Concrete Technology
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Lecture - 33
Durability of Concrete: Carbonation & Chloride Affect

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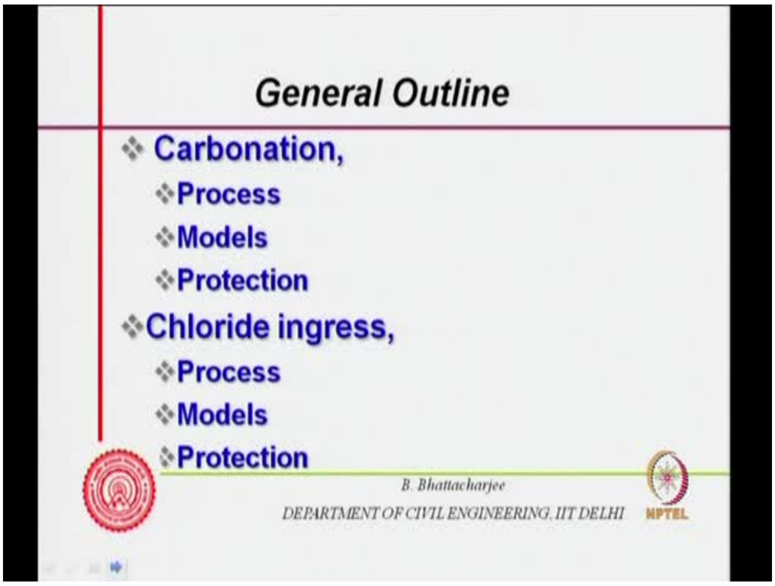

General Outline

- Carbonation,
  - Process
  - Models
  - Protection
- Chloride ingress,
  - Process
  - Models
  - Protection

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Welcome to module 8 lecture 3, in the last lecture you know we just started. I mean we just concluded when we are concluding we talked about the depassive version of rebar, and we just mention about the service life of simplest model for service life of concrete. In our reinforced concrete in the context of rebar corrosion, and we said that 2 phenomena which causes, de-passivation one of them is carbonation the other is chloride.

So, we look into carbonation process models protection chloride ingress process models and protection right. so,, just to recollect the service life with respect to corrosion we define like this in the last class we just mention this diagram same diagram we have looked into in the last class, where we said initially concrete is you know reinforce and reinforce concrete this provides protection to rebar, and with time this may get affected if it is exposed to chloride environment or if it is exposed to atmosphere. Where carbon dioxide from the atmosphere can come and reduce it p h, we also mentioned last class that p h of concrete.

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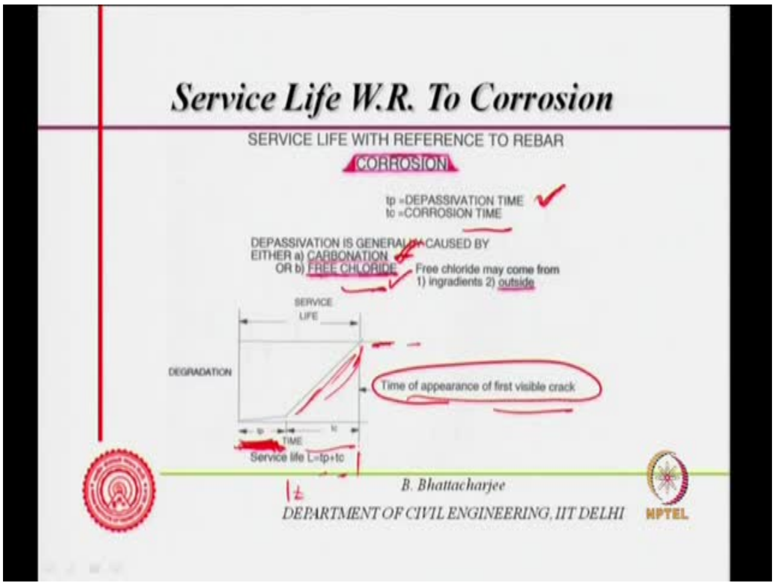

Service Life W.R. To Corrosion

SERVICE LIFE WITH REFERENCE TO REBAR

CORROSION

tp =DEPASSIVATION TIME
tc =CORROSION TIME

DEPASSIVATION IS GENERALLY CAUSED BY
EITHER a) CARBONATION
OR b) FREE CHLORIDE

Free chloride may come from
1) ingradients 2) outside

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At certain p h values high p h values actually the oxide forms passivates the steel in other words forms a layer over the steel bar, which essentially do not impair with the performance of the reinforcement bar and in fact it protects it and that is it passivation layer. so, it essentially oxide coating thin thick dense thin but, dense thin but, dense to which ah f e cannot go into the solution and rate of formation of such oxide is very slow and therefore, we do may not term this as active corrosion, so, this is passive condition now this passive condition broken down during this period of time, and that is what we call as de-passivation time. And this can occur either, because of carbonation or because of free chloride will define free chloride later on.

What is free chloride because there must because then, if it is not free chloride there must be something else bond chloride total chloride we will come to that later on. So, once the de-passivation is occurred that is the layer of oxide which is formed on top of the rebar at high p h level is destroyed at a p h value which is low, when p h tans out we low or sufficient chloride is come then corrosion process might start, and the time after which you have serviceable limit is reached. Which is actually time of appearance of first visible crack you know, the time at which the first visible crack is observed because corrosion process results in cracking, which you will see later on how it does so, when first visible crack is appeared that time we call it service life that is you know there is a limit of serviceability limit, when a first visible crack is appeared this time we call as corrosion time, and total service life is of the element is t p plus t c.

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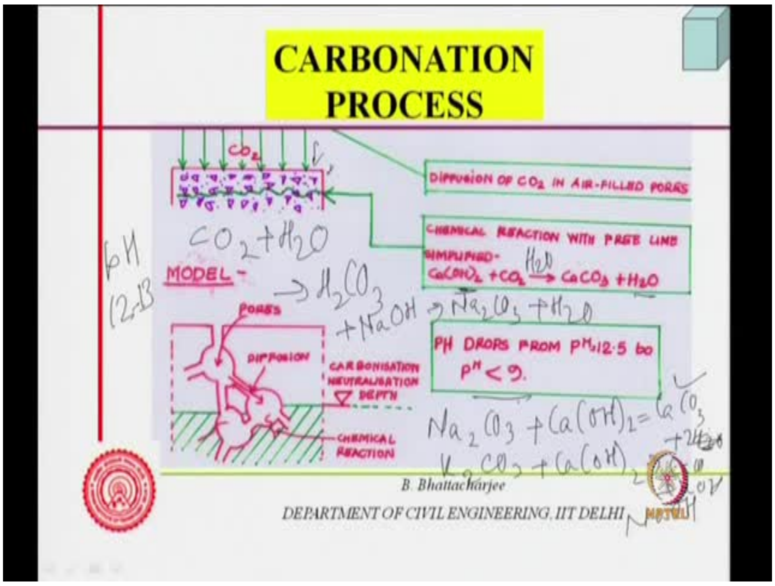

CARBONATION PROCESS

DIFFUSION OF CO_2 IN AIR-FILLED PORES

CHEMICAL REACTION WITH FREE LIME

SIMPLIFIED- $Ca(OH)_2 + CO_2 \xrightarrow{H_2O} CaCO_3 + H_2O$

PH DROPS FROM P^H 12.5 to $P^H < 9$.

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So, service life of the element is t p plus t c, today we will look largely into this phenomena how it get depassivated. First we will look at carbonation and then we will look at chloride, carbonation process if I look at it you see carbon dioxide from the atmosphere penetrates into concrete from the surface as shown here, and it can in presence of moisture it can form you know carbon dioxide plus water can form carbonic acid. And this carbonic acid actually can react with let us say sodium hydroxide to form sodium carbonate plus water. So, sodium hydroxide that is alkies present or potassium hydroxide there are present in the cement material cementitious material concrete system, and it can react forming sodium carbonate and water.

Now this sodium carbonate or potassium carbonate can react with calcium hydroxide in the cement forming calcium carbonate and again water and this also can form in this manner, you know it can form calcium carbonate and sorry sodium hydroxide calcium carbonate and sodium hydroxide this should be sodium hydroxide and this should be 2 sodium hydroxide.

Than this should be potassium hydroxide plus potassium hydroxide, in other words calcium carbonate is formed. And if we write it straight away simple reaction calcium hydroxide plus carbon dioxide in presence of water actually would form calcium carbonate and water. Now since calcium you know the calcium hydroxide or sodium hydroxide material is getting consumed in the process. Therefore, the p h of the concrete will reduce on to start with p h of the concrete is around 12 to 13 So, p h of concrete to start with is around 12 to 13. Which can get reduced down to even lower value than 9 , what we understand is, the intermediate step is sodium hydroxide and potassium hydroxide, calcium hydroxide provides a kind of reserve alkalinity one sodium hydroxide and potassium hydroxide you know they do not get consumed initially.

They are just the in between steps. So, sodium hydroxide and potassium hydroxide they react with carbonic acid which is formed because of the carbon dioxide coming from the atmosphere in presence of moisture this reaction can proceed and sodium carbonate can react with calcium hydroxide forming calcium carbonate. In this process calcium hydroxide which is a sparingly solvable salt we will get dissolved more into the pour solution you know part of it was solvable got dissolved and part is still as specifated. So, this specifated will dissolve more and more as it is consumed from the system to form calcium carbonate, a time will come when even the sodium hydroxide and potassium hydroxide will all get consumed because all alkaline material will get consumed by carbon dioxide.

Under such situation when all alkaline materials including sodium hydroxide and potassium hydroxide has been consumed by carbon dioxide from the atmosphere in presence of moisture forming carbonates p h l reduce down significantly and p h will be less than 9. And when it is less than 9 de-passivation can occur de-passivation can occur at certain lower p h s f e 3 or four, you know the oxides may not be stable and such situation at low p h and actually black rust which I talked about in the last class. May not be stable and now red rust formation may occur, which occupies a lot more volume then the volume that is occupied by black rust or the steel and thereby can cause expensive pressure we will come to that some time later on. Now therefore, you know what we see is there therefore, what we see is p h can get reduced down by consumption of the alkaline material, intermediate steps are not given here.

But, I just discussed then but, how do they how do the carbon dioxide penetrate, it penetrates through the pour in the system penetrates through the pour in the system and has it penetrates and it must moist pour you know the pour must be also moist they must be moisture here, if there is no in case in absence of moisture reaction will not proceed because it occurs in solution phase carbonic acid will not formed.

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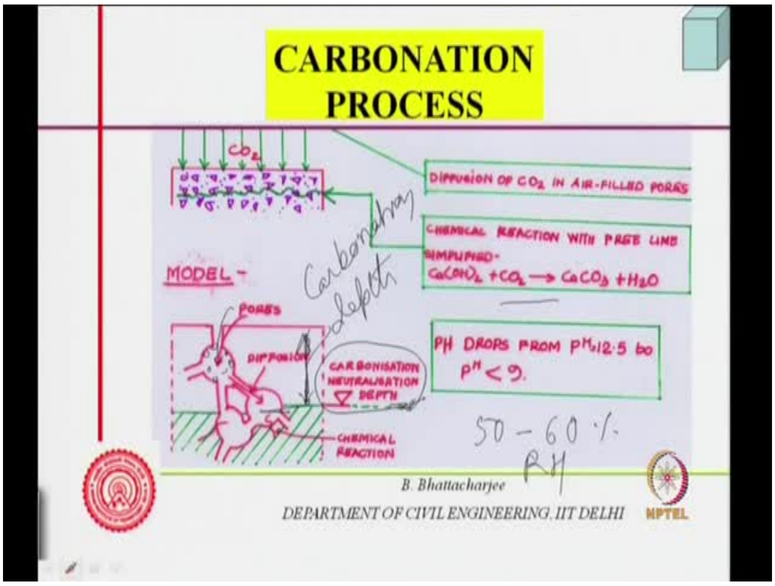

CARBONATION PROCESS

DIFFUSION OF CO_2 IN AIR-FILLED PORES

CHEMICAL REACTION WITH FREE LIME
SIMPLIFIED-
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

PH DROPS FROM P^H 12.5 to
$P^H < 9$.

50 – 60 %
RH

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So, carbon dioxide plus water is necessary and therefore, water has to be there so, it comes to the pours water r h as to be there and as all alkaline material up to this zone this finish we call it the carbonation you know carbonation reaction is occurred, and it is carbonation you know carbonation neutralization so, this is a neutralization depth and that is the carbonation depth. So, we call it carbonation depth. So, up to which carbonation depth up to which all the alkaline material has got neutralized by carbon dioxide coming from outside. So, again the pours are important moisture situation is important. Now even if it is a fully submerged concrete moisture will be available but, carbon dioxide concentration will be very low in dissolved water, and if it is a fully dry concrete reaction will not proceed or the carbon dioxide is there.

This occurs only at in certain validate humidity now if you remember when we talked about carbonation shrinkage around 55 percent humidity carbonation was carbonation shrinkage was maximum. In other words carbonation proceeds maximum at carbonation is maximum at 50 let us say 50 to 60 percent r h. So, 50 to 60 percent r h carbonation is maximum 100 percentage r h it reduces down if it is fully moist actually no carbonation will occur, to have carbonation or to pour carbonation to proceed, I need both oxygen or above carbon dioxide that is air is present in air you know above 3 percentage or so, depending upon the situation and of course, the moisture.

