Admixtures and Special Concretes

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Lecture -23

Chemical Admixtures: Mechanism of corrosion

We will today move on to corrosion inhibiting admixtures and other specialty admixtures that are typically used for concrete applications. So before we look at corrosion inhibiting admixtures, it is important for us to understand the mechanisms that lead to corrosion. So idea is to see what conditions in reinforced concrete can promote corrosion and how do we lead to a protection against corrosion. That was the, that is the kind of strategy we will adopt for this chapter.

Corrosion of rebar:

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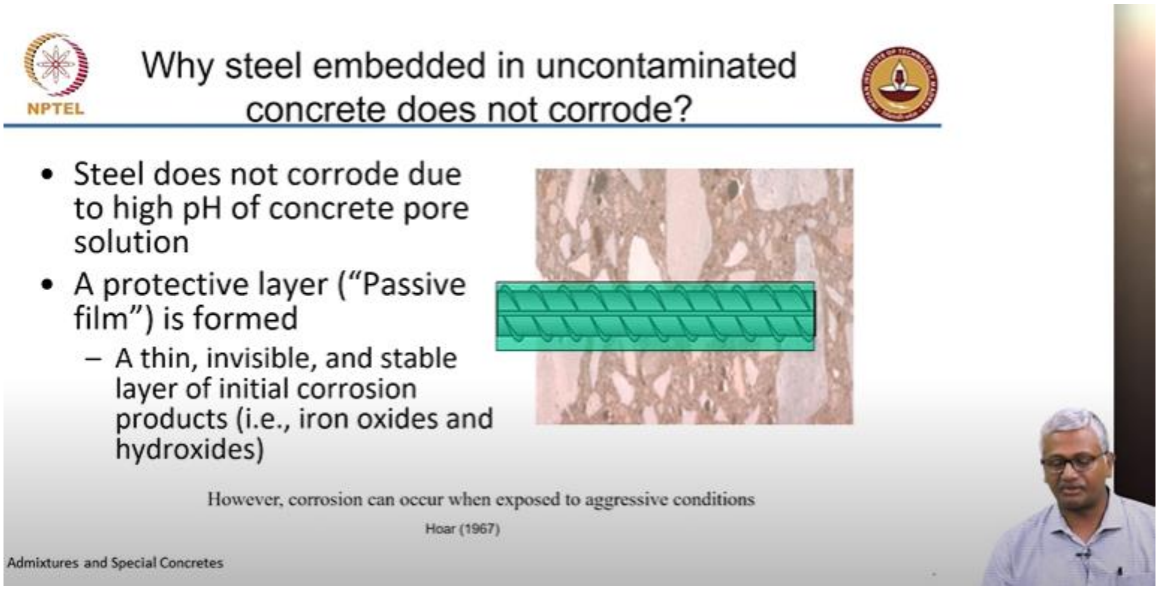

Why steel embedded in uncontaminated concrete does not corrode?

- Steel does not corrode due to high pH of concrete pore solution
- A protective layer ("Passive film") is formed
  - A thin, invisible, and stable layer of initial corrosion products (i.e., iron oxides and hydroxides)

However, corrosion can occur when exposed to aggressive conditions

Hoar (1967)

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Now as you know very well that steel and concrete make a very good combination. Steel is a perfectly good reinforcement for concrete. For what reasons? What are the primary reasons? There is a strain compatibility because the coefficient of thermal expansion of steel is similar to that of concrete and in general the bond between steel and concrete is also good. It is further enhanced obviously by the presence of the ribs that are there in reinforcing parts. Over the years we have moved on from mild steel to cold rolled steel and then finally today we are using what type of steel? TMT but the actual correct name for that is quenched self-tempered QST steel. The common name is TMT, thermo mechanically treated but that is not really a correct name because most steels are thermo mechanically treated.

So basically steel has some thermo treatment, some mechanical treatment. Now steel has an inherent tendency to corrode. Why? Why does steel want to corrode? So the stable form of any metal is its oxide. So iron is no different. It has to stabilize by transforming to an oxide. So there is a natural tendency for steel to corrode with time. Now this corrosion happens in different rates in different types of environments. If you have an acidic environment it is a much faster corrosion. If you have a neutral or an alkaline environment the corrosion rate is controlled by several factors which we will talk about in just a brief while but in concrete we all know very well that the environment is highly alkaline. The pH of concrete is of the range of 12.5, 13 sometimes even more, mostly more than13. In such instances steel in reality corrodes almost immediately but this corrosion layer that forms in the steel as soon as you put that in concrete is actually a passive layer which prevents further corrosion. So this thin, invisible and stable layer of initial corrosion products forms on the steel surface as soon as you embed that in an alkaline medium such as concrete. Of course this layer may take some time to develop but that is what happens initially to the steel as it comes into contact with the highly alkaline environment of the concrete. So high pH of the concrete pore solution leads to the formation of the stable passive layer.

