## **Advanced Concrete Technology Dr. Manu Santhanam Department of Civil Engineering Indian Institute of Technology - Madras**

## **Lecture – 40 Durability Issues in Concrete - Part 4**

So continuing from our discussion yesterday, we will look at some other instances of chemical attack of concrete. We talked about sulphate attack, delayed ettringite formation, chloride attack and we also talked a bit about acid attack which is emerging as in  $(0)$   $(00:30)$  study because there are lot more instances of acid related damage that people are finding in concrete structures.

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## Seawater attack

- Combined effect of sulphates and chlorides
- In addition to chemical attack, other complications are also involved:
	- Tidal zones subjected to drying and wetting (salt crystallization)
	- Splashing action of waves leads to mechanical degradation



So you do not have the problem that you commonly see with sulphate related exposure. So what you think would be a preferred mechanism as far as seawater attack is concerned.

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Since we have both sulphates and chlorides, C3A is not really helping out in the case of sulphates but C3A is important in the case of chlorides. So how should we decide what sort of cement to be used for marine exposure? **"Professor - student conversation starts**" Sorry, (()) (01:25) create expansions because of ettringite formation. (()) (01:35) okay. So if you can reduce the pH and how do you reduce the pH? (())  $(01:39)$ .

Yes, you can use supplementary cementing materials, okay. You can reduce the conditions of expansion-related deterioration because ettringite formation at moderately lower pH will not lead to the same kind of expansion as ettringite formation at very high pH, okay. **"Professor student conversation ends"**

So having a supplementary material will help in that instance further. Using a supplementary material will also reduce the gypsum formation in the system due to sulphate attack. But at the same time as far as chloride attack is concerned, most mineral admixtures also tend to have reactive alumina present in these materials. The reactive alumina tends to further act with the chloride binding.

So irrespective of what type of mineral admixtures that you end up using, the commonly available mineral admixtures either calcined clay or slag or fly ash, most of these will contribute reactive alumina which may end up binding the chloride ions. So apart from the C3A from the cement, there will also be reactive alumina available from mineral admixtures that will end up binding the chloride ions.

So obviously you will have a positive affect whenever mineral admixture is used as cement replacement in marine environments. Now as far as cement itself is concerned, what type of cement would you choose? Would you choose a sulphate resistant cement or would you go with the regular or ordinary Portland cement. **"Professor - student conversation starts**" (()) (03:00) sorry. Why would you go for a sulphate resistant cement? **"Professor - student conversation ends"**

Because you have very low C3A there. So unless you are of course going for a combination of sulphate resistant cement and a pozzolanic material, it may just be beneficial to go for a regular OPC along with the supplementary material because you can have the high the C3A from the OPC again beneficially acting in terms of chloride attack and the aspect clear that you need to consider is that the chloride concentration of seawater is much greater than the sulphate concentration of seawater.

So that is one aspect that has to turn the tide in its favour. So we will talk about that in just a minute. So in addition to this chemical attack, there are other mechanisms of extremely important. One is the tidal zones which are present in seawater that are subjected to drying and wetting here because of effect of tide, you will have drying and wetting of the concrete structures that are in seawater.

And then you will have this splashing action of the waves that leads to mechanical degradation. So if the surface is already getting degraded with the reactions with the sulphates and chlorides, the waves are simply impacting the softened surface and trying to remove the material on the surface. So you obviously have a compounded problem because of the physical degradation. Now chemically what does seawater contain?

This is actually from a textbook, it gives you that seawater concentrations of different ion, ionic species in seawater across range of different types of seas and oceans. So you see here for

example, if you look at the most critical environment that is what is found in the Arabian Gulf. We are talking about the coast of Kuwait, Dubai and all those countries which are in the Arabian Gulf.

So Arabian Gulf has a very high concentration of chloride, almost double the next highest concentration that is found in Mediterranean sea, okay and it has also got a very high concentration of sulphate, 5000 parts per million or mg/litre which is almost double that of the next highest concentration of 3000 in Red Sea, okay. So Arabian Gulf gives a very aggressive sort of an environment for the concrete and added to the fact that you have such high chemicals in the seawater, you also have extremely high temperatures that are there in the Gulf region.

So you can imagine the problem of durability as far as marine exposure is concerned. It is primarily very significant in the Arabian Gulf and in fact, if you design a durable concrete in the Arabian Gulf, you essentially understood the issues related to design of concrete in any environment which is exposed to hot marine conditions. Now please remember when we are designing looking at Atlantic Ocean or at least the Northern Atlantic Ocean, which is present in the colder climates, there you need to consider the fact that you have seawater attack in combination with freezing and thawing.