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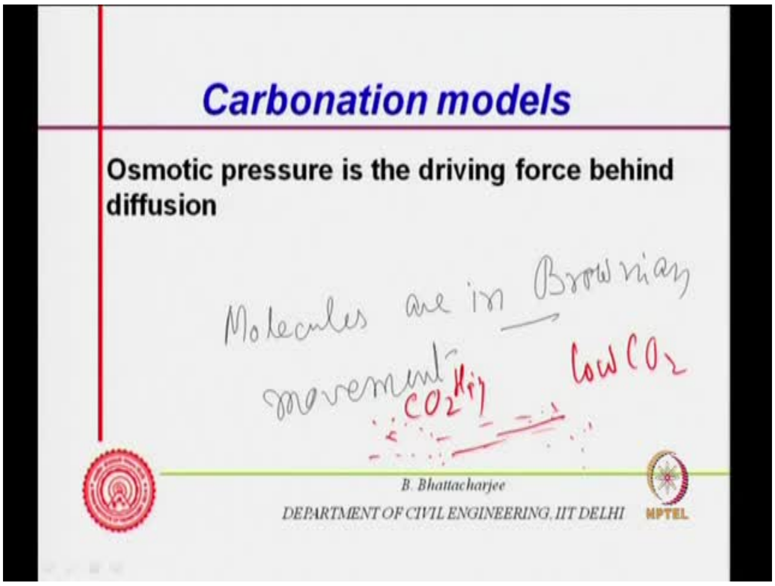

Carbonation models

Osmotic pressure is the driving force behind diffusion

Molecules are in Brownian movement

CO_2 High

Low CO_2

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That is the carbonation process thus actually the carbonation process thus the carbonation process, now we can you know what is your our interest is a carbonation depth, if I call x as a carbonation depth this is important for us carbonation depth is important for us right. And we do module this carbonation depth because when the carbonation depth reaches the reinforcement level that is the time deposition can occur so, therefore, service life with respect to carbonation will be defined when carbonation depth as reached the level or more All right, now how does carbon dioxide comes, see there is the concentration of the carbon dioxide concentration is low in the concrete outside it is more to start with concentration.

So, it is basically molecular diffusion molecules are in Brownian in movement. so, outside carbon dioxide molecule there will be Brownian movement and they collide with each other as long as concentration are same but, where concentration are less carbon dioxide molecule will not be able to interact with the same molecule.

So, what will happen they will penetrate inside they jump you know, so, you have if you have high carbon dioxide concentration here let us say high carbon dioxide concentration, and a less carbon dioxide concentration here low carbon dioxide low c o 2 high c o 2 high the molecule will move along this direction, and since they will not be able to inter you know inter into less molecule will be available for intersection here or collusion more molecule will tend to move, so, they will try to diffuse, so, this is molecular diffusion right.

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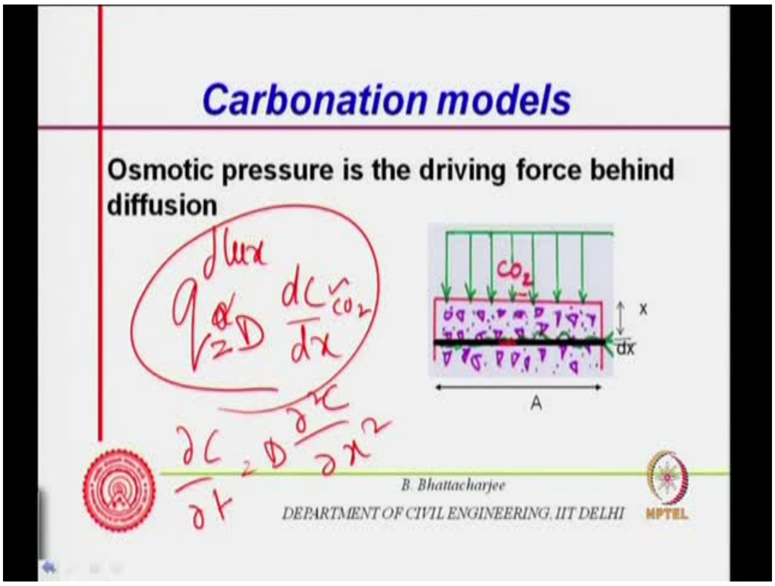

Carbonation models

Osmotic pressure is the driving force behind diffusion

flux

$$q \propto D \frac{dC_{CO_2}}{dx}$$

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

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Basically in liquid situation of course, it is a concentration difference so, concentration difference is a driving force we said in case of liquid last class we mentioned that there could be osmotic pressure difference and that could be the driving force behind such diffusion.

So, carbon dioxide from outside tend to diffuse inside and this diffusion process is governed by fixed diffusion law. So, fixed diffusion law says the flux diffusion flux you know could be in some unit k g per meter square per unit time diffusion flux is proportional to d c d x where c is a rate of you know c is a concentration gradient c is d c d x is a concentration gradient c is a concentration. So, in our case c is c o 2 by d x and the constant of proportionality. I will call it carbon dioxide diffusion coefficient, so, flux q is proportional to d d c concentration gradient of the carbon dioxide, carbon dioxide concentration here would be 0 here will be much higher there is a atmospheric carbon dioxide and therefore, it will this is the x d c d x you know, if I am considering a small length this is let us say carbon dioxide concentration is higher low there one can think in terms of you know its proportional to concentration gradient.

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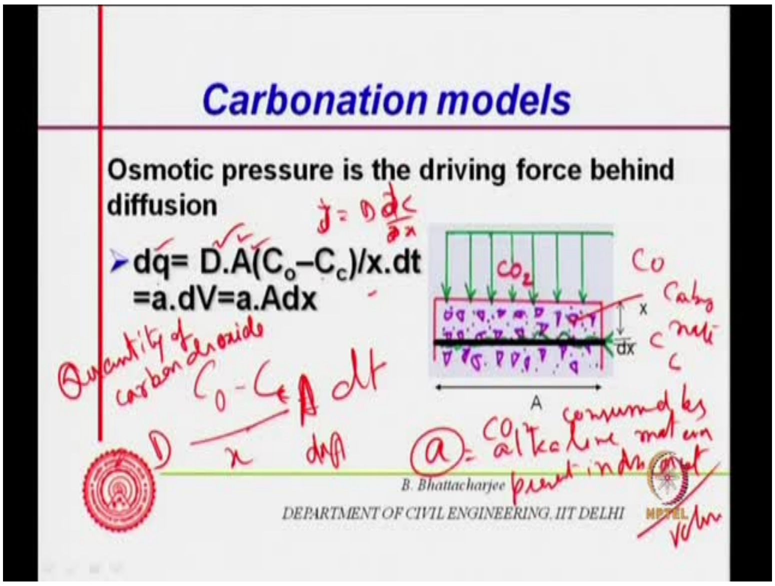

Carbonation models

Osmotic pressure is the driving force behind diffusion

- $dq = D.A(C_o - C_c)/x.dt$
  $= a.dV = a.Adx$

$J = D \frac{dc}{dx}$

Quantity of carbon dioxide

$D \frac{C_0 - C_c}{x} A \, dt$

dA

ⓐ = CO_2 consumed by alkaline material present in unit volume

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Now this is what fixed diffusion law is, and if you are looking at the mass balance then you get actually rate of change of concentration with time, will be given as d c x square is a diffusion equation heat diffusion equation. Quite a number of diffusion equation follows this, so, this is a second equation but, in ways we are not interested the in this manner. Right now we are not interested in this 1, we are not we are only interested in this, so, the flux is proportional to concentration gradient right flux is proportional to concentration gradient, so, d q if I consider the flux at you know the this as already got up to x it has already carbonated.

It has got the concrete has got carbonated up to x. so, concentration between c 0 outside c 0 here, and c in the concrete is here so, the concentration gradient will be given as c 0 minus c divided by x that is you know concentration gradient, d is the d is the diffusion coefficient and if a is the area flux is per unit area, so, quantity the d q is the quantity of carbon dioxide coming to this d x element right. So, it there no this is already carbonated this is carbonated already carbonated like we have shown in the last diagram already carbonated up to x depth x, and now the carbonation is occurring at d x element carbonation is occurring over this d x element.

So, as it comes in the gradient will be c 0 minus c were c 0 is outside c c is the inside divided by x there is a gradient, and we assume that gradient is constant there multiplied by the area a and this is the amount of carbon dioxide that would be coming in you know that flux that would be coming in to d x multiplied by d t that was a rate quantity of carbon dioxide coming in. So, d q stand for quantity of carbon dioxide carbon dioxide in is d c 0, c c divided by, d a c 0 minus multiplied by d t. so, that is the quantity I should have used j for flux j is equals to d dell c dell x you know somebody could have written it like this j is a flux, this is a quantity this I am talking of quantity.

Now, this if it is all getting neutralized, at this moment its getting all neutralized at this moment, let us say a is the alkaline material present small a is a alkaline material present alkaline material that has been neutralized let us say all. The total volume of carbon dioxide coming total volume of total mass of carbon dioxide coming that will dissolve you know that will actually react with the alkaline material present in the d x, so, d x into a is the volume, d x into a is volume, d b volume and total carbon dioxide consume, let us say a is the alkaline you know carbon dioxide consumed by, by alkaline material a is the carbon dioxide consumed by alkaline material which I can find out from stoichiometry if I know the total alkaline material present per unit volume.

Right and multiplied by the matrix factors so, a is the carbon dioxide consumed by the alkaline material present in d x so, a d v you know a is the carbon dioxide consume per unit volume, in the d x element so, a into d v that is a into a d x that is the this must be equal to d q. So, d q is the quantity that comes in, in d t time and it is all consumed. Right, you know for the alkaline material present multiplied by the stoichiometry factor that will give you the carbon dioxide that can be consumed, so, a is the carbon dioxide that can be consumed by the alkaline material present small a is the lower case a in the amount of carbon dioxide that can be consumed by the alkaline material present in unit volume of the concrete.

So, a is the carbon dioxide consumed by alkaline material present in concrete per unit volume unit volume of concrete, so, then a d v or a a small a d x must be the equal to d q. so, that’s that is the idea, it must be equals to d q so, if it is equal to d q then I simply integrated this some constant that is 1 by x into some constant let me call it as k dash d t is equals to you know some other constant that is a k double dash d x so, what I will get if I will get k you know if I integrate d t, and this side it will be some constant let us say k 3 prime x d x integrated so, I will get it x square by 2.

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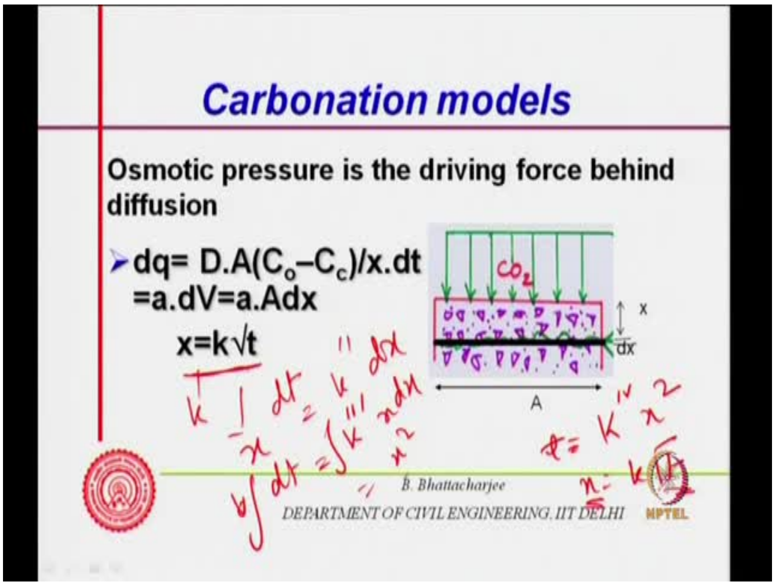

Carbonation models

Osmotic pressure is the driving force behind diffusion

- dq= D.A(C_o–C_c)/x.dt =a.dV=a.Adx

  x=k√t

$k\frac{1}{x}dt = k''dx$

$\int dt = \int k''' x\,dx$

x^2

$t = K'''' x^2$

$x = k\sqrt{t}$

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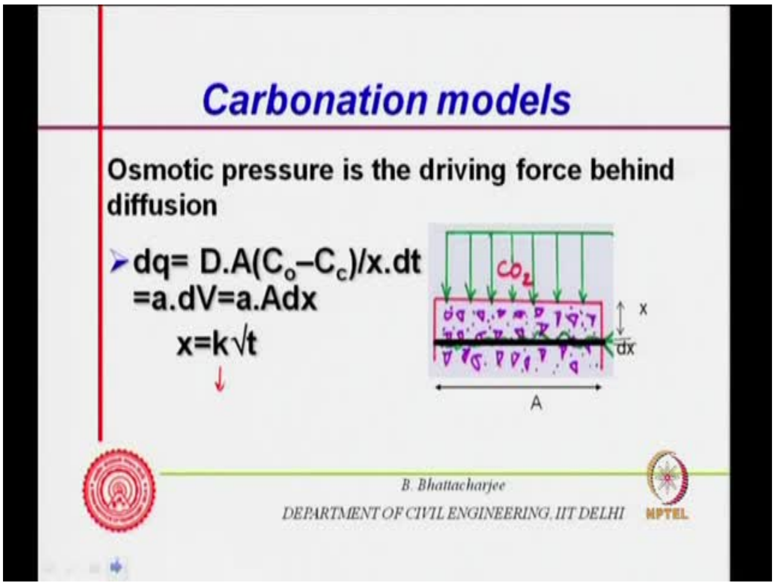

Carbonation models

Osmotic pressure is the driving force behind diffusion

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  x=k√t

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So, in other words k all this can be you know k all this can be put it I can write that t is equal to some constant let me call it as k four prime into x square. In other words I write x equals to k under root t that is what I have done. so, by simple integration I can find out x equals to k under root t now this model is very very simple model absolutely simple stick assuming the properties of this is all uniform after even carbonation and it is not considering many factors, actually does not consider many factor but, one thing comes out from this expression is that x is proportional to root t x is proportional to root t so, this is very simple model and a actually x equal proportional to root t what is come out what comes out from this kind of a model.