Now as you move from reinforcing steel, regular reinforcing steel to corrosion resistant steel or to stainless steel what are you doing essentially there, What changes are you making to steel as it goes from reinforcing steel to corrosion resistant steel to stainless steel? We are adding some alloying elements typically chromium or nickel and these are enhancing the corrosion resistance capabilities of the steel and this corrosion resistance enhancement is primarily because the passive layer that forms on the steel surface in the alkaline environment is much more stable in the case of the corrosion resistant steels especially in the case of stainless steel. Stainless steel is expected to not corrode for a long time. It does not mean it will never corrode but for a long time if the conditions are ideal steel will not corrode, stainless steel will not corrode But reinforcing steel typically has a tendency to start corroding because of change in this environment in its vicinity.

Corrosion cell:

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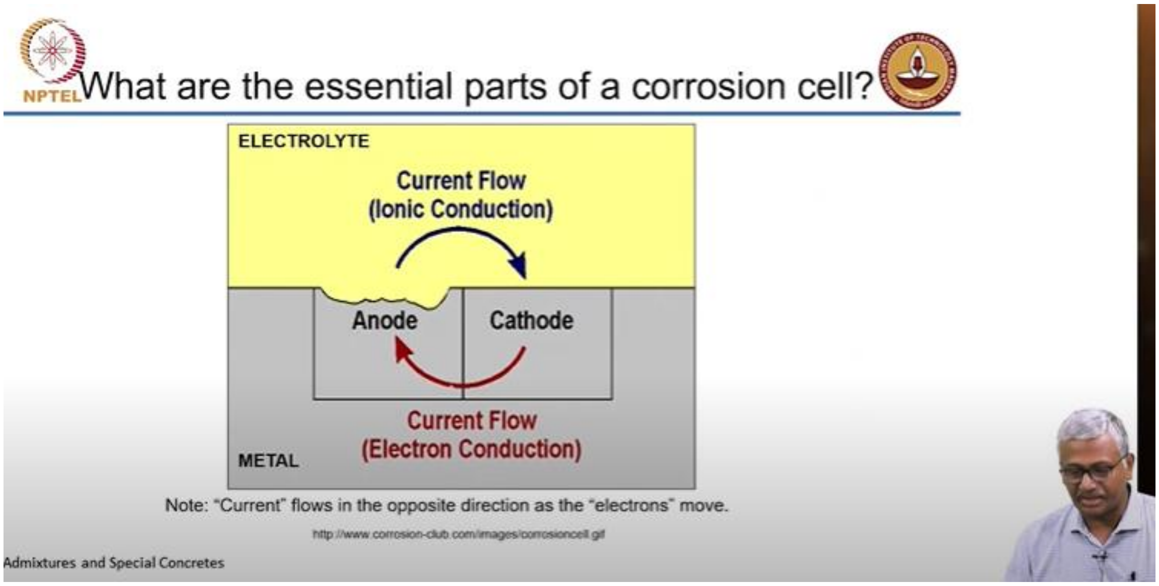

What are the essential parts of a corrosion cell?

ELECTROLYTE

Current Flow
(Ionic Conduction)

Anode

Cathode

Current Flow
(Electron Conduction)

METAL

Note: "Current" flows in the opposite direction as the "electrons" move.

http://www.corrosion-club.com/images/corrosioncell.gif

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Some basic definition of your electrochemical cell that occurs during corrosion. We know that on the same site of steel you have an anode and a cathode.

Anode: $Fe \rightarrow Fe^{2+} + 2e^-$

Cathode: $1/2O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$

So there is a flow of electrons that happens which indicates the conduction offered by the electrons typically the current flow with respect to conduction is in the direction opposite to the flow of the electrons and then there is an ionic conduction that happens and this conduction of the ions has to happen in the electrolyte. For steel embedded in concrete what is the electrolyte? Concrete right the concrete that surrounds the steel is the electrolyte So the obvious understanding from here is that since ionic flow has to happen through the electrolyte if you make the electrolyte less permeable what is going to happen? You will reduce the flow of current. So corrosion rate will be lowered when you have concrete of a high quality surrounding the steel and that is the reason why we see less corrosion potential for concretes where water cement ratio is lower.

Reactions of corrosion:

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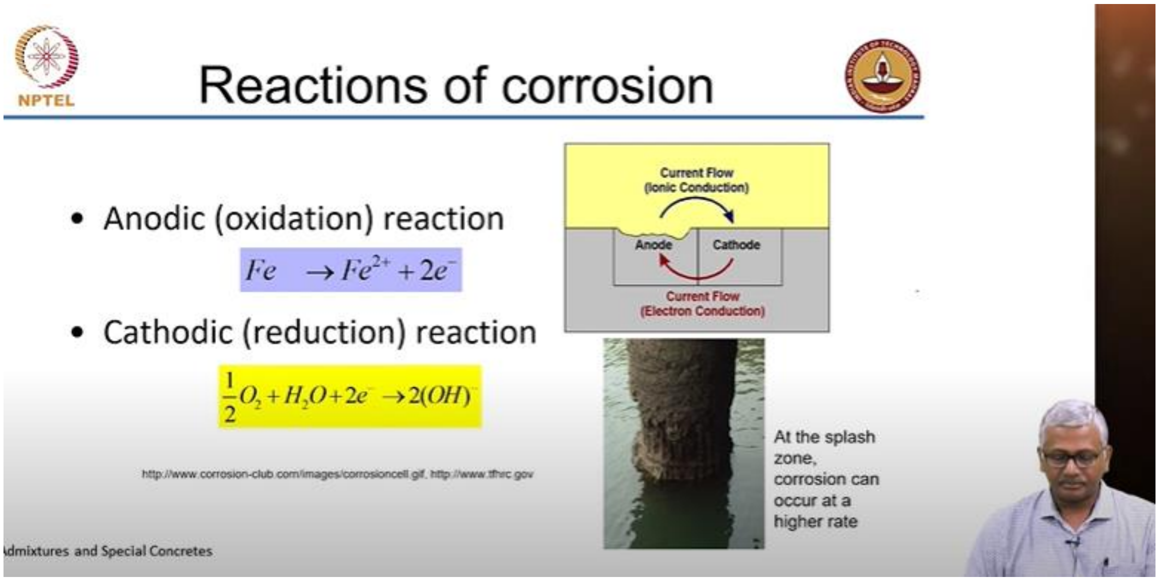

Reactions of corrosion

- Anodic (oxidation) reaction

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

- Cathodic (reduction) reaction

$$\frac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2(OH)^{-}$$

At the splash zone, corrosion can occur at a higher rate

http://www.corrosion-club.com/images/corrosioncell.gif, http://www.tfhrc.gov

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So the anodic and cathodic reactions in perfect balanced conditions are given here and the kind of deterioration that typically happens in a column that is submerged in sea water or partially submerged in sea water is given. The maximum deterioration is seen in the zone which is at the interface of the sea and the air and also where the sea level perhaps changes because of tidal actions and also there is mechanical abrasion because of waves and that causes greater level of deterioration in this kind of a zone. So there are several mechanisms that lead to deterioration of the concrete but primarily we are interested in what causes the corrosion of the reinforcing steel and in sea water the agent that leads to corrosion obviously is what is the in sea water which causes corrosion? Chloride, there is chloride in sea water which causes corrosion.

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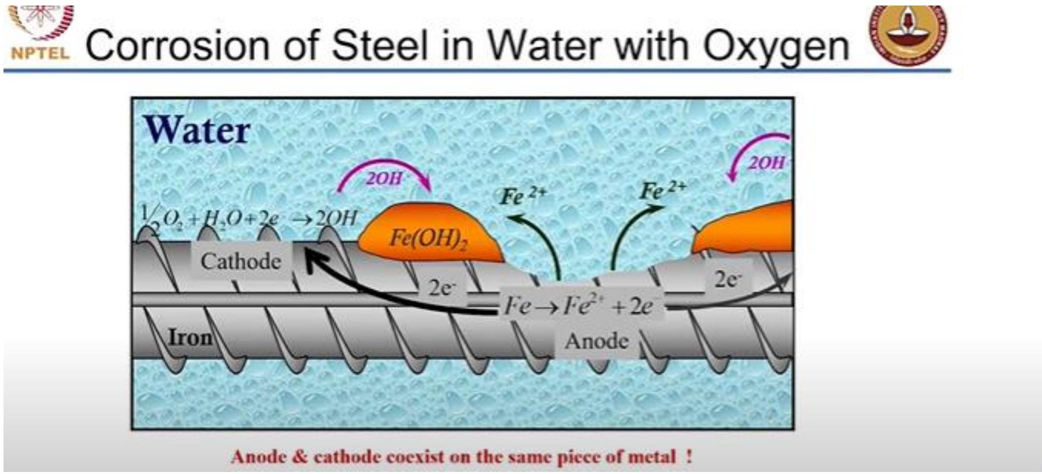

Corrosion of Steel in Water with Oxygen

Anode & cathode coexist on the same piece of metal !

Now again just steel in water with oxygen will have corrosion happening obviously you have the anodic reaction letting out your ferrous ions, you have the cathodic reaction which gives hydroxyl ions and then the combination leads to the formation of what we call as ferrous hydroxide. What is the common name? The corrosion product is called rust.

Now the rust can vary in its composition and therefore its colour depending upon the type of compound that is forming. Early formation happens of ferrous hydroxide then you may have ferric hydroxide that may further change to ferrous oxide or ferric oxide which leads to various different hues and colours of rust that you actually see. But one thing interesting to note is the anodic cathode can exist on the same piece of metal, the same steel bar can have some sites that act as cathode, some that act as anode. Now why does this happen? I would assume that okay when there are two steel bars close together one may behave as cathode other may behave as anode but why should the same steel bar have sites that behave as anode or cathode? Why should potential difference arise on the steel surface?