You have freezing and thawing conditions when you go for the Northern Atlantic regions. So that again adds another layer of complexity to the durability problems that concrete is facing and the performance of concrete can be critically affected by freezing more than the chemical attack happening because of seawater. So you need to consider all these aspects happening together at once and be able to address these through appropriately designed durability investigations, okay.

So just for your information, this is the kind of seawater concentration that you find in different parts of the world. Now the British Research Establishment, BRE created simulated seawater exposure conditions which had this concentration of the ionic species present in the water and a lot of the current standards across the world which gives you stipulations of water-cement ratio and binder content and grade of concrete required for or prescribed for marine exposure conditions.

A lot of those values actually arose from the research done at the British Research Establishment. So we owe a lot of our coded regulations to the research work that was done over a period of 20- 30 years at the BRE. So most of those values we see, water-cement ratio are less than 0.4 or 0.45, all that is arising from this long-term recent study performed at BRE.



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Now of course, this is a classic picture from work done by Mehta. Mehta is one of the pioneering concrete technologist. He is now retired but he worked for lot long years at the University of California, Berkeley and he has worked extensively on durability problems with concrete and this image of his probably is the most widely used image as far as seawater attack is concerned. It very clearly brings to light what are the different environments for the concrete column which is standing in seawater.

You have the atmospheric zone which is above the tide level and you have the tidal zone where you have the affects due to the low and high tides, drying and wetting effects as well as this is the area where the splashing of the waves is also critical and then you have the zone which is always submerged or below the level of the low tide. That means the concrete is continuously immersed in the seawater in that environment.

So the kind of mechanisms that are affecting the performance of concrete will differ based upon

the type of environment. So here you have chemical decomposition if you are under the level of the low tide and we also discussed earlier, you have a constant pressure of the water, so you also have permeation of the water that is happening inside. So the kind of transport mechanisms associated with the different zones would be quite different, okay.

In the case of a splash zone, you have in addition to the chemical attack, you also have the splashing action of the waves, the drying and wetting caused by the tidal effects and also cracking may happen because of freezing conditions and in general, your regular thermal and humidity gradients can also lead to cracking in this zone, okay and then you have the atmospheric zone where the primary effect is the saltwater spray which is going to bring the salt to the surface of the concrete, okay.

So if you have to design concrete for a marine environment, obviously the choice would be to design it for the part that is exposed to this splash zone. You consider that to be the most critical component and design your concrete structure as per that. So all your requirements for concrete cover over the reinforcing steel, the qualities of the cover concrete everything has to be based on the requirement of concrete for the splash zone.

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Now the next problem that is dealt with in a very large extent as far as concrete structures are concerned is carbonation. Now we have talked briefly about carbonation earlier. We talked about the fact that whenever you have mineral additives in concrete, they tend to reduce the amount of calcium hydroxide available in the system and that buffer, the alkaline buffer that you remove from the system, often is responsible for a greater depth of carbon dioxide penetration into the system, okay.

So CO2 attack is generally higher whenever cement is replaced by mineral additives that tend to bind the calcium hydroxide into pozzolanic CSH. So here the idea of carbonation is that carbon dioxide is diffusing into the pores of concrete and reacting with calcium hydroxide first. It will also react with other calcium bearing species. The carbon dioxide will also end up reacting with other calcium bearing species.

I will tell you why that happens and overall, the major result is the reduction of the pH of the system and when the pH goes below critical level, steel starts corroding, okay. So again that was, the primary effect of carbonation is the fact that steel corrosion is initiated in the presence of carbon dioxide environment. Otherwise, the properties of concrete are actually positively increased.

For example, the strength of concrete, right, it is going to be enhanced because of carbonation because you are converting calcium hydroxide into calcium carbonate. So if you take plain concrete and subject it to carbonation, you may actually register a strength increase with time but if you take reinforced concrete, the corrosion of the reinforcement is going to get initiated because of reduction in pH caused by carbonation.

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and a fine · Carbonation typigally occurs in a range of relative humidity (40 - 80%); too dry or too 0.V wet a concrete does not have a carbonation problem . Moisture is essential during this process, to convert the CO<sub>2</sub> into carbonic acid نی  $Ca(OH)_2 \to Ca^{2+} + 2OH$  $CO<sub>3</sub> + 2OH \rightarrow CO<sub>3</sub> + H<sub>2</sub>O$  $Ca^{2+} + CO<sub>2</sub><sup>2</sup> \rightarrow CaCO<sub>2</sub>$ P. H. Emmons. 'Concrete Repair and Maintenance Illustrated.' R. S. Means Company, Kingston, MA

So if you look at the conditions under which carbonation happens, you have to be aware of the fact that when you have a very dry or a very wet condition, gaseous diffusions through a concrete cannot happen easily. If you have a very dry condition, of course, gasses will diffuse in quite easily but carbonation can only be accomplished when there is at least some moisture available because the carbonate or carbon dioxide needs some moisture to convert it to the acid form or carbonic acid form, okay.