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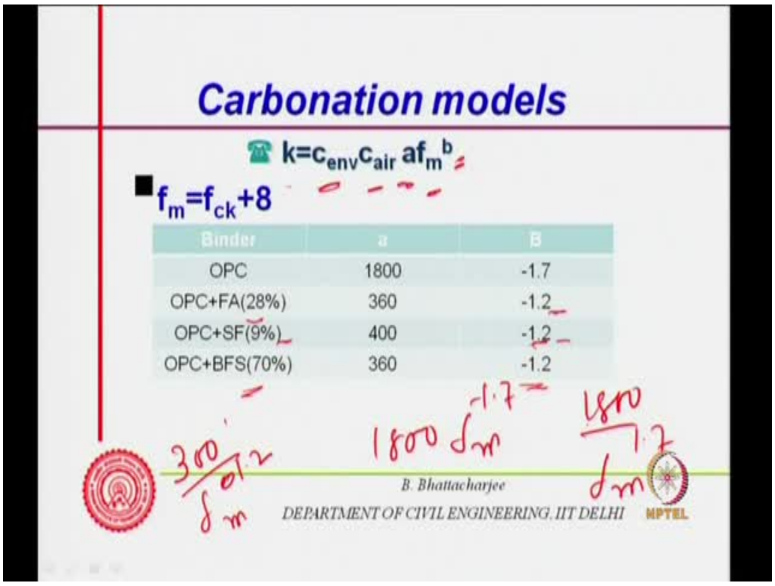

Carbonation models

☎ $k = c_{env} c_{air} a f_m^b$

- $f_m = f_{ck} + 8$

Binder	a	B
OPC	1800	-1.7
OPC+FA(28%)	360	-1.2
OPC+SF(9%)	400	-1.2
OPC+BFS(70%)	360	-1.2

$\frac{360}{f_m^{1.2}}$

$1800 f_m^{-1.7}$

$\frac{1800}{f_m^{1.7}}$

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All right, but there are complex model but, there you know finally, many most of the model makes it some form of t to the power half relationship, because experiment is also this is largely given found to be valid. So, k is the question now k depends upon many factors this is for our qualitative understanding the depth of carbonation at an time is proportional to root t root over t the time from the starting of carbonation, that more or less you know fix in well with the experimental data but, constant of proportionality empirically people have seen that is it a function of c environment c air a and v are 2 constant and strength of the concrete.

So, c environment and c air we have talked about now f m is equal to f c k plus 8 so, its mean strength actually, one can take it that way and a and v for different combinations of blended cement blended cementitious material and o p c are given. for example, for you know f m to the power b it is for o p c a is 1800.

That means k will be higher but, it is also b is minus 1.7 so, this is higher but, this minus 1.7 means the higher the strength actually k would be you know lower higher the strength k will be lower, compare to let us say fly air silica fumes or last one is slag bends normally last one you can go up to 70 percent silica fumes people use about 9 10 percent, and flier use 20 percent so, this is a kind of practical bend which one would use and this values are about empirical is suggested values are 1.2 minus 1.2 etcetera etcetera. And if you calculate out this let us say 1800 into some strength f m to the power

1.7 minus right, or in other words 1800 divided by f m to the power 1.7, you will find this k value comes out to be low compared to 300 into the into divided by f m to the power minus 1.2, I mean 1.2 see 1 this is nearly squaring up and this is say if it is a 50 m p a this will give you somewhere around 2000 or so, while if it is in this case 50 into 1 to the power 1.2 would make it 100 or so, you know, let us say even I mean it is not even its just slightly more than one so, one can find out one can find out what is this value but, 300 divided by it will be 3 this will be much less this much be much less so, bending blended you know this one's actually increases fliers silica fumes.

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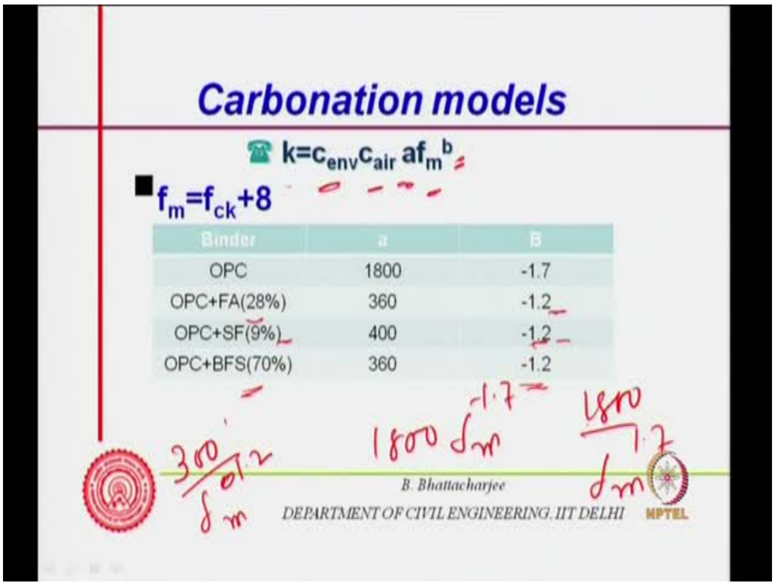

Carbonation models

☎ $k=c_{env}c_{air}\,af_m^{\,b}$

■ $f_m=f_{ck}+8$

Binder	a	B
OPC	1800	-1.7
OPC+FA(28%)	360	-1.2
OPC+SF(9%)	400	-1.2
OPC+BFS(70%)	360	-1.2

$1800\,f_m^{-1.7}$

$\frac{1800}{f_m^{1.7}}$

$\frac{300}{f_m^{1.2}}$

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And this actually increases this increases the k value somewhat so, that means carbonation is likely to be faster for identical condition of environment. And air with blended system with you know fliers blending well we understood. Because, we know that the alkaline materials are consumed by this alkaline materials are consumed by blast one slag silica fumes so, less alkalines a will be now smaller, smaller a in the previous equation. A stands for I mean a is a the alkaline material or carbon dioxide require to consume alkaline material will be less, therefore, this is this is you know this is you know it comes appears like this.

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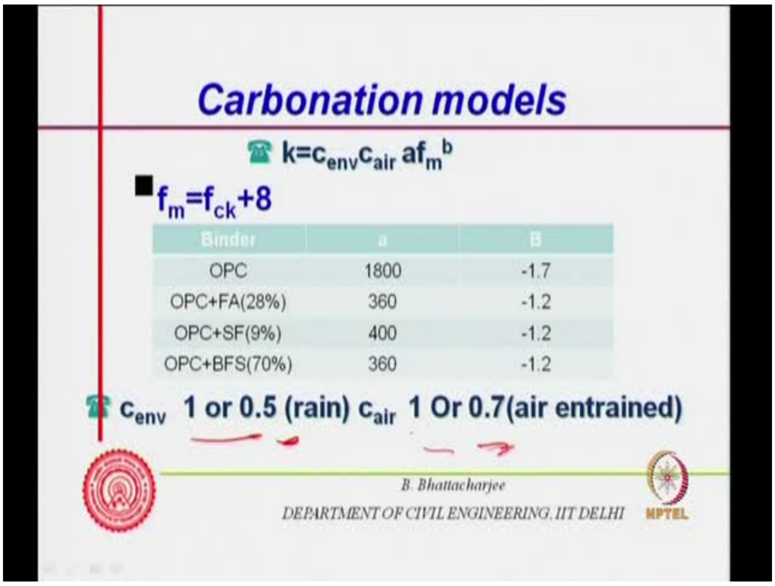

Carbonation models

☎ $k=c_{env}c_{air}\,af_m^{\,b}$

■ $f_m=f_{ck}+8$

Binder	a	B
OPC	1800	-1.7
OPC+FA(28%)	360	-1.2
OPC+SF(9%)	400	-1.2
OPC+BFS(70%)	360	-1.2

☎ c_{env} 1 or 0.5 (rain) c_{air} 1 Or 0.7(air entrained)

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These values are but, that is nothing to worry much actually because although the carbonation process much be faster moisture in air will be slower in this material, and also you know they there is they there microstructure is improved, then their resistivity is resistivity is high for this kind of material whenever you had material resistivity increases significantly as we shall see later on and therefore, actually they don't create much of a problem. When it comes to kinetic sub corrosion, so, they have a tendency to depassivate but, when it comes to kinetic they might improve better, c environment is 1 or 0.5 and for air entrained concrete you know c air is 0.7 otherwise 1. Air entrained concrete is more for us, environmental depend up whether it is exposed because this empirical formula is developed in Europe.

So, Europe if you keep it outside then you know it is partially moist right, I mean inside is partially moist outside if it is continuously wet the values could be lower, so, this continuously wet scenario. Now, root t experimental validation has been shown by some people for example, most of it you know seems to fit to root t curve this also seem to be fitting with root t curve so, this is an artificial climate 20 degree centigrade and 65 percent validity humidity so, 20 per degree centigrade 65 percent r h this one is.

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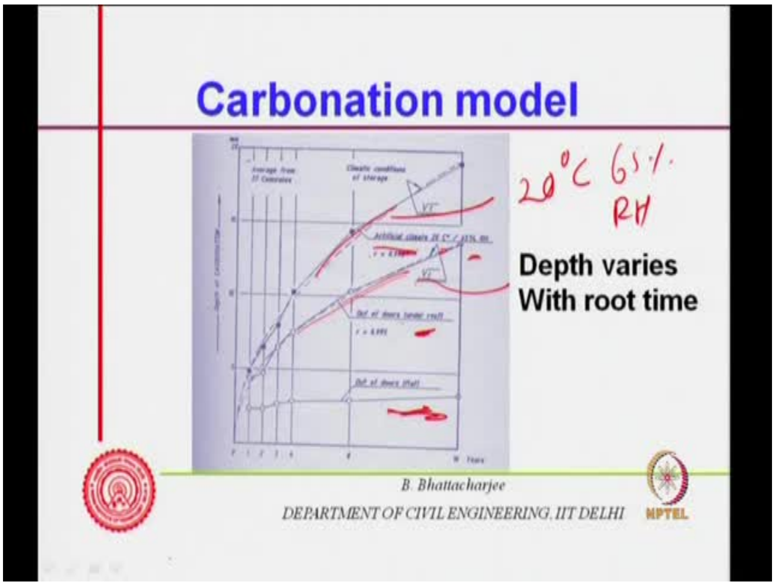

Carbonation model

20°C 65% RH

Depth varies With root time

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And this one is outdoor condition you know so, there is lot of moist condition is prevailing here and this is completely out of door flat this is of course, over a roof so, this is more outdoor you know like it is exposed to rain this is more exposed to rain so, what it shows is that root to relationship after all is quite often following so, this you know relationship although very simple so, depth varies with root time, that becomes a kind of understanding that we try to develop or yet we develop from this situation right.

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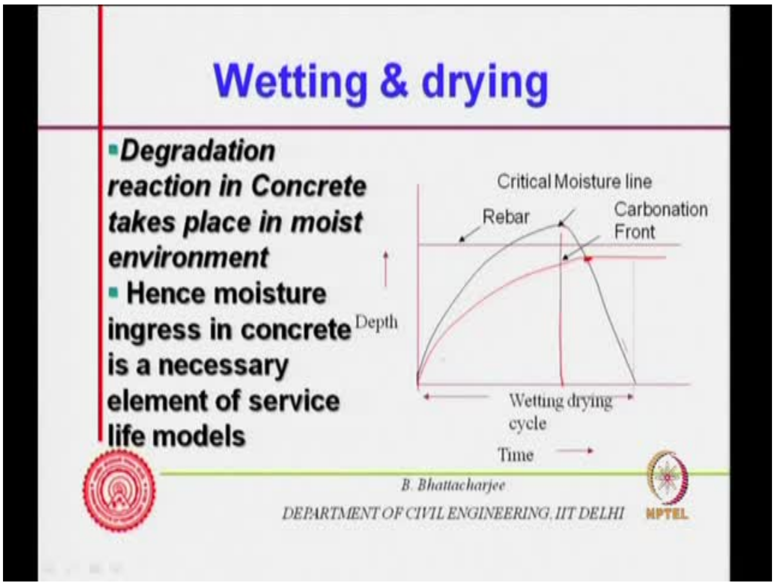

Wetting & drying

- ***Degradation reaction in Concrete takes place in moist environment***
- **Hence moisture ingress in concrete is a necessary element of service life models**

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Now we already said the degradation reaction in concrete takes place in most environment and concrete is not under fully saturated condition in tropical climate exposed concretes are subjected to wetting and drying, even in western situation you know colder climate higher latitude is actually under wetting and drying situation. Hence moisture ingress in concrete is necessary element in service life model all models must look into this wetting and drying, and if you look at it this look at it for example, let us say in the our kind of climatic condition.

This is your reinforcement bar, and if it is a critical moister line there is a critical moister content above which actually it will start carbonation will start now, with in this case it is fully saturated in the beginning then it dries out, shown as if it is fully saturated it dries out to conducive moisture so, above this moister content there will be no carbonation critical moisture level. so, if it dries out so, this zone becomes now critical and carbonation proceeds, here carbonation proceeds here, then the drying stops here suddenly wetting occurs which occurs at very fast rate. And then it has become actually saturated no carbonation will progress.

