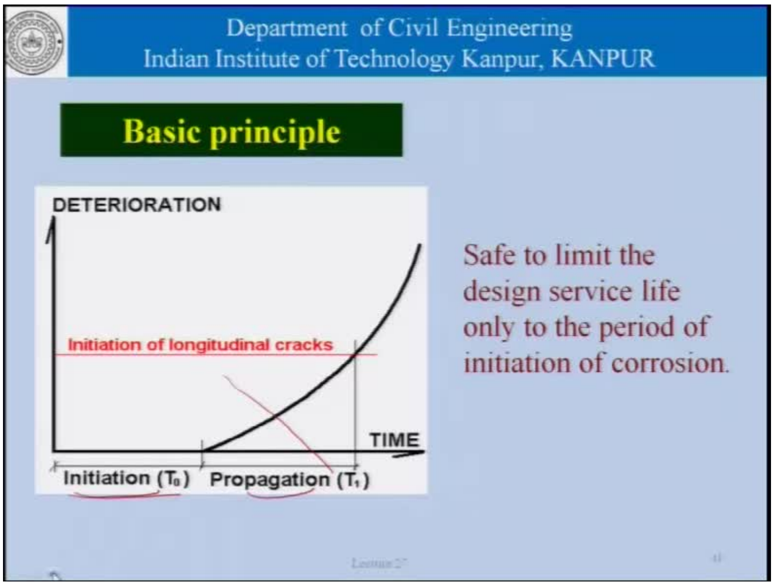

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Basic principle

Safe to limit the design service life only to the period of initiation of corrosion.

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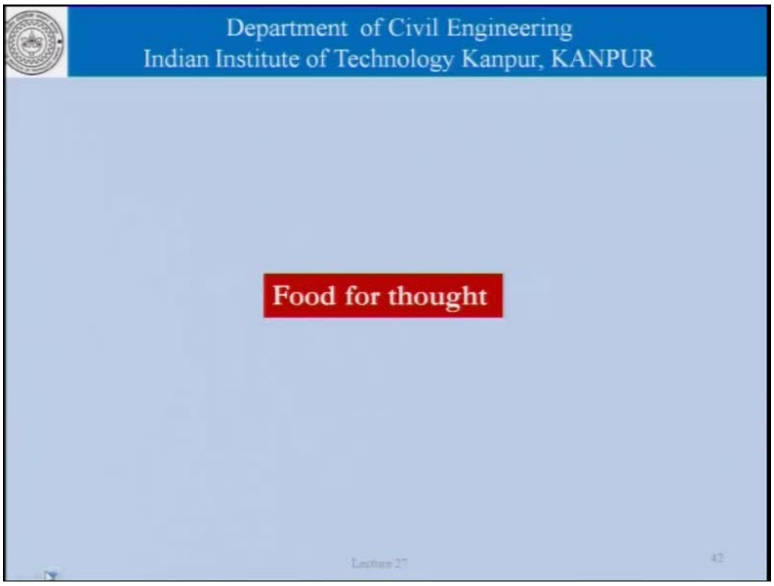

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Food for thought

So, this is what the basic principle was that there is an initiation time and propagation time. And if we do not want to bother about the propagation time, because of engineering considerations and we want to confine ourselves to the initiation time. Then we need to follow. Then we need to have the strategy which we just discovered or we need to follow the strategy that we just formulated that is at the end service life the chloride concentration at the location of the reinforcing bar should be lower than the critical chloride concentration.