Carbon dioxide needs some moisture to convert into carbonic acid which can then react with the cementitious phases to lead to the formation of calcium carbonate. So if there is no moisture available in the system, you will not have the conversion of CO2 into carbonic acid, okay. So the first step in the carbonation reaction after diffusion of CO2 is the conversion of CO2 into carbonic acid and this carbonic acid then reacts with the cementitious phases either calcium hydroxide or CSH or other calcium bearing phases.

Even ettringite for instance can get carbonated and lead to the formation of calcium carbonate and gypsum, okay. So again carbonation can happen based on the reaction of carbonic acid with any of the cementitious phases. So after it becomes an acidic phase, reaction is quite similar to any other acid attack, right. What will acid attack do? It will tend to leach out the calcium. Here, the calcium will be leached and then bound into an insoluble material that is calcium carbonate.

Now calcium carbonate incidentally happens to occur in many different crystal forms. The common crystal form is known as calcite, okay but you may also get other forms of calcium carbonate including Vaterite or Aragonite. The present research is trying to understand what really happens when cementitious systems that incorporates supplementary materials like fly ash and slag get carbonated.

Do we still get the same kind of reaction products? That means is it always calcite that is forming or we are forming other polymorphs of calcium carbonate that has some significance in understanding what is the porosity of the concrete going to be after getting carbonated, okay. I will talk about that just in a minute. So for a very dry environment, you do not have sufficient moisture available to convert CO2 into carbonic acid, okay.

So at very dry conditions, less than 40% relative humidity, you do not really have a danger of carbonation. Now when you go to very wet conditions, 80% or more, CO2 diffusion is impeded because you have pores that are saturated with moisture. So if you have pores saturated with moisture, gaseous diffusion cannot happen easily, okay. So the critical concentration or critical relative humidity is 40-80% and more critical the peak happens typically between 60-70%.

The peak carbonation attack will happen primarily at humidities of 60-70%. Now if you look at coastal environments, your humidity is typically will be always of the order of 75-80 or even more, okay. Very rarely will you get humidity levels that are less than 70%. You can have several days where humidity is less than 70% but on a persistent basis, you will not have humidities which are lower than 75-80% in a coastal zone but when you move inland, it is quite a reality that you can actually get this range of humidities almost on a constant basis affecting your concrete structure.

So you have to be clear about the fact that when you are moving away from the coast, the dominant mechanism of damage of your concrete will change from chloride attack to carbonation, carbon dioxide attack and both chloride and carbon dioxide are closely associated with the initiation of corrosion of the reinforcing steel, okay. So from both these perspectives, you need to address the issue of corrosion which we will take up in the next chapter.

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Now what do supplementary materials do to carbonation? We have done an extensive research program here which tries to look at how the rate of carbonation changes when cement is substituted by supplementary materials like slag and fly ash at different percentage replacements. So here you have 15%, 30% and 50% of slag. 15%, 30% and 50% of class F fly ash and 15% and 30% of class C fly ash.

And here we were doing carbonation inside the accelerated carbonation chamber which I discussed in the last chapter which is simulating a condition of carbonation which has CO2 concentration which is nearly 25-40 times that of atmospheric carbonation, okay. So what we were able to get from this is the fact that when you have 15% or 30% slag, your carbonation rates or the extent of carbonation depth is not that much different as compared to OPC.

But when you move to 50%, the carbonation depths are increased as compared to OPC. With fly ash, even 15% of fly ash, class F fly ash, that means the low calcium fly ash, even at 15%, the extent of carbonation or carbon dioxide penetration is greater than that of Portland cement. So when we are using PPC, you can expect that the depth of carbonation is going to be greater when PPC is used instead of OPC.

Now of course, at 30% and 50%, the carbonation depths are further increased when you

substitute cement with fly ash. With class C fly ash, you do not see that much of an increase at 15% but you see some increase at 30%. Again class C fly ash is contributing lot of calcium. So any system that is rich in calcium like slag for instance or class C fly ash, at lower dosages will not really suffer the same extent of carbonation as a type F fly ash.