So any concentrations may be different in different portions of your concrete, what else? What else may happen? Well, we are assuming that concrete is uniform. Actually that is an interesting case because it may happen sometimes that the same rod may actually encounter two different confidence but as far as possible we have to minimize that happening. The differences due to concrete have to be minimized but steel itself inherently will have some issues. What are those issues? For instance, at this location and at this location would there be any difference? What I meant to ask you is in the ribbed sections versus the non-ribbed sections would there be a difference? There will perhaps be some local strains in the ribbed portions which may attribute to that site being more active than the other site. What else can your composition of the steel may not be perfectly uniform across the entire surface? Differences in composition may make one site more reactive than the other site. If you look at microstructure of steel there are different phases present, some are more reliable to corrode as compared to the others.

Now in cold rolled steels or cold worked steels you are doing cold working, you are twisting when the temperature is low. So obviously you are inducing some internal residual strains in the system and those residual strains if they are not distributed uniformly you will definitely have some sites that act as anodic as compared to the others. Even a simple thing like a steel bar which is stored in the external atmosphere gets coated with dust at one location and you put this without cleaning you are then creating again differences on the same steel bar. One is covered with dust, the other is open so the access to moisture and oxygen is less in the zone covered with dust and more in the zone that is open. So there are differences that you are creating on steel bar sites which are not uniform. So that is why the same steel bar can act as both anode and cathode.

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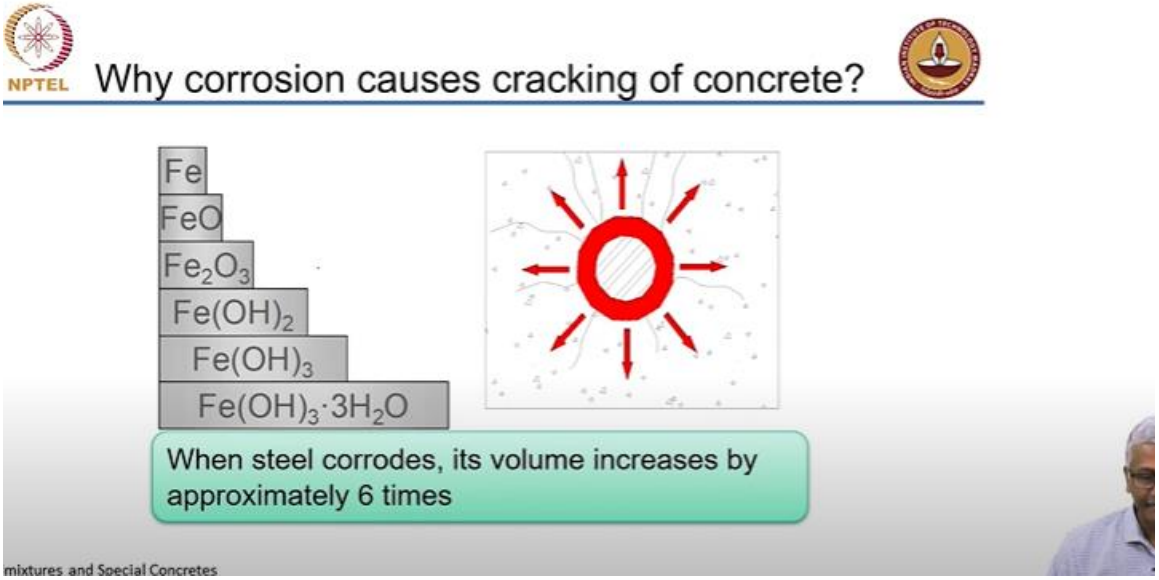

Why corrosion causes cracking of concrete?

When steel corrodes, its volume increases by approximately 6 times

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And corrosion or rust formation essentially leads to cracking and why does this cracking happen because your oxides and hydroxides of iron have a much greater volume than the original steel up to 6 to 8 times increase in volume can actually happen when steel corrodes leading to distress or tension in the concrete outside and tension in concrete is always accompanied by cracking.

Types of corrosion:

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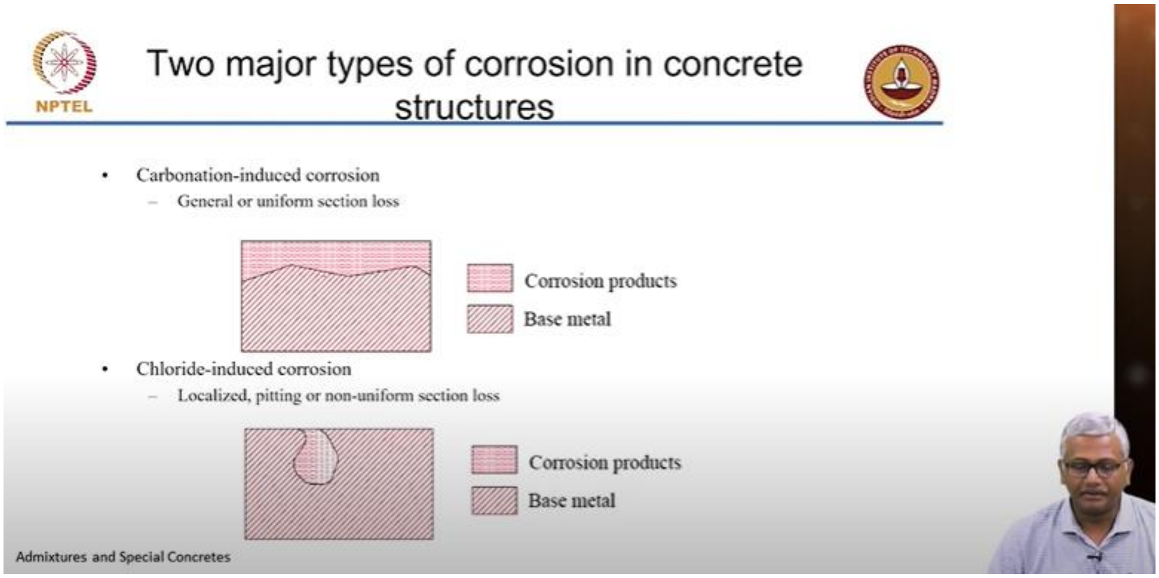

Two major types of corrosion in concrete structures

- Carbonation-induced corrosion
  - General or uniform section loss

- Chloride-induced corrosion
  - Localized, pitting or non-uniform section loss

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Now as far as concrete or reinforced concrete is concerned two major things that we need to worry about with respect to the cause of the corrosion itself. One is corrosion that is caused by chlorides, the other is corrosion that is caused by carbonation. Now this relates to the general atmosphere in which your reinforced concrete structure is servicing. A coastal structure obviously has much greater chances for chloride related damage and the issue with chloride is that it leads to a rapid pitting on the surface of the steel. So the loss is more non-uniform and that is quite dangerous because there are some sections of the steel where the cross section becomes so small that your load carrying ability of the steel bar is not there anymore. On the other hand in carbonation, the carbonation or the CO_2 penetration into the concrete, so let us say this is your reinforced concrete structure and that is your steel in between. So the CO_2 that comes in from the external atmosphere has to penetrate this concrete and generally moves as a front that is the CO_2 which has entered the concrete and it more or less approaches the steel surface all at the same time. So you get a more uniform rate of corrosion. Uniform corrosion is not as detrimental to the concrete or to the structural capacity of the concrete as the formation of a single large pit which may happen at certain locations.

So very important to understand that chloride induced corrosion can lead to much more devastating failures as opposed to carbonation induced corrosion. In what environments will carbonation happen? Generally most polluted areas but more often it happens wherever the relative humidity ideally is between 40 to 80%. Maximum happens between 60 and 70%. Maximum rate of carbonation, carbon dioxide induced corrosion or rather carbon dioxide penetration is possible in the 60 to 70% relative humidity range but it can happen all the way up to 80%. Beyond that the concrete is almost getting saturated. So if the pores of concrete are saturated with water it is not easy for the gas to diffuse. There is no space for the gas to come in and there is only so much of CO_2 that can dissolve in water. But what about the other end, very dry concrete less than 40% RH. Why is carbonation not a problem there? Moisture is not there. You need moisture to convert CO_2 into carbonic acid and that is what leads to the corrosion of the steel. Acidic conditions may not get generated because there is no moisture available. So you need to have some moisture but not a lot of moisture. Partially saturated systems are prone to carbonation and then you have wetting and drying cycles that may happen because of natural exposure of the concrete and that may also change the rate at which CO_2 penetration happens. So you have to be careful about modelling this kind of phenomenon. In the lab we always do this with accelerated carbonation exposure. We increase the carbonation concentration and allow the carbon dioxide to move in much faster but in reality it is much slower. What is the atmospheric composition of carbon dioxide? The concentration of carbon dioxide in the atmosphere, what you and I are breathing now? Point 0.04%, about 400 ppm, 0.04% is the CO_2 concentration but if you look at experiments which are done in the lab we do it at either 1%, 3%, 4%, sometimes 50% of CO_2 also is used. That is very high amount and correlating those experiments becomes quite difficult. But anyway we need to understand the rate of CO_2 penetration into concrete and more than that we need to understand what the instances are where corrosion will happen. For that I will go back to this diagram here. When steel is corroding it needs oxygen and moisture for corrosion to happen. For steel to corrode oxygen and moisture are necessary to be present at the cathodic sites Without that you are not really causing or propagating corrosion which may initiate but propagation requires oxygen and moisture to be present. And if your concrete is impermeable you will further restrict the possibility of corrosion because oxygen and moisture are not available. Similarly if you are in zones where carbon dioxide penetration is high but then there is not sufficient moisture available to cause the corrosion you may get CO_2 penetration deep into the concrete but perhaps there may not be much chances of corrosion. And this is indeed the case wherever people see that the extent of rainfall is limited because unless you have rain there is no moisture that comes into the concrete. If you have prolonged periods of rain followed by periods of drying where CO_2 can penetrate again followed by rains in such cases you need to be very careful about carbonation induced corrosion. But if your atmosphere is mostly dry even though the humidity may be 50-60% you may not really get corrosion due to carbonation.