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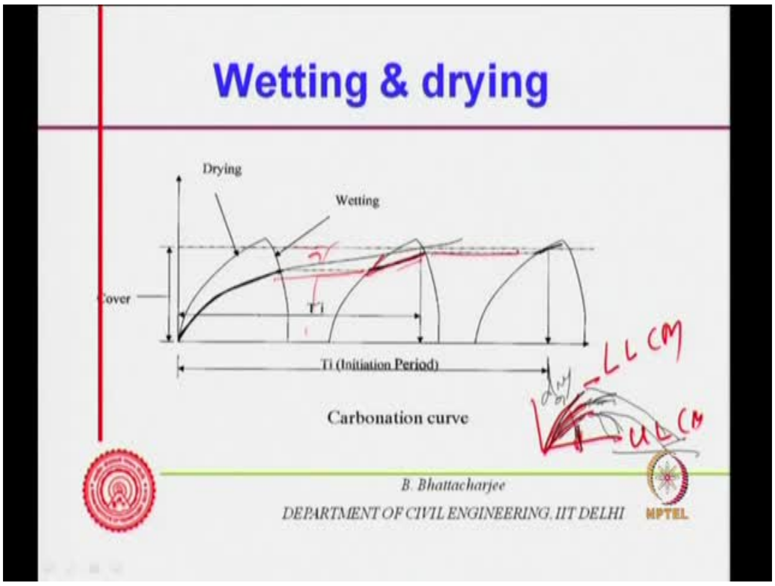

Wetting & drying

Carbonation curve

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So, carbonation will progress within only within this envelop. And this process will repeated, will be repeated and you can see this in this diagram this process will repeat now after this no carbonation, there might be a drying period dry this there might be waiting period. Then this is all saturated situation no carbonation occurs it starts again when moisture contains releases below critical level continuously. The same kind of slope same kind of relationship and in steps it actually happens, so, if you have cycles of wetting and drying right, then carbonation will also progress in steps carbonation will also progress in steps right carbonation will progress in steps this is when it was fully wet if it was fully saturated but, if it was fully dry then also similar situation progress the moisture form but, this will be more complex for example, you have fully dry then critical moisture level you know in present critical moisture level here it will be more, then critical moisture level and there is the way critical moisture upper limit of critical moisture content lower limit of critical moisture content upper limit of critical moisture content.

Carbonation will only progress in between, when it is fully dry and getting saturated, so, only beyond certain moisture level lower limit of critical moisture content up this is dry, then moisture reaches a critical lower limit of critical moisture content carbonation, and then as wetting is continuing this would be upper limit of moisture carbonation will progress only in between.

And this is during wetting phase once it is wetted wetting is over drying starts, this will come back like this and this will also follow like this, this is a longer because drying takes much longer time. So, carbonation will follow you know only during the critical moisture situation modeling that is relatively difficult, and people have not done any modeling on those so, far.

So, this is, but in the Indian tropical scenario it will be like that consider let us say situations of any part of let us say composite monsoon climate of central and northern India you have monsoon season of 2 months. So, this time during this time period wetting will continue after that drying starts.

And before the monsoon season it was fully dry so, during the monsoon season wetting would start and the concrete will become moist and conducive if the situation is conducive for the cover concrete carbonation will progress and winter comes it will become more dry after monsoon season August September it tends to be dry it will possible continue and when it becomes fully dry humidity becomes very very low again it will cease to carbonation will cease.

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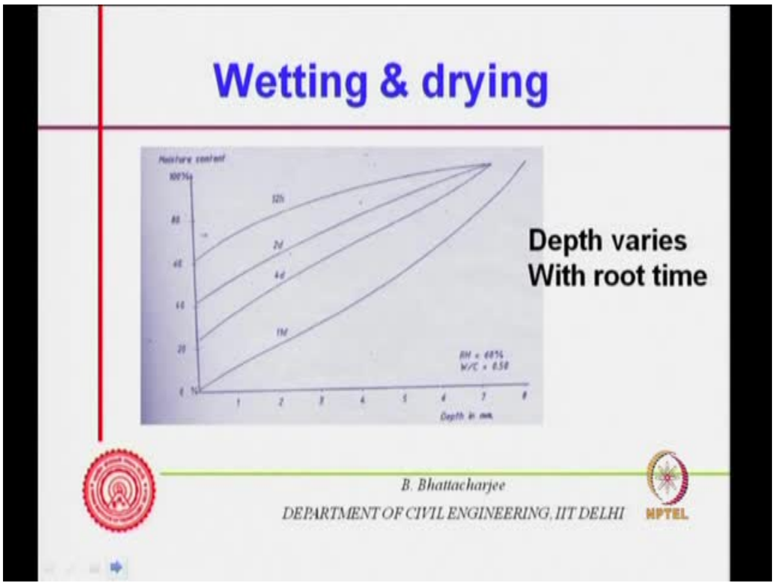

Wetting & drying

Depth varies
With root time

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So it will actually occur between some time from the month of you know during the monsoon period to winter period after that it would stop when it has become fully dry. And again start next year. so, you will have cycles of carbonation in exposed concrete in Indian scenario when it is exposed to rain of course, in any other condition it could be different. But, you see other case the modeling is simple when you have situation of you know originally saturated which could be in the condition of Europe where you know it is mostly saturated some time it becomes dry, then it will again become saturated.

Now, moisture diffusion or moisture movement it can be expressed through what is called Richards equation which you have not looked into here at the movement. And its Richards equation which can be written like this d theta relative moisture contain d t is equals to dell d x of d which is the function of theta into d theta d x.

So, let me write it like this dell again let me write it clearly like again let me just write it clearly again you know it can be written like dell theta d t, where theta is relative moisture content dell dell x of d, which is a function of theta dell theta dell x this is Richards equation, and through this actually you can solve and find out the moisture profile. However it has been if you look at observed at the diagram. You know 1 hour 2 hour drying 3 hour drying 12 hour drying even drying could be somewhat related to this however the boundary condition will be different. Only the capillary moisture flow will be like this. Vapor transmission equation is also similar it can be also modeled in the similar manner, whatever it is this is how drying follows drying follows and it can also be shown to be proportional to depth varies with root time.

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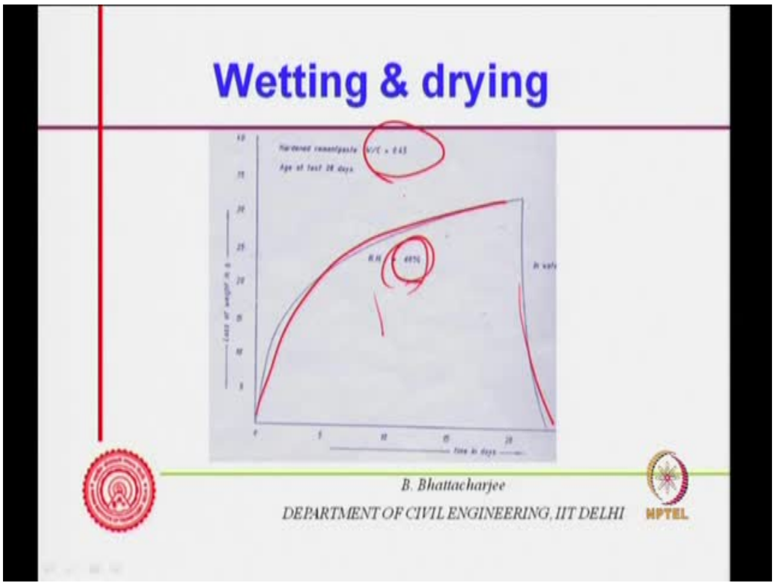

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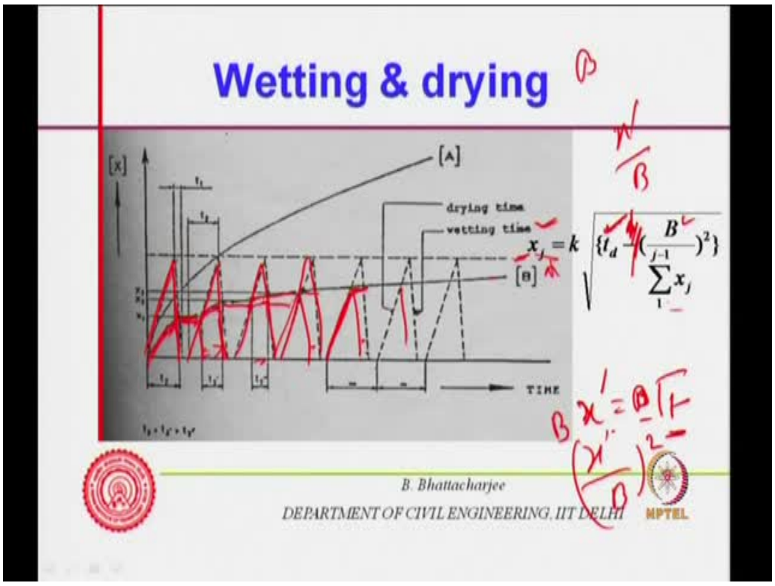

Wetting & drying

$$x_j = k\sqrt{\{t_d - (\frac{B}{\sum_1^{j-1} x_j})^2\}}$$

B

$\frac{x}{B}$

$x' = B\sqrt{t}$

$(\frac{x'}{B})^2$

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It can be shown in the simple manner like we have done earlier in a you know simple model one can show that this got root of time therefore, if this is my you know critical moisture line before that it was all saturated, so, relative humidity is 6 6 56 percent 65 percent and this is wetting, wetting is instant areas drying takes longer time, so, this could be the cycle of drying and wetting. So, like drying and wetting right, for given concrete experimental also somewhat this can be validated.

So, then you will have actually the carbonation front will progress in this manner, in the first cycle you see this is this one can approximate the wet drying and wetting because wetting model is instantaneous then again drying and wetting then there is small gap, drying and wetting small gap drying and wetting, so, this is the conducive moisture condition during which carbonation progress.

So carbonation progress is here but, then it will not progress further till this point again progress in this manner stop here progress in this manner. And it follows till it reaches the cover depth, which is the cover depth is here this is your cover so, it reaches the cover depth. Now, one can simply one can see that during the second cycle the duration during which carbonation is occurring is smaller, in the third cycle it is still smaller, forth cycle it is still smaller, fifth cycle it is smaller and so, on so, for. Now what is this time this is the time require for drying of the already carbonated depth, so, this is the time required drying of the already carbonated depth you know, this is the drying this is wetting drying wetting, so, this is the time required, so, the carbonation font in the first cycle reaches here then it remains constant second cycle it reaches there, third cycle it reaches there and so, on so, forth.

So, if you see the forth cycle the carbonation will only start when the depth up to which forth cycle carbonation will occur the drying must you know takes place up to that depth. So, one can algebraically formulate a formula like this where b is the constant you know the moisture penetration depth if I call it x dash is b under root t. Because, we said moisture penetration is also proportional to under root t so, b is the constant of proportionality, so, x j j going from 1 to j minus 1, where this is x j is a carbonation depth progress of carbonation depth during j h cycle so, sum up all the carbonation depth prior to j h cycle, b divided by this because b is equals to so, we want to find of the t so, t will be you know t would be x dash square s dash by b square, x dash by b square right, t would be x dash by b square so, t would be x dash by b square so, therefore, this square of this gives me b divided by that gives me the time one of what it gives me the time so, total time required up to which drying you know dry this time must be subtracted from total drying time.

Total drying time minus this time must be subtracted this must be subtracted from drying time I think it is one over, that it should be one over that because time would b x divided by b x divided by b or if I write it other round one by you know b x dash is equal to root t b x dash equals to root t. so, then I will have t equals to b x square you know this should be one over that one over that so, this should be one over that one over b divided by this square so, you can find out this time and k under root that will give you k because k is the constant of proportionality for carbonation.

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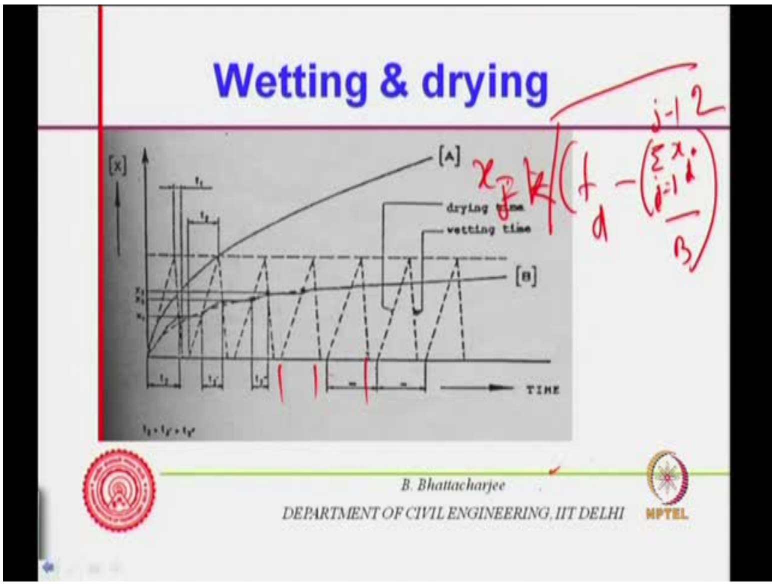
Wetting & drying

$$x_j = k\sqrt{\left(t_d - \left(\frac{\sum_{i=1}^{j-1} x_i}{B}\right)^2\right)}$$

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So x j will be k one over this and this process every cycle you can find out how much is the progress of carbonation. Actually let me write this out clearly x j is equals to t d where t d is the drying time that is this period which is constant for all you know wetting drying wetting drying cycle or the time every cycle time during which moisture condition is conducive, so, t d now if you look at x dash that is the moisture penetration depth b under root t so, unit o b is at actually distance or length.

