

**Maintenance and Repair of Concrete Structures**  
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**Lecture 6**  
**Deterioration of Cementitious Systems**  
**(Introduction, Sulphate attack, Biofouling and Acid attack)**

Hi, in the last module on deterioration of embedded metal or the steel reinforcement in the concrete, we discussed mainly about how the various types of steel can get corroded, corrosion mechanisms of different types of steels etc., are covered. In this module we are going to talk about deterioration of the cementitious system or the plain concrete itself.

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**Outline of Module on  
Deterioration of cementitious systems**



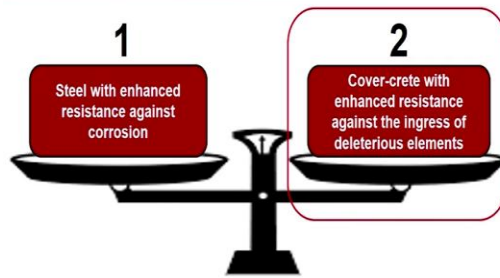
- Introduction to durable concrete systems
- Sulphate attack
- Biofouling and biogenic acid attack
- Freeze and thaw
- Alkali-Silica reaction
- Shrinkage and creep
- Other damage/ deterioration mechanisms



So, this is the outline of this module where we will talk about what are the essentials for a durable concrete system and then various deterioration mechanisms. In this particular lecture we will cover sulphate attack, biofouling and biogenic acid attack. In the coming lectures we will talk about freeze-thaw attack, alkali-silica reaction, shrinkage and creep and also some other deterioration mechanisms such as or damage mechanisms such as fire attack or what will happen to concrete at elevated temperature and then also looking at erosion and some other mechanisms.

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As discussed earlier, a balanced approach is needed to enhance the service life



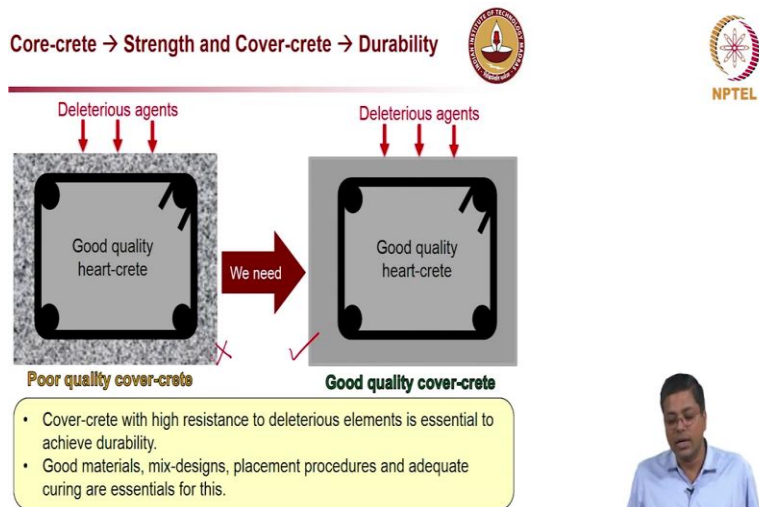
Synergistic effects need to be considered



Now, as we discussed in the previous module, a balanced approach is very much necessary for ensuring durable reinforced concrete systems and enhance the service life. Now, when I say balanced approach it is to do with both the steel and the concrete here you can see on this balance on the left side, item number 1 we are talking mainly about the corrosion resistance of the steel.

And the number 2 is mainly on the corrosion resistance or in other words the degradation or damage of the concrete cover, which is necessary for preventing the deleterious elements to enter the concrete which eventually leads to cracking and then corrosion of the steel. So, synergistic effects need to be considered both of steel and concrete.