But chloride as long as it is present in the vicinity will certainly cause corrosion and it is not just in coastal structures you get chloride corrosion you may also get sometimes in inland structures where chloride concentrations are high in the groundwater. For instance in Delhi interestingly the chloride concentration in the groundwater are very high. And there is a study that was done by our environmental engineering group which showed that the burning of micro plastics also increases the chloride load of the soil. And this chloride eventually makes its way to the groundwater and that can also lead to corrosion. Nobody would have thought this. Imagine of course most of the studies in Delhi were done with respect to understanding the issues of pollution because of crop burning but this micro plastic burning was another big problem like your small polythene covers and all that they make their way into the composting yard they get burnt and this micro plastics will release this chloride available in the system and that also adds to the load of chloride in the soil. It combines with the water or dissolves in the water and is available for corrosion of the steel. So you would not never imagine that chlorides would be present in a place like Delhi but yes groundwater there has fairly high chlorides in some regions.

Carbonation induced corrosion:

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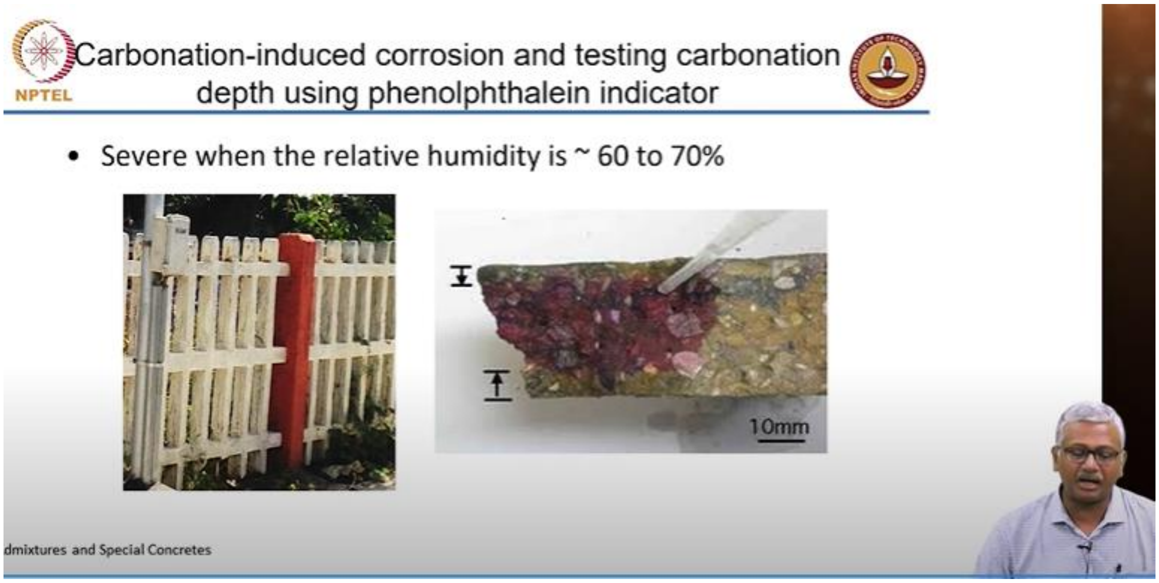

Carbonation-induced corrosion and testing carbonation depth using phenolphthalein indicator

- Severe when the relative humidity is ~ 60 to 70%

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So this is a typical case of a carbonation induced corrosion. You have very thin members, thin reinforced concrete members so it is not going to take long for the CO_2 to penetrate to the extent of the steel and if there is rainfall that provides moisture you will definitely get corrosion that leads to cracks like this. So this is a telltale sign of corrosion. All along the steel there is cracking that is a very clear sign of corrosion happening. So to assess corrosion what typically is done is you take a sample of the concrete and you spray phenolphthalein on the cut surface. You split it so that you expose the surface and you spray phenolphthalein wherever you get no coloration is the zone that is carbonated. Wherever you get pink coloration is the zone which is not carbonated which is high pH. You would have done phenolphthalein test in chemistry lab in school. So in alkaline environments it turns pink. It is colorless when the pH reduces to around 9. So why does carbonation reduce pH? Because it combines with your calcium hydroxide to make calcium carbonate and it reduces the alkaline buffer that is present in your system. So pH reduces when CO_2 enters the concrete.