Divided by root over t root over t so, if I square it up so, x t would be x dash square by b square so, constant b you know b square what is unit of b is as length root over t to the power half root over you know length t to the power half so, length for you need go minus half therefore, this would be you know this would be simply sigma x j, j going from 1 to j minus 1 or x i, i going from divided by b square and whole of this things should be under root multiplied by k.

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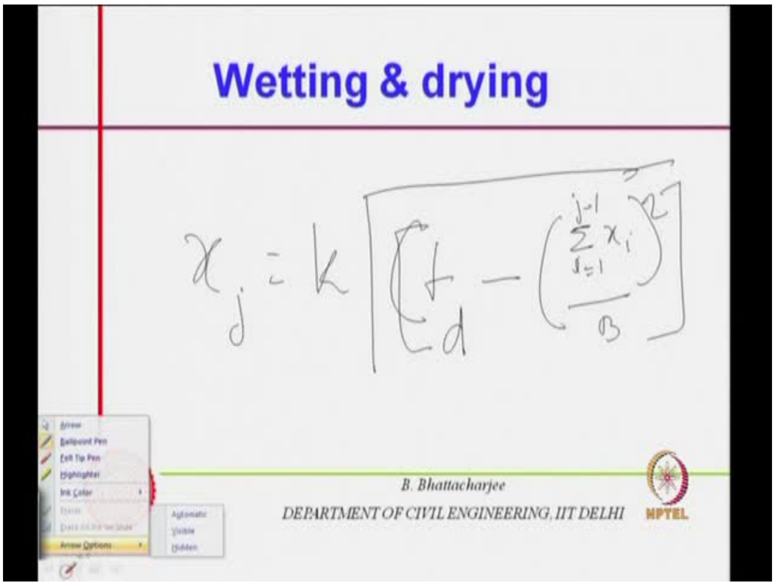

Wetting & drying

$$x_j = k\sqrt{\left[t_d - \left(\frac{\sum_{i=1}^{j-1} x_i}{B}\right)^2\right]}$$

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So, let me write it again clearly write this one clearly again let me write this one clearly again the x j at the x j you know this let me erase this out actually and write clearly x j that is the carbonation depth at any cycle depth cycle will be given as k under root t d where t d is the cycle time or effective duration in every cycle during its carbonation can occur minus or put it like this minus sigma x i, i going from 1 to j minus 1 by b square, so, this would be the you know so, next x x j so, x j is the carbonation depth progress of carbonation depth in j h cycle progress of carbonation depth in j h cycle and this you can repeat and find out.

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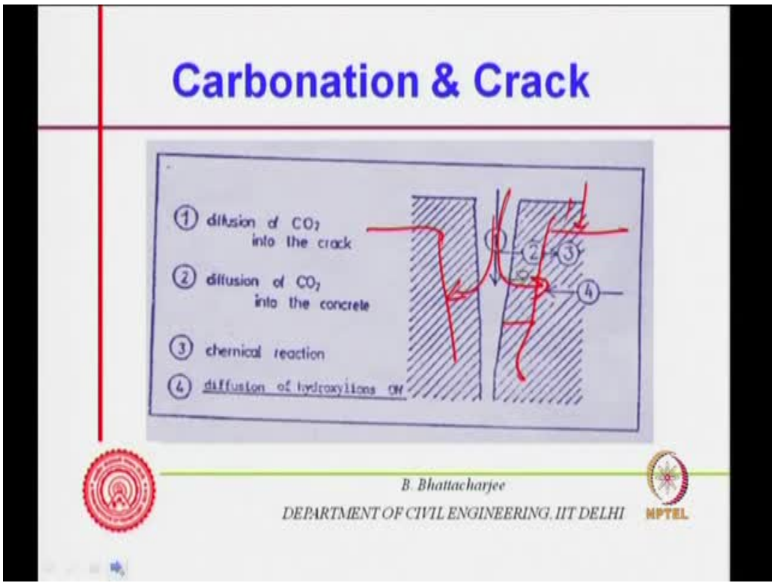

Carbonation & Crack

① diffusion of CO_2 into the crack

② diffusion of CO_2 into the concrete

③ chemical reaction

④ diffusion of hydroxylions OH

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Protection against carbonation

- Presence of both moisture & air is necessary. Water saturated concrete exhibit lower rate of carbonation.

☎ Service life w.r.t carbonation is the time when carbonation front reaches rebar level

■ Impervious surface concrete, Lower w/c and adequate cover depth improves protection against carbonation

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So this is how we find out this is how we can actually model this well but, what is important for us to understand is actually, what is important for us and when it reaches the cover depth service life will so, what is important for us to understand is that the carbonation progress is instant and it would depending upon wetting and drying cycle. Right, this is the simple model there is a model for specific condition actual condition should be model under wetting and drying. If you have a crack carbonation can penetrate along this direction, diffusion of carbon dioxide first into the crack and then inside, in a crack concrete carbonation font might reach in this manner. So, if have rework somewhere it is coming then there is a problem. What is protection against carbonation moisture and air is necessary water saturated concrete exhibit lower rate of carbonation. So, keep concrete out of moisture time when carbonation front reaches the rebar level.

That is we have understood and impart we have surface concrete lower water cement ratio adequate cover depth improves protection against carbonation, so, this is all about carbonation. Now, we can look into chloride we have 2 types of you know when we have measuring chloride we have 2 types of chloride for example, we take some concrete grind it to powder and dissolve it in acid you get acid soluble chloride. I mean you actually dissolve it in h n o 3 6 normal h n o 3 concentrated nitric acid then you get acid soluble chloride, dissolved it in distilled water. and find out by silver nitrate test the quantity of chloride this water soluble chloride that is water soluble chloride you know that is water soluble chloride, so, we distinguish 2 types of chlorides in concrete 1 is water soluble and another is acid soluble de-passivation takes place.

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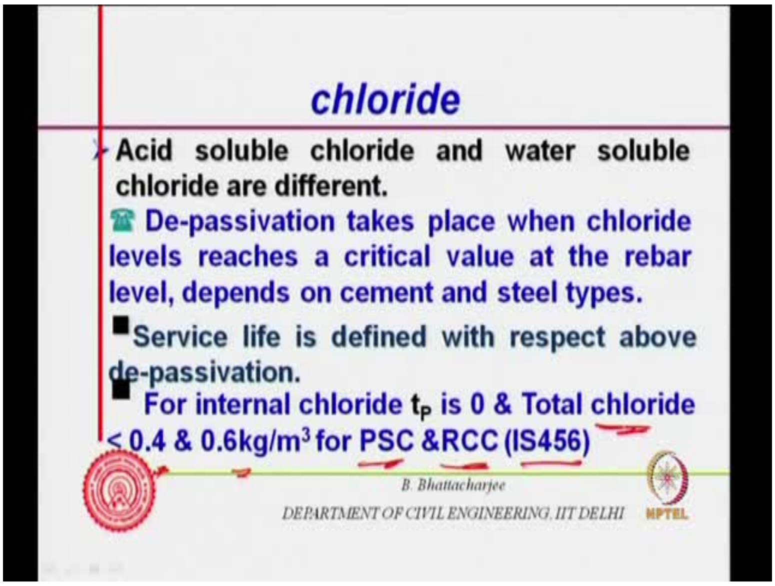

chloride

- Acid soluble chloride and water soluble chloride are different.
- ☎ De-passivation takes place when chloride levels reaches a critical value at the rebar level, depends on cement and steel types.
- ■ Service life is defined with respect above de-passivation.
- ■ For internal chloride t_P is 0 & Total chloride $\leq$ 0.4 & 0.6kg/m^3 for PSC &RCC (IS456)

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When chloride level reaches a critical value at the rebar this is sometime called fresh hold chloride level. And it depends upon cement and steel types. And service life is define with respect to above de-passivation of course, internal chloride is the chloride coming from ingredients and i s 456 2000 tells you that this internal chloride which is acid soluble chloride total chloride you know should be less than 0.4 or 0.6 k g per meter cube for r c c for pestered concrete 0.4 k g per meter cube. so, this is total chloride is important for ingredients, because some of this acid soluble chloride may tend to be water soluble chloride in future, so, if you have sufficient chloride right in the beginning the t p de-passivation time could be even 0.

So, it is important that keep the concrete new concrete free of chloride or below the values that has been suggested in the coal 0.4 k g per meter cube or 0.6 k g per meter cube, some of the total chloride remains physically and chemically bound some chloride with the cement like c 3 a reacting with calcium chloride gives you chloroeliminate salts and higher c 3 therefore, improves the chloride binding so, this is the chemically combined chloride these are called friedel salts. Right, so, chloroeliminate salts they are friedel salts and c 3 are bind c some could be physically absorbed and they are also immobile not able to move not water soluble, so, chemically bound chloride as not what so, water soluble and they would not contribute to de-passivation but, they can later on become soluble there could be a problem.

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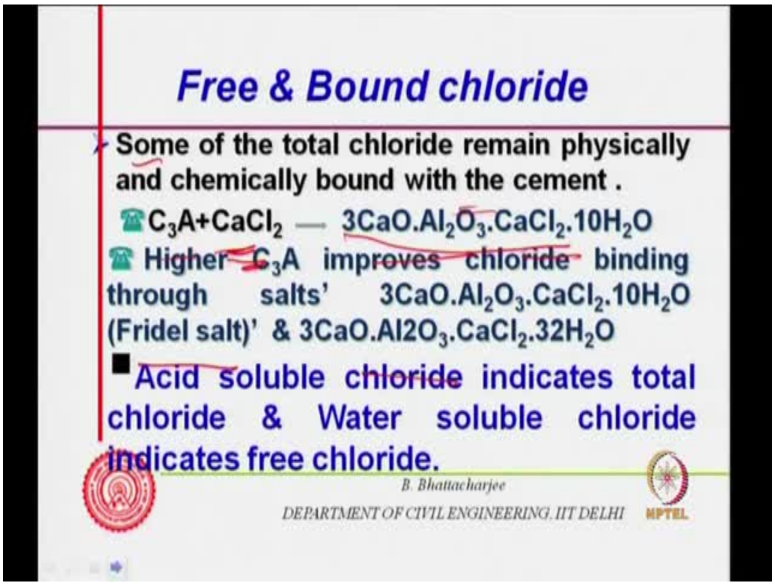

Free & Bound chloride

- Some of the total chloride remain physically and chemically bound with the cement .
- ☎ $C_3A+CaCl_2$ — $3CaO.Al_2O_3.CaCl_2.10H_2O$
- ☎ Higher C_3A improves chloride binding through salts' $3CaO.Al_2O_3.CaCl_2.10H_2O$ (Fridel salt)' & $3CaO.Al2O_3.CaCl_2.32H_2O$
- ■ Acid soluble chloride indicates total chloride & Water soluble chloride indicates free chloride.

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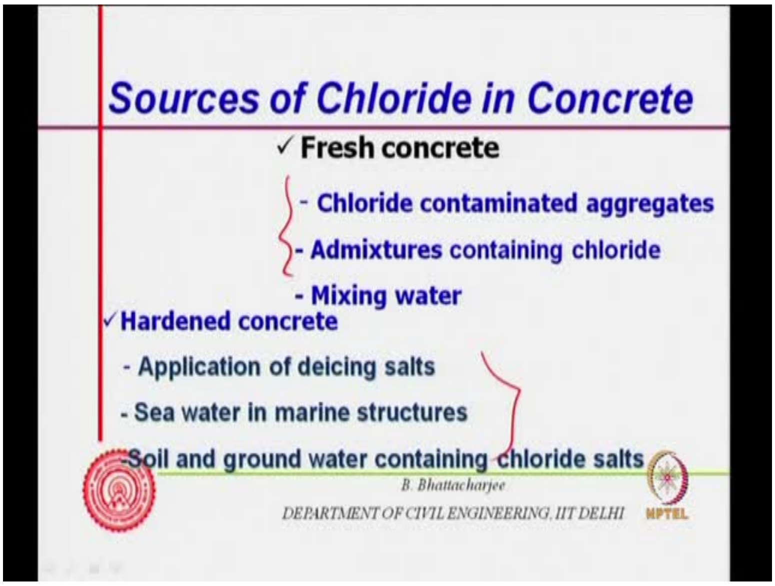

Sources of Chloride in Concrete

✓ Fresh concrete
- Chloride contaminated aggregates
- Admixtures containing chloride
- Mixing water

✓ Hardened concrete
- Application of deicing salts
- Sea water in marine structures
- Soil and ground water containing chloride salts

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So therefore, total chloride when you are measuring with acid soluble chloride that actually include the bound chloride and free chloride both, so, free chloride bound chloride both are there All right acid soluble chloride indicates total chloride and water soluble chloride indicates free chloride so, total minus free chloride gives you bound chloride.

Sources of chloride in concrete well if it is fresh concrete it may come from ingredients called chloride contaminated aggregates admixtures containing chloride which is of course, restricted this days mixing water quite often ground water contaminated with chloride if it is used in concrete, and that is the case in many of them north Indian scenario. And then in harden concrete because they can come from outside deicing salts that is very common in northern I mean Europe developed you know northern countries.