So you have to understand that. The depth of carbonation will directly depend on how much carbon dioxide can be consumed by the calcium bearing phases in the system. So what we have seen is generally the carbonation depth is higher primarily because of this lesser carbonatable content. That means you have reduced the amount of calcium bearing compounds in the system because there is more silica infusion, you have reduced calcium, you put more silica in the system.

There is coarsening of the pore structure that happens due to the carbon dioxide penetration, okay. I will talk about why that happens in just a minute and that leads ultimately to an increase in total porosity. Now why I am saying this? So in normal cement, I told you that carbonation actually increases the strength of the concrete. Why? Because you are converting the calcium hydroxide phase into calcium carbonate, okay.

Now when your PC with SCM, what happens? You do not have much calcium hydroxide. So the CO2 will directly react with the CSH, okay and that will produce calcium carbonate and silica gel. The silica gel just like what we saw in the case of sulphate attack tends to be noncementitious and porous. So that is where your porosity of the system is getting increased and further in the last slide, I talked about the fact that your calcium carbonate can form in different crystalline forms, okay.

The overall space occupied by these different polymorphs is quite different, okay. So it turns out that this calcium carbonate that forms here is a very dense phase, is a very dense phase. So that means, what it will do? It will occupy less or more volume? Less volume. It is a very dense phase, occupies very less volume. So although the calcium carbonate itself is a strong and dense material, it is now occupying a lesser volume because of which it creates a coarsening of the pore structure.

So when concretes with supplementary cementing materials get carbonated, you do form dense phases but you end up coarsening the pore structure and increasing the total porosity because of which more CO2 can now penetrate the system, right. You create more porosity, so more CO2 penetrate the system. So that is why we generally end up seeing greater depths of carbonation, okay.

But again you have to understand the fact that this increased depth of carbonation does not necessarily mean an increased rate of corrosion because corrosion will also demand the presence of water and we know that in concretes that are saturated, carbonation is not really a big issue, okay. So when you have drying and wetting environments, that is where you will have the issue of in the drying environment, you will have CO2 penetration.

In the wetting environment, you will have the access to corrosion. So it is not that simple to convert this rate of carbonation to the rate of corrosion. It has to be understood by the help of experimental investigations whether carbonated concrete when it is prepared with different types of binders, will lead to the same or different levels of corrosion of reinforced steel.



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So again this is just showing you some research data based on the extent of carbonatable content present in your system against the depth of carbonation. So here with OPC, fly ash, slag and silica fume, this graph simply presents the extent of carbonatable material that is present in the system. That means the calcium bearing phases that are present in the system and for the same materials, the depth of carbonation is given for different concretes with different water to cement ratios.

So you see here when you use silica fume, you do not really create a much greater depth of carbonation as compared to OPC but with fly ash and slag, you generally end up having a greater depth of carbonation, more, greater with fly ash and less with slag. So of course here you should understand fly ash is at 30% and slag is at 50%, okay. We are always looking at that as the reference mixture for fly ash and slag based systems and silica fume typically will be 5%-10%, okay.

That will be a reference mixture because we have seen from our understanding of supplementary materials that these materials are typically used at such dosage levels. Now what you have to also understand is in all these systems, you need to specify at what age you started carbonating these systems. Why is that important? Because with increase in age, your structure also is changing, you produce more CSH, you consume more calcium hydroxide and pozzolanic materials are available, you are changing your pore structure with time, right.

Because of that you need to specify what age the concrete has achieved before it was exposed to the carbonation environment and it has been seen that especially with fly ash and slag, the longer your cure, the better the resistance that you have to carbonation. The longer you cure, the better the resistance to carbonation.

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Now what happens to the pore structure itself? These are results from our lab based on mercury intrusion porosimetry studies for concretes that have been carbonated. These concretes are first of all made with fly ash and with the LC3 2 different binder systems. So the solid lines are noncarbonated and the dash lines are the carbonated system. So what is happening here if you compare the 2 green curves, as we have discussed earlier with results of MIP, if you have a shift in the diameter that means you have coarsened your pore structure, you have basically made it more open.

The threshold diameter which is basically the critical diameter beyond which a lot of intrusion of mercury occurs that has been increased upon carbonation and both fly ash based systems and LC3 based systems are showing that increase in the threshold diameter and also there is an increase in the total porosity in the LC3 system that you see here after carbonation. So concretes with mineral admixtures will tend to coarsen a lot more as compared to concretes with ordinary Portland cement.