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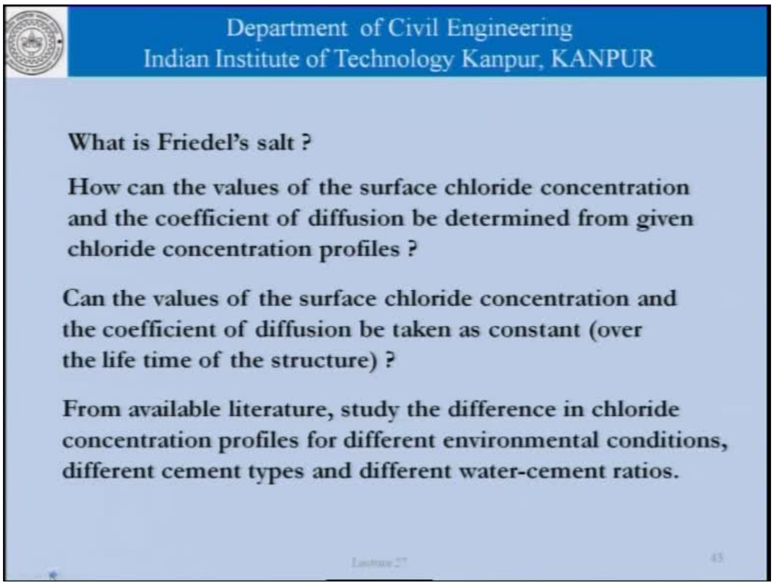

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What is Friedel's salt ?

How can the values of the surface chloride concentration and the coefficient of diffusion be determined from given chloride concentration profiles ?

Can the values of the surface chloride concentration and the coefficient of diffusion be taken as constant (over the life time of the structure) ?

From available literature, study the difference in chloride concentration profiles for different environmental conditions, different cement types and different water-cement ratios.

Now, before we close the discussion today, I would like to leave some questions, what is Friedel’s law? We talked in terms of chlorides being fixed in hydration products and that should give you and that should give you a hint as to what is Friedel’s salt. The second question which I would like to leave for you is how can the values of service, how can the values of the surface chloride concentration and the coefficient of diffusion be determined from the chloride concentration profiles in the discussion. Today, we just said that given a concentration profile with a certain number of points we can do it in an iterative manner. Please try to see how actually that iteration process will work.

Can the values of the surface chloride concentration and the coefficient of diffusion be taken as constant they are taken as constant s they may be taken as constant that is also another s. But what are the implications of doing so is it realistic is it not realistic and so on. From available literature try to study the difference in the chloride concentration profiles for different environmental conditions, different cement types and different water cement ratios. And you will get the kind of results that I showed you in one of the picture they will give you information about chloride concentration profiles from different kinds of environments. If we take a structure or a sample from a highway which has been exposed to 10 cycles of deicing salt every year and the sample has been drawn after 10 years.

Now, chloride concentration profile there would be quite different from a marine structure where the sample or the core has been taken from the submerged part of the structure or the tidal zone or the splash zone or a structure which is away from the coastline. The distance to the coastline may be 500 meters may be 100 meters and there if you try to take the concentration gradient or the concentration variation of chlorides within concrete. These are the kinds of thing that we need to study and assimilate bring bring them together on a common platform. And then try to figure out what really is happening, as far as chloride penetration in concrete is concerned.

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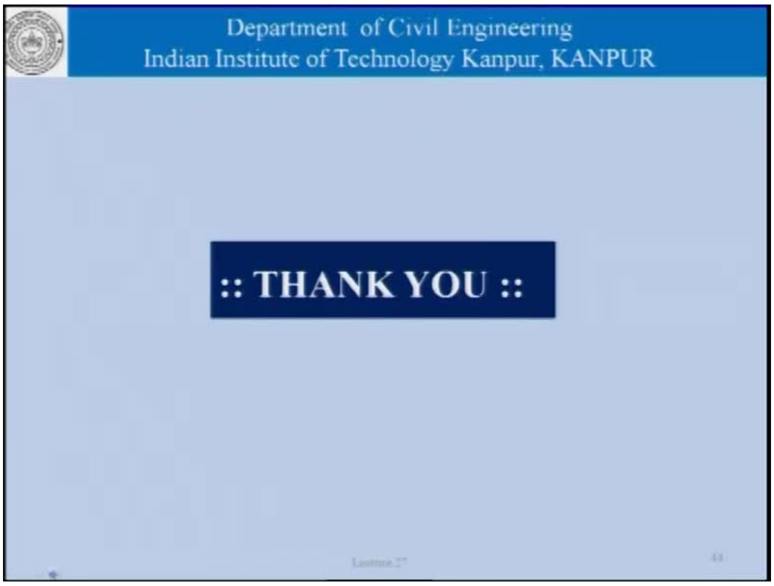

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:: THANK YOU ::

With that let us close the discussion. Thank you.