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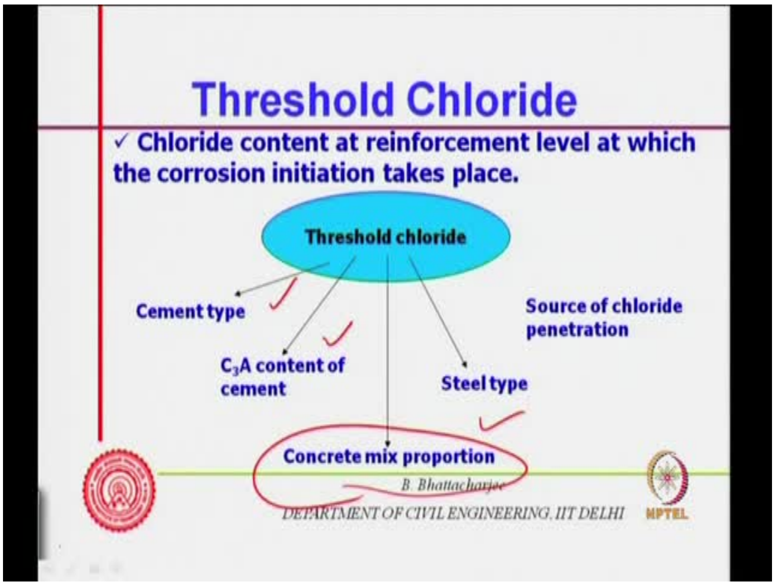

Threshold Chloride

- ✓ Chloride content at reinforcement level at which the corrosion initiation takes place.

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Europe or United States of America as chloride salts are used as deicing salts sea water in marine structures chloride can come we have discussed this earlier and soil and ground water containing chloride salts, so, these are sources of chloride these are called internal chloride, and these are external chloride which will come through in this.

Chloride content at reinforcement level at which the corrosion initiation takes place are called threshold chloride. But, it will vary with the cement type c 3 a content of cement because cement type mixed proportion steel type not all steel will get depassivated for example, a corrosion resistance steel may not get depassivated easily so, sources of chloride penetration it will depend upon that also, all put together threshold chloride will vary from cement to cement steel to steel so, that is it cannot be unique.

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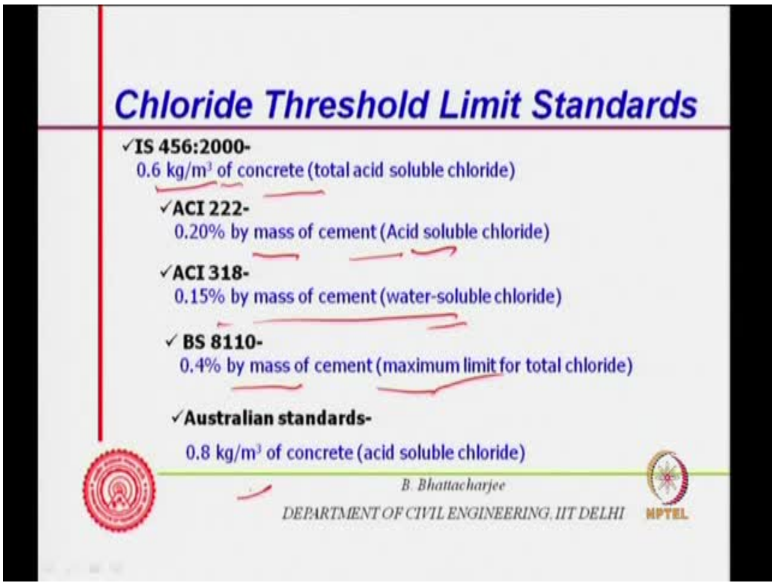

Chloride Threshold Limit Standards

- ✓**IS 456:2000-**
  0.6 kg/m^3 of concrete (total acid soluble chloride)
- ✓**ACI 222-**
  0.20% by mass of cement (Acid soluble chloride)
- ✓**ACI 318-**
  0.15% by mass of cement (water-soluble chloride)
- ✓ **BS 8110-**
  0.4% by mass of cement (maximum limit for total chloride)
- ✓**Australian standards-**
  0.8 kg/m^3 of concrete (acid soluble chloride)

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And therefore, you find that a various codes of different values you know for example, i s 456 you said this for r c c only 0.6 k g per meter cube a c i 220 0.2 0 by mass of cement acid soluble chloride 318 0.1 5 by mass of cement water soluble chloride, so, this is acid soluble this is water soluble b s 8 1 1 0 0.4 percent by mass of chloride and this is for total chloride, and Australia standard 0.8 k g per meter cube of concrete acid soluble chloride.

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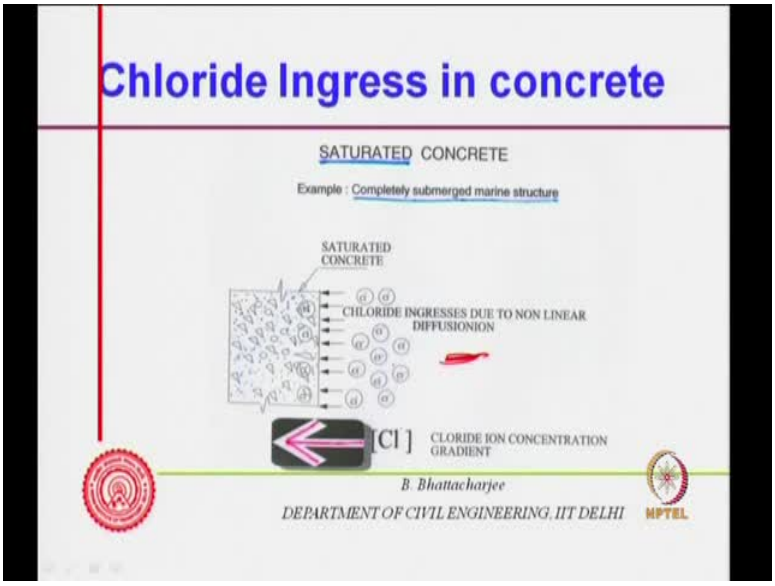

Chloride Ingress in concrete

SATURATED CONCRETE

Example : Completely submerged marine structure

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So, you see it varies and also it must be varying because of the experience also it varies cement type and steel type. One thing you must remember that carbonation as well as chloride is not a problem for say for concrete except for of course, carbonation shrinkage its actually problem of the reinforcement because they initiate the reinforcement corrosion so, for concrete they are not problem.

Therefore, we should address actually reinforcement corrosion or some indicators of reinforcement corrosion whether it is initiated or not with respect to chloride as well as carbonation right so, in saturated concrete if the concrete is saturated the concentration of the chloride ion will be high here and it may not be there inside chloride may diffuse by fixed diffusion equation. And actually for charged particle it is electrical potential.

Now if there is a concentration gradient of the charged particle then the potential will also they will be potential gradient will also be existing and that would cause driving of the chloride you know ions chloride ions so, that is what we looked into saturated condition chloride ions chloride ions actually saturated condition you know chloride ions chloride ions in saturated conditions chloride ions are penetrating.

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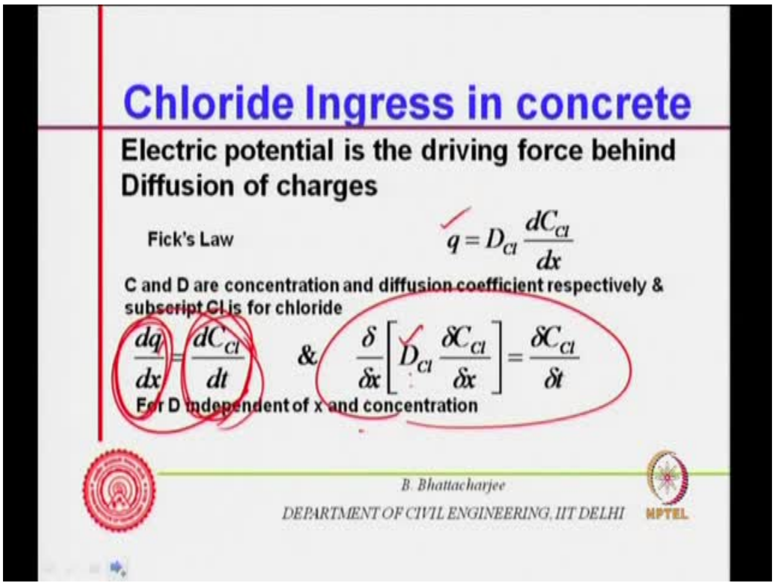

Chloride Ingress in concrete

Electric potential is the driving force behind Diffusion of charges

Fick's Law $q = D_{Cl}\frac{dC_{Cl}}{dx}$

C and D are concentration and diffusion coefficient respectively & subscript Cl is for chloride

$$\frac{dq}{dx} = \frac{dC_{Cl}}{dt} \quad \& \quad \frac{\delta}{\delta x}\left[D_{Cl}\frac{\delta C_{Cl}}{\delta x}\right] = \frac{\delta C_{Cl}}{\delta t}$$

For D independent of x and concentration

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These are all chloride ions so, if the chloride ions penetrates they this you know high chloride ions concentration higher potential here less chloride ions concentration lower potential so, the chloride ion move because of the potential difference and it also can be expressed in form of the fixed diffusion equation same fixed diffusion equation. Right, so, this is the flux here and if you look at the mass balance then it can be written like this if d c l is a function of the you know if this can be simplified d c l is not the function of the chloride concentration this can be taken out or of the space then it can be taken out.

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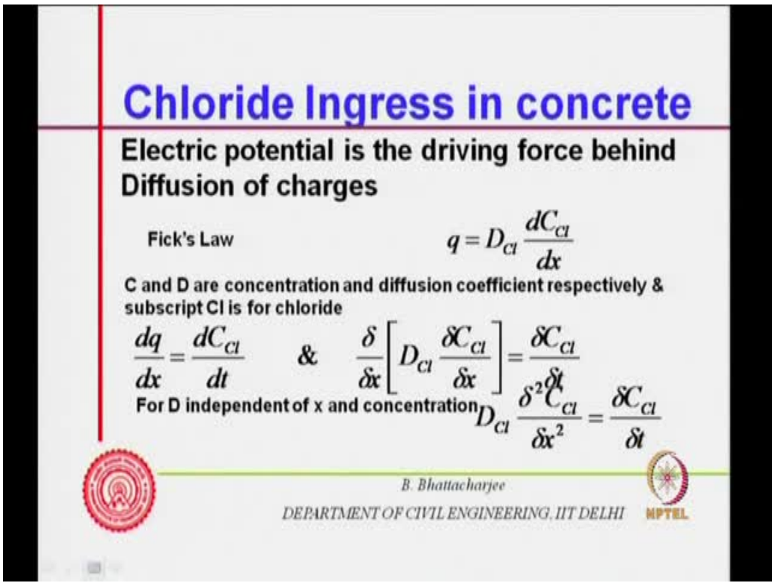

Chloride Ingress in concrete

Electric potential is the driving force behind Diffusion of charges

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$$\frac{dq}{dx} = \frac{dC_{Cl}}{dt} \quad \& \quad \frac{\delta}{\delta x}\left[D_{Cl}\frac{\delta C_{Cl}}{\delta x}\right] = \frac{\delta C_{Cl}}{\delta t}$$

For D independent of x and concentration $D_{Cl}\frac{\delta^2 C_{Cl}}{\delta x^2} = \frac{\delta C_{Cl}}{\delta t}$

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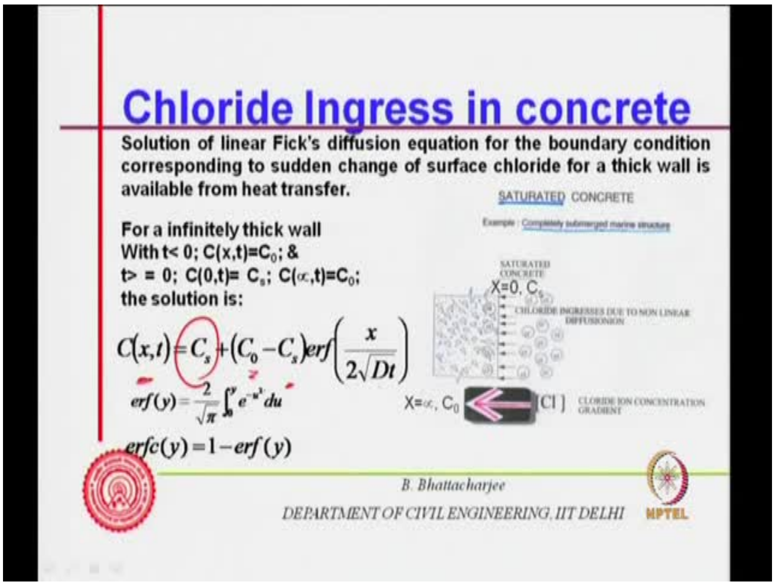

Chloride Ingress in concrete

Solution of linear Fick's diffusion equation for the boundary condition corresponding to sudden change of surface chloride for a thick wall is available from heat transfer.

For a infinitely thick wall
With t< 0; C(x,t)=C$_0$; &
t> = 0; C(0,t)= C$_s$; C(∝,t)=C$_0$;
the solution is:

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

$$erf(y) = \frac{2}{\sqrt{\pi}}\int_0^y e^{-u^2}du$$

$$erfc(y) = 1 - erf(y)$$

SATURATED CONCRETE

Example : Completely submerged marine structure

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So, if it is not the function of the space or the chloride concentration itself can taken out and it will be a linear equation, so, this is what it is mass balance will show you this kind of an equation this is the flux coming in and rate of change of this flux is rate of flux whatever flux you know chloride coming in must minus going out must gone increasing the concentration.