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And again microstructurally, you can also see the effects. On the left, you have a non-carbonated mortar which shows the regular cementitious hydration products like calcium hydroxide, CSH and ettringite and on the right, you have the formation of the calcium carbonate, extensive deposit of calcium carbonate along with some silica gel around a group of hydrating cementitious particles.

So these are C2S particles, okay. There is CSH presumably which would have been surrounding it earlier but the CSH has been converted to calcium carbonate and amorphous silica gel, okay. Because of this, you have a loss of your cementitious characteristic, you have an increase in the extent of porosity that happens in your system.

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And again, this is showing you the x-ray analysis taken on a point by point basis in the CSH which shows you the extent of carbonation that is happening in these systems. So you have a reduction in calcium to silica ratio in the inner CSH. That means your calcium is getting removed from this system. Any acidic condition will tend to remove calcium from the system, okay. Carbonation also essentially is an acidic condition similar to your other acid attack.

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# Carbonation shrinkage

- Even though the total volume of the products is greater than the reactants, there is a shrinkage associated with the dissolution of the CH
- Magnitude is not large
- Weight gains due to carbonation have been noticed



Now what is not very clearly understood about carbonation is the fact that there is also a shrinkage associated with this process. We have talked about the fact that your calcium carbonate forms is a denser phase. So the product ends up occupying a lesser volume as opposed to the reactant. So there is a shrinkage associated with this process of carbonation and magnitude is not large, okay and in fact in systems which are subjected to carbonation, you can also detect the weight change, usually a weight increase corresponding to carbonation but there is a volume decrease.

So that means you are ending up forming much denser phases with the help of carbonation but this subject is not very clearly understood because there is no clear way of actually assessing the extent of this shrinkage that happens because obviously it is compounded by other problems like drying shrinkage at the same time.

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So with that we come to the end of this chapter. I would like to acknowledge Prof. Doug Hooton form University of Toronto and Prof, Paramasivam from National University of Singapore for some of the diagrams and illustrations as well as some research results which were not from our laboratory, okay.

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So far we have discussed about the general mechanisms affecting durability problems with concrete and we took an extensive, we took an extensive understanding of chemical attack of concrete that is brought about by different types of chemical species, okay. One common issue that you would have seen in most of these chemical attack was the fact that the alkalinity of the concrete was getting reduced and conditions that are favourable for corrosion by getting created because of this reduction in alkalinity.

Corrosion is a problem that we have talked about before affects the structural integrity of the entire structure rather than just the integrity of the concrete because here we are talking about the reinforcement which is getting deteriorated inside the concrete and reinforcement deterioration leads to a loss of structural capacity.

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## Introduction



So corrosion happens to be a problem that we need to deal with on a more serious note as compared to some of the other durability problems which are usually fixable with some regular measures like reduction in water-cement ratio and reducing permeability of the system. With corrosion, we need to be a little bit more careful because the kind of mechanisms that lead to corrosion, the kind of protection systems that we device have to ensure that the service life of the concrete is not getting affected.

Service life of the structure is not getting affected. So of course, you must have come across these figures before that corrosion of reinforcing steel in concrete leads to large amounts of money being spent in repairs. So we are talking about 5% of the developed nations GDP just to repair corrosion-related damage.

And particularly when you talk about reinforced concrete bridge desk in the US alone, the estimated that the yearly cost is varying between 50-200 million dollars just for bridge desk constructed with reinforced concrete. So you can just extrapolate this to the extent of reinforced concrete structures around the world and see the kind of damage that is inflicted by corrosion and the extent of money spent in repairing corrosion related damage.

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## Corrosive environments

Marine, coastal, and carbonation



So first before we talk about the process of corrosion, let us take a look at what are these corrosive environments for which we need to design the concrete and of course this is taken from the fact that corrosion is primarily initiated by 2 major environments. One is chloride reduced corrosion, the other is carbon dioxide or CO2-induced corrosion. So we will look at marine, coastal and carbonation based environments.

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## $IS456 - Exposure classes$

- Severe: Concrete completely immersed in sea water; Concrete exposed to coastal environment (???)
- Very Severe: Concrete surfaces exposed to sea water spray
- Extreme: Surface of members in tidal zone

If you look at IS456, the Indian Standards which are currently in practice for buildings, the exposure classes that are defined in IS456 are divided into severe, very severe and extreme. There is some definition given as to what these means but there is no clarity in defining the exposure environment which is classified as coastal environment. Now we had discussion earlier that some other codes give you a little bit more guideline as to how far from the coast you can consider as a coastal environment.

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Nevertheless, what we have in IS456 is a description for the mixed design of concrete for the specific environment. You have a requirement for example if you consider the severe environment, you have a requirement of at least 30 Mega Pascal concrete. You need to have a requirement of maximum 0.45 water-cement ratio.