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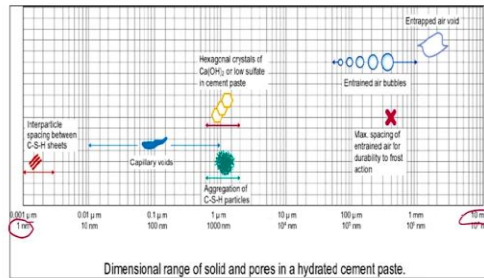
Now, on the left side you see a picture, which indicates how a typical reinforced concrete system will look like. Over there you can see steel reinforcement which is the black solid line inside which the concrete we can call heart-crete and the concrete outside the steel reinforcement we are going to call it as cover-crete. Now, core-crete or the heart-crete influences a lot on the strength of the reinforced concrete system whereas the cover-crete influences a lot on the durability of the concrete system.

So, if you look carefully on the picture on the left side you will see that the cover-crete is of a different texture basically to indicate that if you do not have a good concreting practice you might have a very good heart-crete but the cover-crete might be still very porous in nature. So what we need is something like on the right side where good quality heart-crete or core-crete and at the same time good quality cover-crete are essential.

When you talk about this good quality cover-crete and core-crete, how do we achieve it? It's possible by having good materials, good mix designs and then very good placement procedure and also adequate curing. All these are necessary to ensure good quality heart-crete and cover-crete.

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Size of pores/voids in concrete could range from 1 to  $10^7$  nm



Size and distribution of pores influence the rate of ingress of deleterious elements through cover-concrete

Mehta and Monteiro (1993)

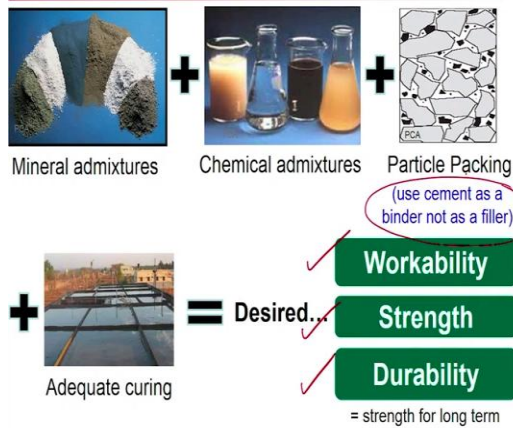


When you talk about concrete the size of pores and how they are distributed in concrete is very important to consider. As in this picture, you can see the size of these pores range all the way from 1 nanometer to about 10 millimeter. So, this is the range of different types of pores or voids that can be present in concrete which might very well influence the rate at which different deleterious elements such as chloride, moisture, oxygen, carbon dioxide, sulfate and all this can enter the concrete.

So, having a very compact micro structure is very important to reduce the rate of ingress of these deleterious elements through the cover concrete which means you need to have very small pore size or very compact micro structure.

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Mineral/chemical admixtures and adequate curing can influence the properties of concrete



How do we achieve this highly compact micro structure? We can use different type of chemical and mineral admixtures and adequate curing. I am emphasizing again on adequate curing because it is not just having good quality materials and design procedures but also after placing the concrete you need to have very good curing. If you do not cure the concrete properly, you may not really achieve durable concrete systems.

It is just like having different type of vegetables. You can have dishes made with same vegetable but the way you make the curry or the way you make the dish is very influential on how at the end, the taste of that dish would be. So, you can probably use a good analogy here also in concrete. We add different ingredients mineral and chemical admixtures then pack them very well.

And then at the end you have to pack and then place and then cure the concrete very well that is very much important to achieve decided workability, strength and durability. What is durability? It is nothing but strength in long term. So, one thing to mention here is the use of cement. Cement should be considered not as filler, but as a binder. In other words, when we talk about mix design, we should think about having minimal amount of cement which will play a role mainly as a binder or glue to hold all the aggregate particles together that should be the idea.

Why I am saying that is there are many cases where people say, if you want to increase the strength you go for more cement content which is not the right thing to do always because cement is the one which is probably most reactive element in the concrete. So, whenever we talk about long term chemical degradation, it is the cement which gets reacted and thereby changes the properties of the concrete. So if you have minimal cement that is always going to be probably more durable concrete system.