That is the idea concentration of mass so, this is the flux rate of change of flux with space that must be equals to change in concentration of the chloride within that space so, finally, this is the diffusion equation this is the diffusion. D is the independent of x and concentration and therefore, you can simply write this kind of an equation you can simply write this kind of a equation. But, this is only valid for saturated condition this is only valid for saturated condition. Now solution of fixed diffusion equation for a specific boundary condition is available, so, it can be solved today with finitely maintain so many types of tools available it is not really difficult to solve so, you can solve it and since you can solve it therefore, it is not very difficult to use this but, most commonly people have adopted to a specific solution for a specific boundary condition.

For example, for a specific boundary condition of sudden change of surface chloride for a thick wall this is available for heat transfer situation for example, this is a boundary condition for infinitely thick wall you know a semi infinite medium where t less than 0 concentration was c 0 everywhere and t greater than 0 at x equals to 0 this is your system at x equals to 0 this is semi infinite medium this is infinity at x equals to 0 certainly you have changed the chloride concentration to c s where other side it has still remain same c 0 it was not changed the solution is given by error function solution, solution is given by you know this is the condition at x equals to infinity it is always c 0 here x equals to 0 it is certainly changed to c s for this solution is available and this is given by c x t at any point the chloride concentration is given as c s.

Where c s is the surface concentration which is kept constant plus c 0 minus c s, c 0 is initial concentration and at x equals to infinity it still remains same minus c s into error function gausses error function of x by 2 d where d is the diffusion coefficient and t is time, where error function of any y is any variable is given by this equation so, this is the known solution but, this is not valid for all situations although apparently lot of people use this for all kind of situation. It is only valid for saturated chloride saturated condition that means possible where no flux zone submerged concrete concentration outside is constant rankled water, no change in concentration and this boundary condition is followed. It cannot be used everywhere but, that is what has been done quite often and error function complementary is called 1 minus e r f y case gone you know so, this value will vary from 0 to 1

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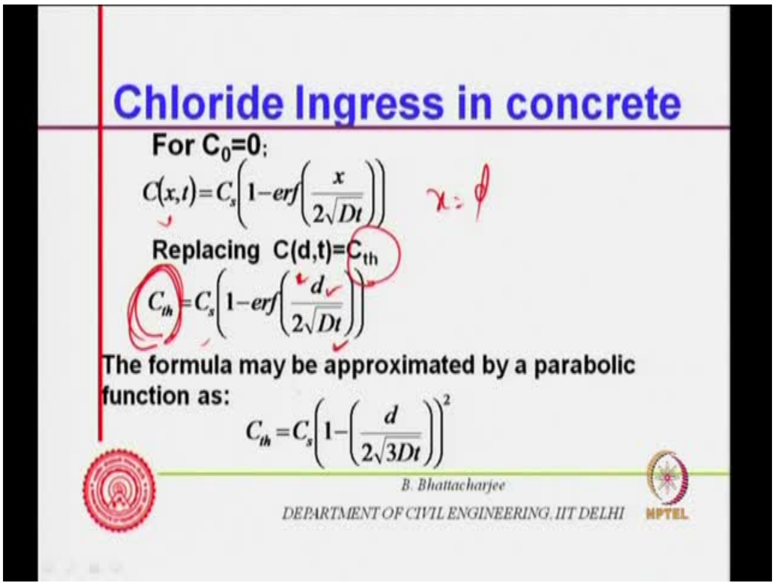

Chloride Ingress in concrete

For $C_0=0$;

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

Replacing $C(d,t)=C_{th}$

$$C_{th}=C_s\left(1-erf\left(\frac{d}{2\sqrt{Dt}}\right)\right)$$

The formula may be approximated by a parabolic function as:

$$C_{th}=C_s\left(1-\left(\frac{d}{2\sqrt{3Dt}}\right)\right)^2$$

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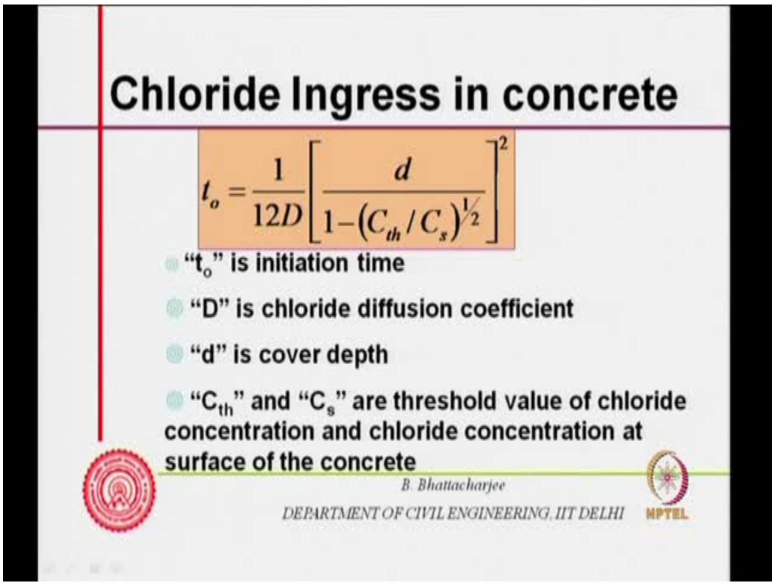

Chloride Ingress in concrete

$$\boxed{t_o=\frac{1}{12D}\left[\frac{d}{1-(C_{th}/C_s)^{\frac{1}{2}}}\right]^2}$$

- "t_o" is initiation time
- "D" is chloride diffusion coefficient
- "d" is cover depth
- "C_{th}" and "C_s" are threshold value of chloride concentration and chloride concentration at surface of the concrete

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And 1 minus this error function y is complementary error function and you can actually get a you know error function is equal to 0 error function infinity is equals to 1 so, it varies from 0 to 1 so, 1 minus this is called complementary error function and one can use this so, for c 0 equals to 0 this equation can be written in this manner. That is initial chloride concentration is 0 one can write in this manner, where x is any distance this are diffusion coefficient and t is a time.

Replacing c d t is equals to you know at cover depth it is as threshold so, this c s t I replace it by d at x equals to d x equals to d and at time at sometime c equals to t h then I get c t h on this side this equals to c s where this is equals to d, this is the then this t is the service line this t is the service line then when the chloride level at the rebar level at d d is the cover depth the rebar level as reached threshold. And one can actually the formula may be approximated by a parabolic function like this error function it can be you know actually approximated by a parabolic function and you can get service life like this an expression for service life like this.

Right but, there are lot of uncertainty in this one for example, c t h as we said it varies there are you know threshold values would depend upon cement type steel type etcetera etcetera and is not constant it not sure how you measure the diffusion coefficient, there is no way really systematic way to measure the diffusion coefficient. So, t 0 is the initiation time or t p plus de-passivation time this and lot of people use this calculation but, this is absolutely inaccurate one can possible use experience rather than using something which does not exactly represent the real life situation not the exact boundary condition.

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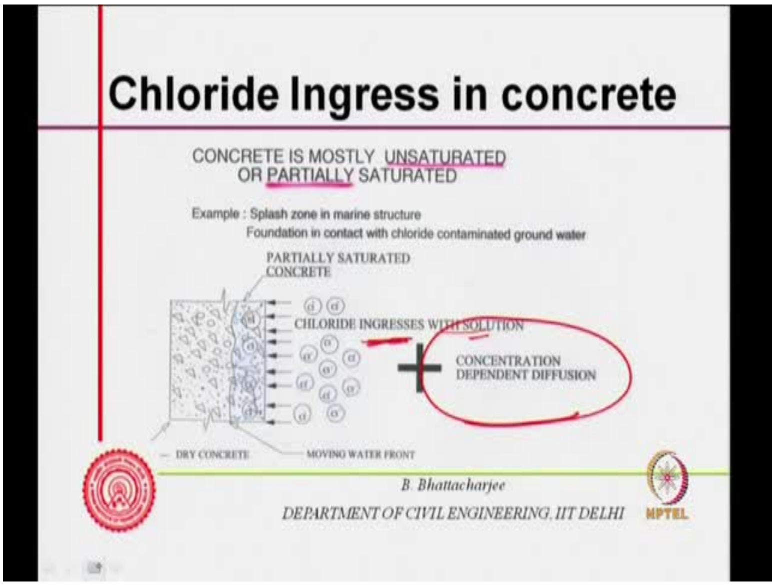

Chloride Ingress in concrete

CONCRETE IS MOSTLY UNSATURATED
OR PARTIALLY SATURATED

Example : Splash zone in marine structure
Foundation in contact with chloride contaminated ground water

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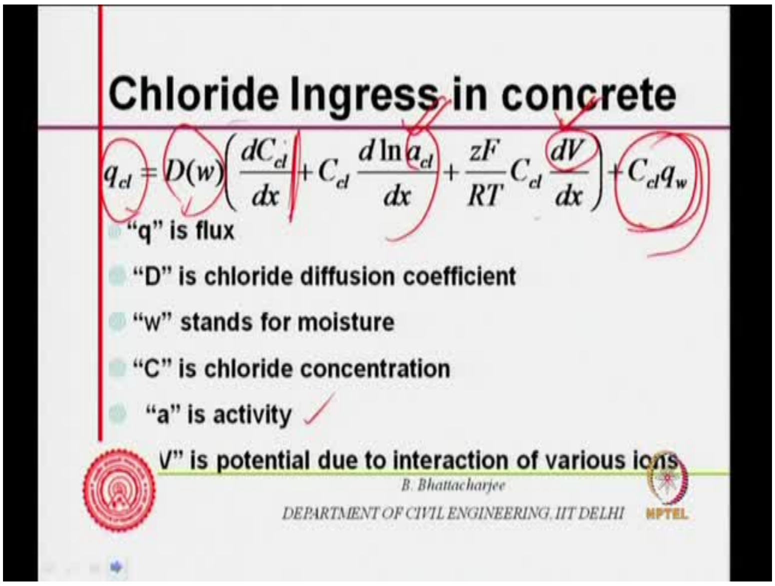

Chloride Ingress in concrete

$$q_{cl} = D(w)\left(\frac{dC_{cl}}{dx} + C_{cl}\frac{d\ln a_{cl}}{dx} + \frac{zF}{RT}C_{cl}\frac{dV}{dx}\right) + C_{cl}q_w$$

- "q" is flux
- "D" is chloride diffusion coefficient
- "w" stands for moisture
- "C" is chloride concentration
- "a" is activity
- V" is potential due to interaction of various ions

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Saturated concretes are rare but, people do use them, unsaturated concrete, concrete is mostly unsaturated and this flux concentration dependant flux is same as earlier we talked about but, the chloride can migrate with solution because unsaturated solution can go in so, chloride cannot migrate sorry chloride can ingress migration is under electric field so, ingresses it can go under the capillary section and that flux is much higher usually so, you know in flux zone and foundation and many other places where concrete unsaturated one can use this. Unsaturated concrete is the most important one and equation for this is fairly complex. I just take a half a minute and conclude our discussion on this and continued on next lecture on the same one.

Now, you can see that this is the flux of chloride, d is the diffusion coefficient so, this is under concentration gradient this could be under activation you know because reaction might be taking place and if there is a external potential applied migration can be occurring so, migration potential activation potential reaction actually activity reaction potential and this is due to the section water section you know the capillary section or solution flux. Now this flux is much more than this flux, and this is the diffusion coefficient so, if you are looking at the total flux that should be some of the solutions flux plus the flux this may not be there if there is no external field you can neglect this at least 2 fluxes 1 must consider. And once since there is a total chloride and free chloride one must look at the mass balance of the total chloride and under such condition you know one must take the equation would turn out to be this flux change is equals to some bind chloride binding factor must be taken into account.

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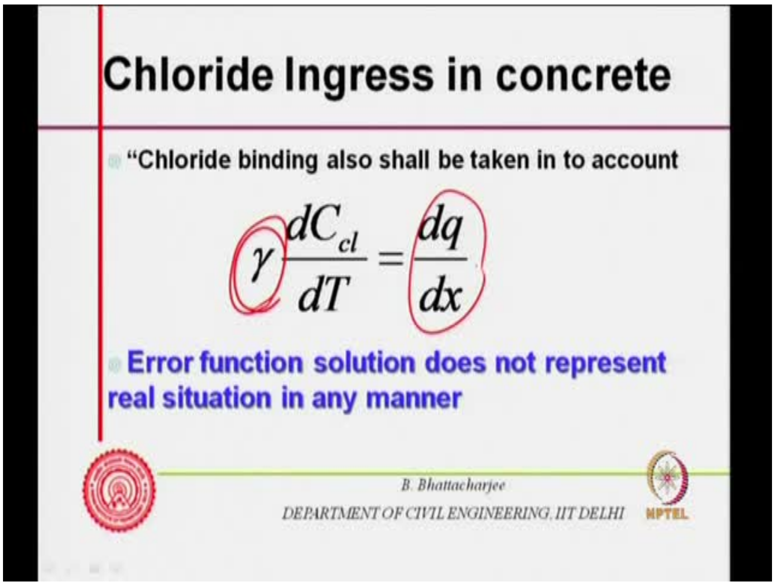

Chloride Ingress in concrete

- “Chloride binding also shall be taken in to account

$$\gamma \frac{dC_{cl}}{dT} = \frac{dq}{dx}$$

- **Error function solution does not represent real situation in any manner**

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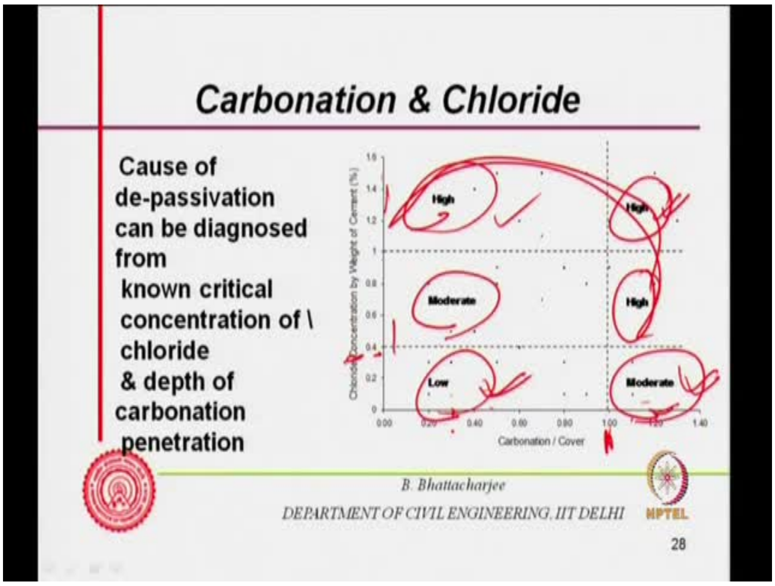

Carbonation & Chloride

Cause of de-passivation can be diagnosed from known critical concentration of \ chloride & depth of carbonation penetration

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So, equation would be much more complex then what actually you have done. Therefore, solution does not represent real situation in most of the cases in any manner, it does not chloride banding this is the factor of chloride banding total chloride to free chloride ratio you must balance the total chloride and the flux rate of change of flux which you have used earlier it would be something like this so, quickly we can look into you know cause of de-passivation can be diagnosed from chloride concentration if you have both chloride some diagrams are available for example, carbonation depth to covered depth one the risk is relatively low but, if it is more than 1 that is carbonation only chloride is relatively less here both chloride and carbonation, carbonation is less but, chloride is high risk of corrosion is high here.