Chloride induced corrosion:

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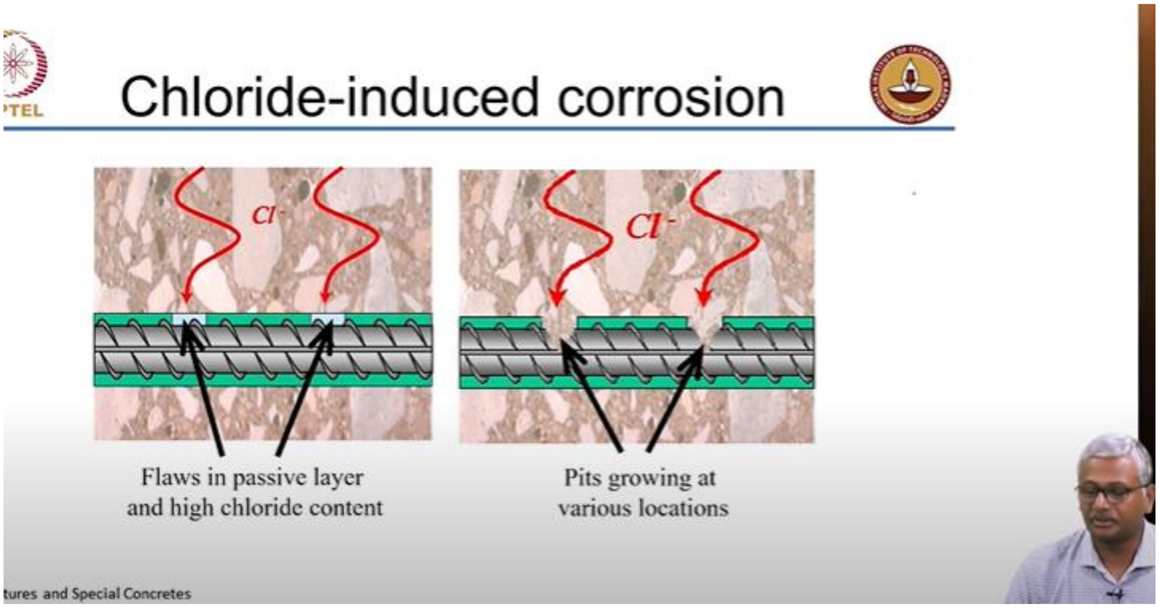
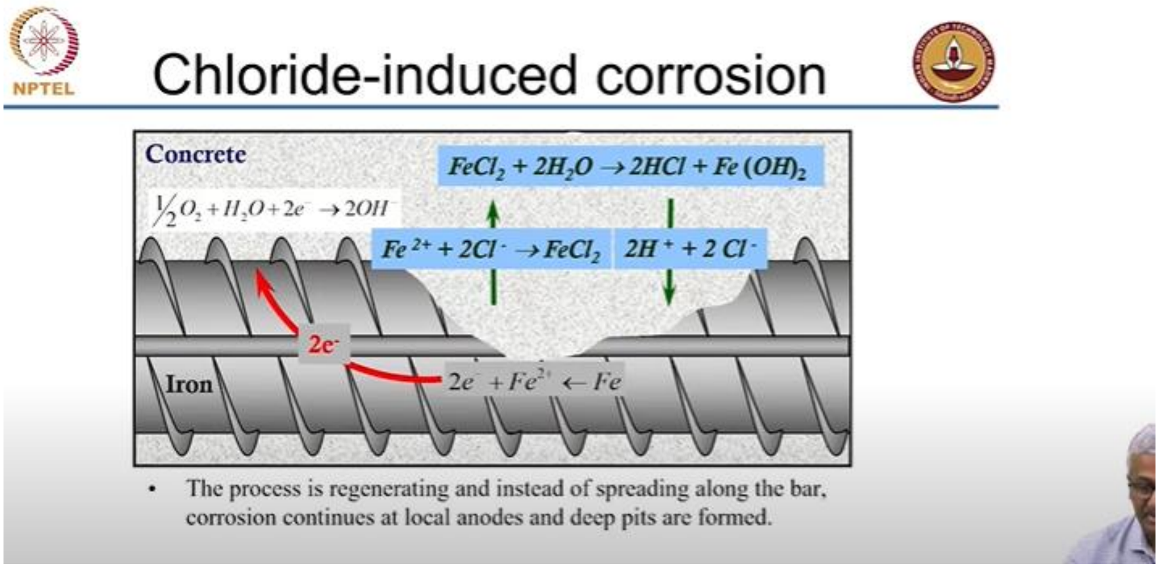


Chloride-induced corrosion

Flaws in passive layer
and high chloride content

Pits growing at
various locations



Chloride-induced corrosion

$FeCl_2 + 2H_2O \rightarrow 2HCl + Fe(OH)_2$

$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

$Fe^{2+} + 2Cl^- \rightarrow FeCl_2$

$2H^+ + 2Cl^-$

$2e^- + Fe^{2+} \leftarrow Fe$

- The process is regenerating and instead of spreading along the bar, corrosion continues at local anodes and deep pits are formed.