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**What are mineral admixtures OR  
supplementary cementitious materials (SCMs)?**



- 'Mineral admixture' is a common name used in India
- A finely ground solid material that, when used in conjunction with Portland cement, contributes to the properties of the hardened concrete through hydraulic or pozzolanic activity or both
- Contains some form of amorphous reactive silica, which in the presence of water, combines with calcium hydroxide to form calcium silicate hydrate similar to that formed in the hydration of Portland cement

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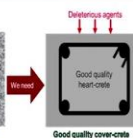
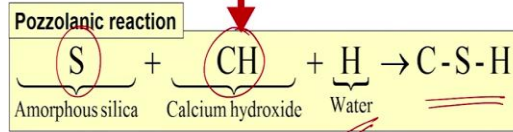


Now, what are mineral admixtures? First, I would say what? This mineral admixture it is a actually a common name used in India but not outside Indian border. So outside it is more technically correct name is supplementary cementitious materials or SCMS. So, I would like you to actually talk in terms of SCMS and not you know, when you especially when you start writing documents, we should really talk about SCMS and not probably the main admixtures.

What is an SCM? A finely ground solid material that when used in conjunction with Portland cement contributes to the properties of the hardened concrete through hydraulic or pozzolanic activities or both. The main ingredient which is the component which we are looking for in SCMs is the amorphous or reactive silica which in presence of water combines with calcium hydroxide to form calcium silicate hydrate which is basically the glue which you are talking about in cement hydration.

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Pozzolanic reactions occur when sufficient CH from the cement hydration is available



Use of SCMs, low-water binder ratio, and superplasticizers, good placement, compaction, and adequate curing can help in achieving highly compact microstructure and high resistance against the ingress of deleterious elements through coverconcrete.



Now, this reactive silica is very important to have. It is not just silica. So, when you talk about SCMs, you have to really ensure that particular SCM has sufficient amount of amorphous silica. Now, here the first equation on the top of the slide, it shows a typical Portland cement hydration reaction where you can see  $C_3S$  and  $C_2S$  are the reactants along with water they form CSH and CH.

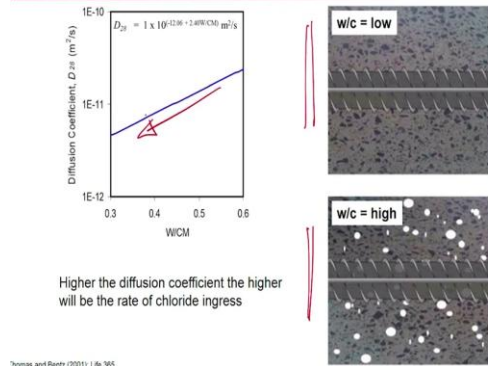
Now, when we talk about these SCMs or pozzolanic reaction, we are essentially talking about using this calcium hydroxide which is formed because of the cement hydration reaction. And that calcium hydroxide reacts with the amorphous silica which is present in the SCM. When there is sufficient water or moisture it forms more CSH. Now, the CSH is formed by replacing or by consuming calcium hydroxide.

So, the space which is occupied by calcium hydroxide is now going to be occupied by CSH. So that enables it to form a more compact micro structure, which is stronger and also durable in most cases. Now, the outcome of this entire discussion is the use of SCMs, low water binder ratio, sufficient quantities of super plasticizers, good placement, compaction procedures and adequate curing.

All these, if you are ensuring then it is very easy to achieve highly compact micro structure and thereby high resistance against the ingress of deleterious elements through concrete. So we can have durable concrete.