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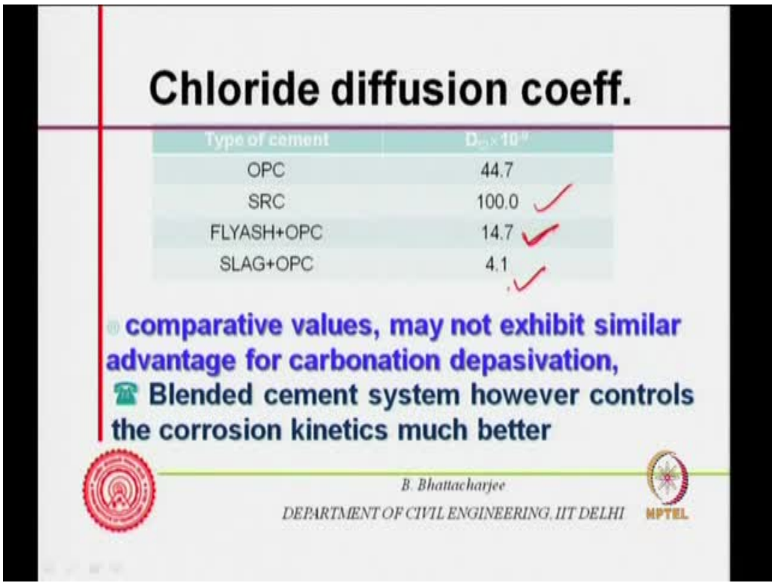

Chloride diffusion coeff.

Type of cement	$D_{cl} \times 10^{9}$
OPC	44.7
SRC	100.0 ✓
FLYASH+OPC	14.7 ✓
SLAG+OPC	4.1 ✓

- comparative values, may not exhibit similar advantage for carbonation depasivation,
- ☎ Blended cement system however controls the corrosion kinetics much better

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Both carbonation chloride is high risk of corrosion is high this is high so, chloride risk is high both carbonation chloride is there only carbonation chloride is not there the and it has not reached to the cover depth risk of corrosion is low otherwise if it cross the cover depth carbonation is cross the cover depth but, chloride is low moderate this zone is moderate where carbonation is less but, chloride is reached its threshold well these are some guidelines available but, you may not be very you know it can be used in incentive concrete chloride concrete chloride diffusion coefficient it is been seen that sulfide resistance even gives you high chloride diffusion coefficient compared to slag or a you know slag of each combination or flier of each combination. So, surface resistance cement is no good or chloride situation blenders cement however controls the corrosion kinetics much better that is well understood they you know but, with respect to carbonation of course, we have already said that is it may not be very good.

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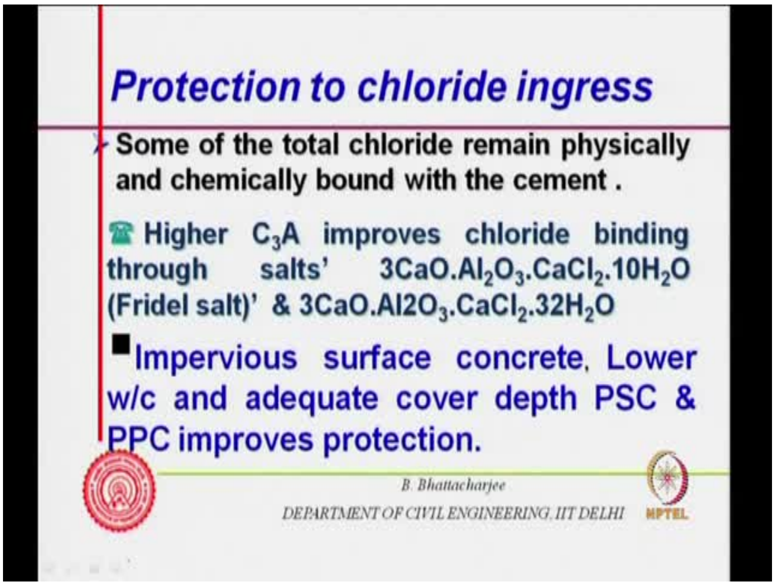

Protection to chloride ingress

- Some of the total chloride remain physically and chemically bound with the cement .

☎ Higher C_3A improves chloride binding through salts' $3CaO.Al_2O_3.CaCl_2.10H_2O$ (Fridel salt)' & $3CaO.Al2O_3.CaCl_2.32H_2O$

■ Impervious surface concrete, Lower w/c and adequate cover depth PSC & PPC improves protection.

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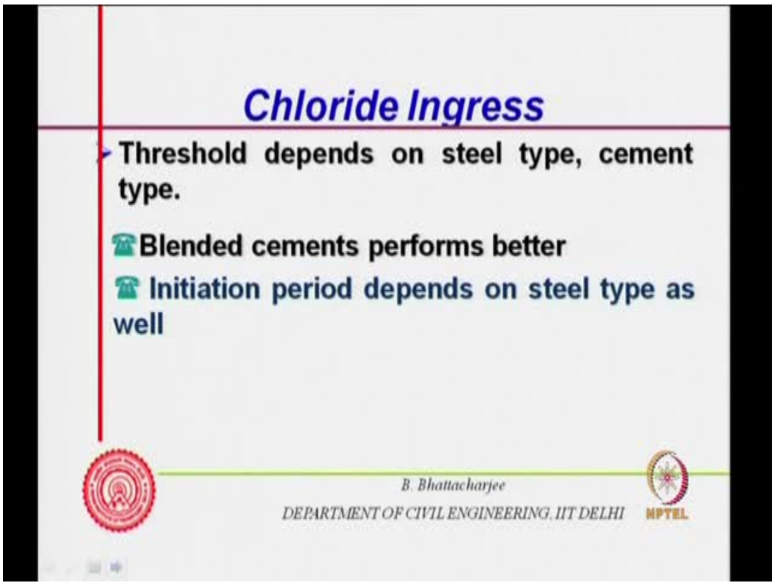

Chloride Ingress

- Threshold depends on steel type, cement type.

☎ Blended cements performs better

☎ Initiation period depends on steel type as well

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I think I think will close down here and start from you know like basically protection same as some sound the total chloride remain physically and chemically bounded cement that is what we have said. So, protection would be this already we have seen blended cement performs better so, you know what we have seen is protection would mean impervious concrete impervious concrete c 3 a higher c 3 a c 3 a would actually do well as for as chloride high improves chloride binding but, may not do sulfide very well.

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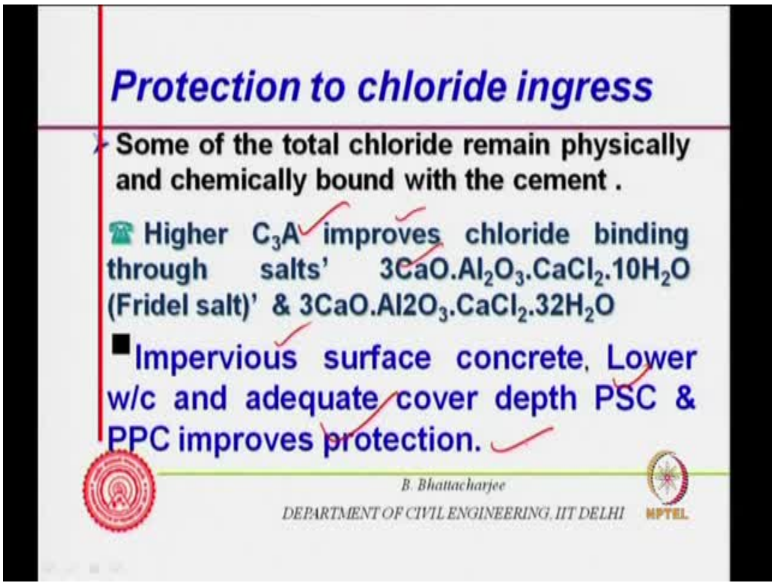

Protection to chloride ingress

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While slag cement is better both sulfide as well as chloride, so, higher c 3 implies chloride right and impervious surface concrete lower water cement ratio adequate cover depth t p c etcetera improves chloride. Threshold chloride depends on steel blended cement performs better and initiation period depends on steel type ratio as soluble chloride to water soluble chloride is this that is gamma values is something like this.

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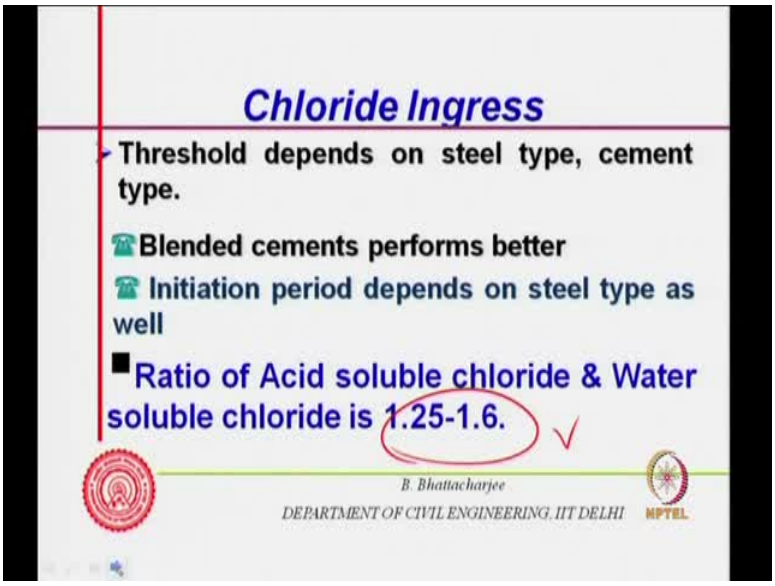

Chloride Ingress

- Threshold depends on steel type, cement type.

☎ Blended cements performs better

☎ Initiation period depends on steel type as well

■ Ratio of Acid soluble chloride & Water soluble chloride is 1.25-1.6. ✓

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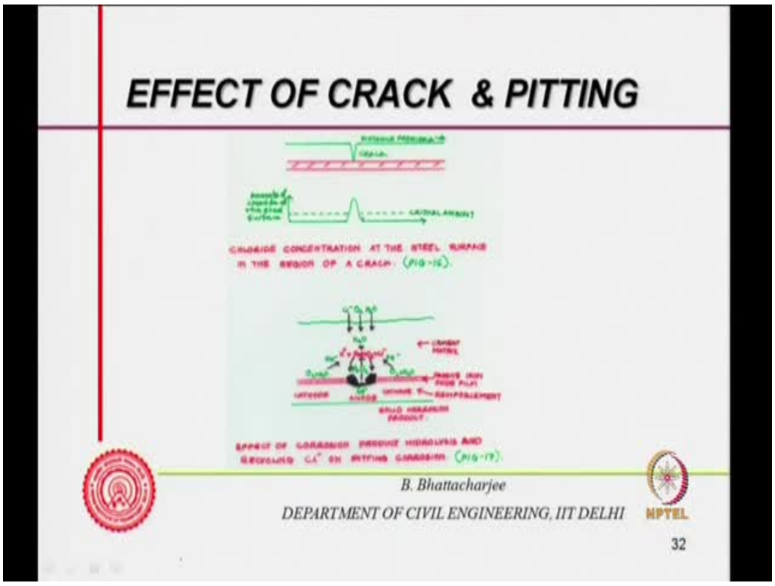

EFFECT OF CRACK & PITTING

CHLORIDE CONCENTRATION AT THE STEEL SURFACE IN THE REGION OF A CRACK (FIG-16).

EFFECT OF CORROSION PRODUCT HYDROLYSIS AND RECYCLING Cl^- ON PITTING CORROSION (FIG-17).

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So, if you have a crack than chloride can penetrate and it can cause what is called heating corrosion that is what is shown here. So, with this we can actually summarize our discussion we have looked into carbonation and chloride together and as far as chloride is concerned we said that the c 3 a it gives better binding carbonation impervious concrete and low water cement ratio is better, and you know de-passivation time we have looked into we have looked into some of the models and with this.

Thank you.