And you have requirement of minimum 320 kilograms per cubic meter cement content in your system, okay. So once you do your concrete mixture design for a particular environment, you need to check the resultant proportions against these numbers and see whether your design that has been chosen satisfies the criterion. If so, then it is deemed to satisfy the criterion for durability.

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## **EN206 Exposure Classes**

- XS1 Exposed to airborne salt but not in direct contact with seawater (structures near to or on the coast)
- XS2 Permanently submerged (parts of marine structures)
- XS3 Tidal, splash or spray zones (parts of marine structures)



Now EN206 comes up with a slightly better enhanced definition of these exposure classes where they have the seawater based chlorides separated from chlorides coming from other sources, okay. The seawater based environments are divided into 3 classes, XS1, XS2 and XS3. This is exactly based on the kind of aspect that we saw in the last chapter for the distinction on the zones which are attacking a column standing in seawater.

So you have the atmospheric zone, you have the tidal zone and you have the submerged zone. So this is basically the seawater chloride classification, okay. Apart from this, they also have a classification for chloride attack from other sources. For example, when you have chlorides in ground water like the situation as in Delhi, okay. In Delhi, which is so far away from the coast, a lot of chloride exists in the ground water and that chloride has created a lot of corrosion-related problems.

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Now the table that they provide for the prescription for the different types of cements to be used and the quantity of the cement and so on and the water to cement ratio, etc., it is a little bit more intricate as compared to what we have in the IS456. I will just take a look at one or 2 of these 10 classes. So again as I said they have different exposure classes. There is a seawater based exposure class.

There is a chloride other than seawater based exposure class. There is an exposure class for carbonation-induced corrosion which is not present in the IS456 standards. There is another exposure classification for freeze-thaw attack which was covered to some extent in IS456 but not explicitly. Then there is other aggressive chemical environments for example sulphate and acid attack which again are treated to some extent in IS456 also.

So here what the European classifications do is that they give you the maximum water to cement ratio to be used in these environments, the minimum strength class of the concrete and that strength class is specified in terms of C followed by 2 numbers and this C basically means the concrete strength grade, just like we have M in India, they use C. But then 20-25, when it says 20-25, 20 is the strength measured on cylinders and 25 is the strength measured on cubes.

So one is the cylinder strength, the other is the cube strength because in Europe, certain countries use cylinder, certain countries use cubical specimens. So they provide a table which has both cylinders and cubes specified. They also provide the minimum nominal cover for these environments and you can see these covers are actually varying significantly based on the different types of exposure classes.

In our codes, we have only cover specified for the exposure classes either for foundations which are exposed to sulphated soils or you have the environmental classification of severe, very severe and extreme based on which again the cover is specified, okay. Air content range is obviously important from the point of view of freezing and thawing attack and that is also specified based on that and cement type again addresses the issue of using special types of cements in certain environments.

For example, when you have sulphate bearing environment, you need to look at combinations of cement that induce good sulphate resistance. So sulphate resistant Portland cement is used as well as combinations, composite cement combinations that we have talked about in cement composition chapter, okay. So again here with chlorides, they are generally trending to prescribed cements which are rich in slag or fly ash, okay.

Most of these cements are slag based cements which are clearly specified for the seawater. Again for the exposure classes for chloride other than seawater for the lowest exposure class, they ask you to use any cement but then when you go for a higher level of exposure XD2 and XD3, there are requirements for slag based or fly ash based cements, okay.

So again, this gives you again a description for a durability environment that addresses corrosion as well as other chemical attack. Of course, we are here going to be talking primarily about the carbonation and chloride-induced corrosions. So we are restricting our discussion to the exposure classes according to these.

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## Other codes

AS 3600 (2009):

Distance from coast defined in three categories: 1) Up to 1 km 2) Beyond 1 km and up to 50 km

3) Beyond 50 km with different exposure classifications.

No other codes give guidelines to select coastal zone! Only CPWD has a recommendation to treat distance up to  $10 \text{ km}$  as coastal  $\rightarrow$ Severe to Very Severe environment applies

Now as I said earlier, there are certain codes around the world which address the exposure classifications a little bit better. For example, the Australian standards, they describe that up to 1 km, there is one environment, coastal environment. Between 1 and 50 km, there is secondary coastal environment and beyond 50, you have an inland environment and again CPWD talks about 10 km from the coast as a coastal zone. That means within 10 km as per IS456, all our structures come under the severe category of exposure.