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**Use low w/c and superplasticizers to enhance the workability, strength and durability**



Thomas and Benz (2001), Life 365



I am going to show you one slide on water binder ratio, 2 slides on SCMs; how they really influence the rate of ingress of these deleterious elements? When you have a very low water cement ratio, the chance of having micro pores is very less which is this case here. So you can see that in the picture, I am not really showing any micro pores for low water cement ratio whereas in the second picture on the bottom right with high water cement ratio micro pores are present.

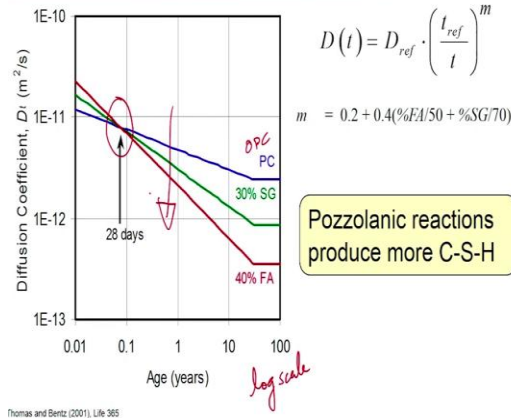
Whatever the amount of water which is not used in the cement hydration reaction, it is going to be now left. It will be unused water which eventually dries and leave air voids. So, this white circular and elliptical shapes which I am showing there is all indicating that there are possibility of more air voids in the concrete when you have a higher water binder ratio. We should use lower water binder ratios and if the water binder ratio is low.

If it is leading to workability related issues then handle that by using chemical admixtures such as super plasticizers and not by adding more water. So, the point here is when you have a lower water binder ratio, the rate of diffusion or ingress of various chemicals into the concrete is going to be less, you can see that on this graph.

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**Adding fly ash and/or slag can improve the strength and durability of concrete**

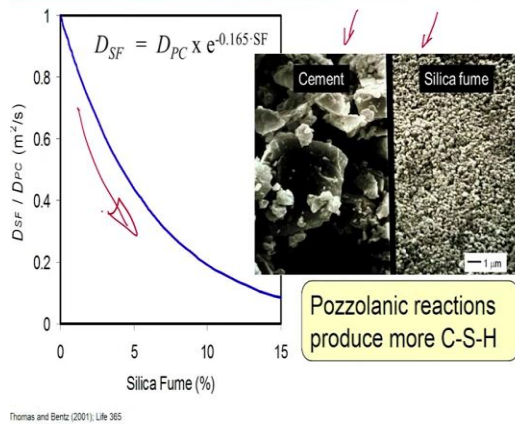


When you talk about fly ash or slag which are the two widely used supplementary cementitious materials. Until 28 days you might not see significant difference between the diffusion coefficients of OPC or Ordinary Portland Cement. And then there is not much difference in the diffusion coefficient of ordinary Portland cement based concrete or concrete with slag or fly ash replacement within 28 days.

But as the time passes, on the x axis which is in log scale. You can see that definitely as time passes the diffusion coefficient of slag and fly ash is significantly less than that of ordinary Portland cement concrete. So, definitely in the long run as the concrete continues to hydrate and then make more and more CSH and then effectively or get more and more compact microstructure as time passes which leads to reduction in the rate of ingress of different elements into the concrete.

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## Adding silica fume can improve the strength and durability of concrete



Thomas and Bentz (2001), Lih 365



Now, if you are talking about silica fume which is also a very good SCM with very fine particle size. So, the silica film has a dual role both as a pozzolanic material and at the same time it also has a little bit of filler effect depending on how much silica fume is used. As you see in this micro graph here you can see that cement particles are much larger than the silica fume particles.

So, all the space between the cement grades can probably get filled or the very fine pores available can also get filled by the silica fume particle depending on how much is the dosage definitely you can see the rate of ingress is going to be less when you add silica fume.