In chloride induced corrosion depending on the locations where permeability is greater maybe because of some cracks appearing in the surface or maybe because of some other defects that are present in the concrete in some locations you have chlorides entering more and chlorides have a tendency to completely eat away the passive film. So here the passive film is indicated by the light green layer. The chlorides will have a tendency to completely eat away the passive film and indeed what happens is actually in the process you are actually generating more acidic environment in the system and this acid further damages the steel. So you get pit formation this is called pitting corrosion and that is really problematic because it reduces now look at this cross section it is now reduced by more than half. So your load carrying capacity of the structure is getting severely limited now because of the pitting formation. Other regions may be free of corrosion but then there are some regions where this can happen so your steel will just snap. You may not get lot of corrosion products forming in this case. You are not seeing lot of corrosion products forming even without that also you can cause significant damage. But of course $Fe(OH)_2$ is also going to form and that will further add to the damage by cracking the concrete. If concrete cracks more chlorides get in the reaction is speeded up even more. So if you typically look at the damage due to corrosion and you plot that with respect to time you will see this kind of a relationship initially there is very little damage then there is suddenly high damage and finally very high damage. So there are 3 essential zones this is the zone where the steel is mostly passivated that is because the film is intact in that zone. So while I put some damage here but actually there is close to 0 damage in that zone.

So if you have to design a structure for 50 years you have to ascertain that this passivation of the steel will not get broken for 50 years that is a safe design. That means you do not want corrosion to start at all during the life cycle of the structure. You can also adopt a slightly more risky design approach where you say that okay I will allow up to 10% damage to happen and that will allow you to design for a greater service life but then you need to have some detection of whether corrosion is actually happening in your system or not and any repair is needed to further enhance the service life. But the problem is when it starts getting into this region beyond the passivation the properties become unpredictable the extent of cracking starts dictating the rate at which your chlorides come in and because of that cracking happening the later age damage basically increases significantly.

So again I am not talking about modelling in this chapter but what I will essentially talk about where we can actually start looking at solutions to increase the service life. Mostly we will want to work in this time for deep passivation of the steel that is where we want to really focus our recovery or our strategies for increasing corrosion resistance of the reinforced concrete.

Pitting corrosion:

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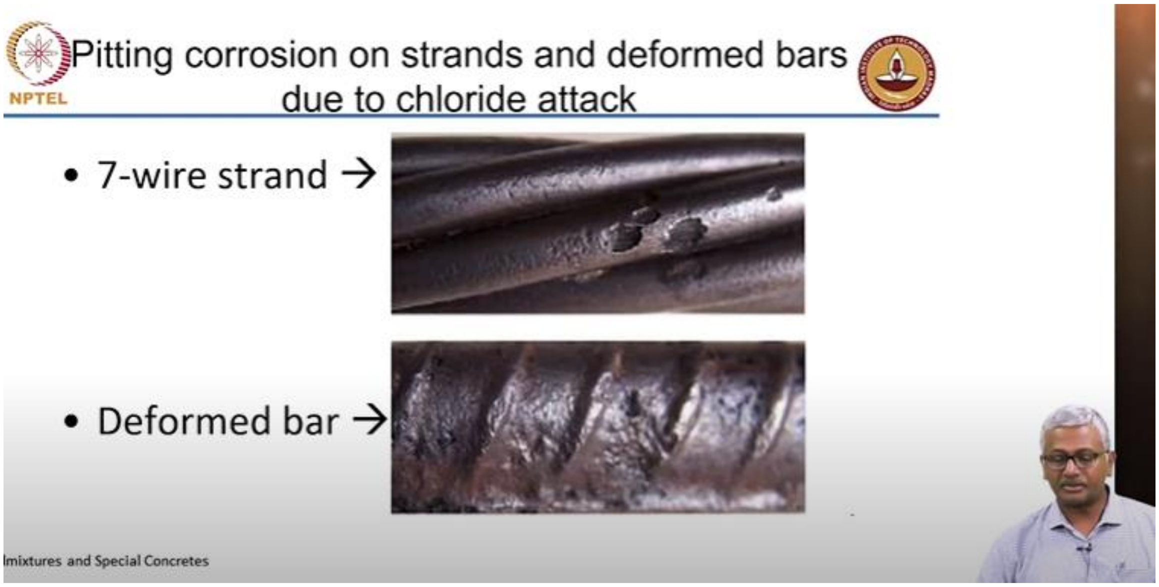

Pitting corrosion on strands and deformed bars due to chloride attack

- 7-wire strand →
- Deformed bar →

So this is again an example of pitting corrosion happening in prestressed strands so you can see very clearly pit formation on the surface of prestressed strands. In prestressing concrete or prestressed concrete corrosion of the strands is even more dangerous because we know that we rely on that for the load carrying capacity. In reinforced concrete there is sufficient redundancy so if one steel gets corroded we have sufficient redistribution that can actually happen. Lot of cracking can happen before the failure happens but in prestressed concrete one crack can lead to complete collapse especially when it is leading to a steel strand damage that will lead to a complete collapse.