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Now what we did was evaluated the durability classifications or rather the exposure classifications given in different standards and came up with the slight improvement on what is currently available in the IS codes. There is lot of literature on this now, lot of people have been trying to address this issue. This is a shortcoming with our IS456 and we wanted to add some data to show that concrete structures that were built for CPWD, the student who worked with me was actually from the CPWD.

So for CPWD construction, the kind of concrete mixed proportions that were chosen based on the exposure to environment taken from IS456 led to sometimes inappropriate choices for the water to cement ratio and the cement content, okay. So based on that and based on the fact that so much development has taken place around the world, especially in the European standards and American standards, what we did was tried to bring those about and apply them to how we can change exposure classifications in the Indian construction.

Once again, the air-borne chloride exposure class was defined separately as opposed to the seawater exposure class, okay. So air-borne chloride exposure class was divided based on the distance from the coast. So up to 10 km was considered the closest to the coast. Beyond 10 and up to 50 km was another and then inland environment is something which is beyond 50 km. So here we are pulling the experience from the Australian code as well as CPWD and applying them together to the definition of air-borne chloride exposure.

So here D1, D2 and D3 are the names given for the exposure classification. Again this, prescript as specification for the grade of concrete cementitious content and water to cement ratio along with the cover is the specified for this. So this is again a new proposal. It has not yet been discussed by the code, codal agencies. It will take some time before these take effect. IS456 is in the process of revision and we are going to be submitting this also as a positive consideration for changing the exposure classification.

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The seawater exposure class is a lot simpler now. We have SW1 and 2. An SW1 is concrete completely immersed and concrete in spray or tidal zone. Why do we not consider the atmospheric zone concrete in this case? The atmospheric zone concrete which is subjected to seawater spray, why is that not addressed here? Because that gets covered in the air-borne chloride exposure class under the D1 category.

So you do not need to create that category again to seawater. You can just address it with 2 categories. So again, you have minimum grade of concrete and then you have cementitious content max water-cement ratio and clear cover. We are not deviating too much from what is already there in the standards. What we are simply trying to tell is that you can modify the classification systems to make it more appropriate with respect to the deterioration mechanisms.

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## Carbonation exposure class



#### Ramalingam and Santhanam. 2012

And then the carbonation exposure class, which is until now not available in our systems, can

consider again the benefits of what has been already prescribed in international standards and basically these are values taken directly from the European standards, okay. So again 3 different exposure classes with different grades of concrete. Of course, the definition of these exposure classes has to be given. C0 is concrete that is completely dry or completely wet, okay. That means there is no danger of carbonation.

C2 is the concrete that is most critical which is shelter basically, right. That means there is sufficiently high humidity to build up greater depths of carbonation. C1 is something that is subjected to drying and wetting. That means it is not as critical as C2 in terms of carbonation in depth, okay. So these are different service environments. You can see that the requirement for durability in terms of carbonation exposure is not that stringent as it is in terms of seawater exposure. The water-cement ratio required in seawater exposure is usually much lower than in the case of carbonation exposure, okay.

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So coming back to corrosion, so why does steel not corrode in a regular concrete which is unattacked? You know this very well that regular concrete has a high pH and in this high pH, there is a passive layer that forms on the system, okay. So this is the steel embedded inside concrete and around the steel, there is a passive layer and this passive layer is basically a mixture of stable corrosion products that happen in an alkaline environments. These are ion oxides and hydroxides. More typically it is called gamma FeOOH.

Basically this is ion hydroxides and oxides which are forming in a stable condition. This is actually corrosion of the steel which is happening in an alkaline environment but that alkaline corrosion leads to a protective barrier being formed on the steel surface, okay. So corrosion can occur when this concrete is subjected to aggressive conditions and this passive barrier on the surface breaks down because of some reasons. And again coming back to the reasons that causes passive barrier to breakdown, one is chloride, the other is carbonation.

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So once the corrosion initiates, okay, the sides on which the ion or Fe gets transformed to Fe2+ is where the anodes are located and the side where the electrons given out by the anode are taken up and have the formation of hydroxyl ions OH- is the cathodic region, okay. So there is current flow that is happening through the concrete that surrounds the reinforcing steel and this is where we discussed earlier that the parameter that really controls this factor is the resistivity of the concrete.

The more resistive the concrete, the more difficult it will be for the current to flow in the electrolyte that is concrete which is surrounding the reinforcing steel, okay. But within the steel, there is obviously current flow happening between the cathode and the anode. Electrons are moving in this direction, there is a current flow in this direction.

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So now if you look at this entire system, that looks more like a battery cell because there is a current flow and electron flow. I will talk about that later again. It is called the galvanic cell. So we call this process as a galvanic corrosion process. So oxidation reaction involves transformation of Fe into Fe2+. You give out 2 electrons.

The reduction reaction involves dissolved oxygen and moisture to produce hydroxyl ions, okay. So again this is giving you an example of concrete in the splash zone which has been heavily corroded and completely the concrete around steel has been spalled and removed from the system.

# Corrosion of Steel in Water with Oxyger Water  $0. + H_1 0 + 2e$ Cathode Anode & cathode coexist on the same piece of metal !

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Again, if you have corrosion of steel in water with oxygen, okay, you have the formation of the hydration, sorry, the corrosion products which is FeOH2 in the beginning, okay and this FeOH2 starts getting further oxidized and converted to other forms of hydroxide and then later to oxides because of which the color of the rust that you get at different stages could be quite different. At early stages, you see the reddish rust, then you see the brown rust and finally you see the black rust.

So these are different forms of hydroxides and oxides that are forming across the different processes that are happening in the system. Now what is interesting is? The anode and cathode are not really 2 different pieces of steel but they are existing on the same steel surface and that requires some idea as to why that actually happens in the system.

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So let us look at that. Before we see that of course this is again a depiction of your galvanic cell which is showing the ionic current through the electrolyte and the electron current happening through the concrete, sorry through the steel. So that is why it resembles more of a galvanic cell and this process is called a galvanic corrosion process.

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# Why do anodes form?

- · Compositional variances on the steel surface
- · Presence of dust/dirt etc. partially on the steel surface
- · Presence of local differences in applied stress
- Microstructural variations in the steel: (1) The ferrite phase is more active than the cementite phase, (2) Grain boundary atoms are more active compared to the bulk
- · Strained zones produced during cold working of metals may be more active
- · Presence of stress concentrations
- · Differences in oxygen concentration at different sites on the steel: generally, the site with a lower oxygen concentration becomes anodic

So why do anodes form on the surface of the steel? Again we know that most steel which is used for reinforcement is subjected to some sort of a mechanical treatment before it is actually used, okay. Mechanical treatment can create zones of residual stresses or strains. When you have residual strains or stresses present on the steel surface, that makes those sides more electrochemically active.

So more electrochemically active means the site has more propensity to become anodic, okay. Then you may have compositional variances on the steel surface. Steel of course we know has a very well defined composition but then there will be local differences in the composition of the surface that may lead to greater propensity for attack. Presence of dust or dirt partially on the steel surface.

Now when we store our steel bars on the site, often times we do not take care about cleaning them. So there is dust or dirt accumulation. So when there is dust or dirt accumulation, there is a shortage of oxygen and moisture when you put the steel inside the concrete. So those sites may become anodic because there is no oxygen and moisture available at that point and local differences in applied stress could also lead to this microstructural variation in the steel.

Strains induced during cold working of the steel, stress concentrations and differences in oxygen and moisture concentration will lead to creation of anodic and cathodic sites on the same steel surface and that is very critical for us to address because now this is not really one steel corroding because of another. It is happening on the same steel surface. So obviously the one thing we need to understand from here is that steel has to be used in an extremely cleaned state inside the concrete.

If you go to job sites, people seem to believe that the more rust that is on the steel, the better will be the bond of the steel and the concrete, that is obviously not correct because if you want to have a better bond, obviously you have the ribs that are formed on the surface of the steel and steel in general has a good bond anyway with the concrete, okay and the ribs are only further enhancing that bond.

The scale that is produced because of corrosion, because of improper storage of steel on the site, has to be cleaned properly before the steel is used in the concrete, okay. Because otherwise, it can create these differences even before you put the steel inside the concrete. Epoxy coating, another problem is that if you do not coat the epoxy properly on the steel, if you leave some zones, pin holes or blisters are created on the steel surface.

And those are the zones where epoxy is not coating the steel and you can directly create a difference between that point and the rest of the steel surface and start initiating the process of corrosion. So you need to be extremely careful with the use of steel. Unfortunately at job sites, we do not seem to pay much attention to these very simple aspects. Again bending of the steel bar, when you bend, there are likely chances of more defects or cracks forming at the bends.

Especially when you have coating on the steel, when you do bending, the coating will tend to break near the bends. Again that creates sites of local differences in the electrochemical potential. So all that has to be taken into account but the problem is there are so many factors that you cannot really address all of these and what you need to understand is steel will eventually corrode inside the concrete. Eventually steel will corrode.

The question is you need to prolong that process of corrosion until the end of service of the concrete structure. Thank you.