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## Chemical admixtures can be used to achieve various desired properties



- These are ingredients other than Portland cement, cementitious materials, water, and aggregates that may be added to impart a specific quality to either the plastic (fresh) or hardened concrete
- ASTM C494 provides specifications on chemical admixtures, in general
- For attaining uniformity, it is recommended to mix the admixture with the mixing water



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We also talked about chemical admixtures. I am showing here 6 widely used chemical admixtures. First one is super plasticizer, which is used mainly for handling the workability related issues and then you have an air entrainer which also helps in enhancing the flow properties, but at the same time, it is also used widely for addressing the freeze-thaw attack in concrete structures. You introduce small air bubbles, as you see in this picture these small black circles which are all air bubbles introduced into the concrete by this air entraining admixtures.

They help in providing sufficient space during the winter when water gets into the concrete it starts expanding and try to become ice. If there are no air voids, then you will have significant expansive stresses. So, that can be avoided by providing these small air bubbles in concrete will talk much more in detail in the next lecture on that. And then you have retarders which are mainly to slow down the reaction rate, especially for cases like what you see in that picture, it is a concrete truck stuck in traffic.

If the concrete has already started mixing or hydrating and then you are stuck in the traffic and you have time to reach the construction site. So, the best thing to do there is to reduce the rate of reaction so that you can still have good concrete by the time you reach the construction site. Now, number four over here is the corrosion inhibitors, which are mainly used to enhance the corrosion resistance of the steel rebar or the steel- concrete system.

What it does is, while mixed with concrete, it actually helps in providing a better passive film or a more resistant passive film. So, the point to note here is this inhibitor they will come into action maybe after a decade or two depending on the corrosive environment or how corrosive the environment is. Now, shrinkage reducing admixture, this is number five, shrinkage reducing admixture is used especially when the concrete can be more prone to cracking or in very thin elements which can be more prone to cracking.

So, we tend to use shrinkage reducing admixture and number 6 which is an accelerator, an accelerator which is mainly used when you talk about very low temperature or cold climate where you want the concrete or the cement to hydrate faster, so you tend to use accelerator. There are different types of these admixtures available to cater to different requirements of the concrete.

Now, one thing is quantity of these admixtures which are added to the concrete is very small. So, to attain uniform distribution or making sure that these admixtures are available in the entire concrete in a uniform manner, it is recommended to add these admixtures to the water and then use that mixing water rather than adding directly to the concrete being mixed. Now, the ASTM C494 provides specifications for typical chemical admixtures.

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## Why to use chemical admixtures?



- To achieve/enhance certain desired properties in fresh and hardened stages
- To ensure quality during the stages of mixing, transporting, placing and curing in adverse weather conditions
- To face emergencies during site operations
- To reduce the overall cost to achieve the same desired properties for ensuring durability



116



Main advantages of using these admixtures are to achieve and enhance certain desired properties in both fresh and hardened states. Like for fresh state super plasticizer, air entrainer, retarder, and accelerator all these are mainly handling the properties during the fresh state whereas corrosion inhibitor and shrinkage reducing admixtures are mainly for the hardened state depending on what type of shrinkage, whether you are talking about plastic shrinkage or later. Also to ensure quality during the stages of mixing, transporting, placing and curing in adverse weather conditions and to face emergencies during site operations.

This is one emergency, which we briefly discussed. And then to reduce the overall cost to achieve the same desired properties to ensure durability. Why we are saying overall cost is because when you talk about these admixtures into the concrete, the unit cost of the concrete might increase slightly. However, you have to think about the entire system.

If you really look into that basically you will end up in having a peaceful concreting to that manner. So, definitely the overall cost is going to decrease, because you will not have much of hassle in placing the concrete and at the end you will get a good product. So, essentially the overall cost is going to be better.

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## Other relevant NPTEL courses from our group



- Modern Construction Materials
  - Prof. Ravindra Gettu
- Advanced Concrete Technology
  - Prof. Manu Santhanam
- Advanced Topics in Science and Technology of Concrete
  - Multiple experts
- Characterization of construction materials
  - Prof. Manu Santhanam and Dr. Piyush Chaunsali

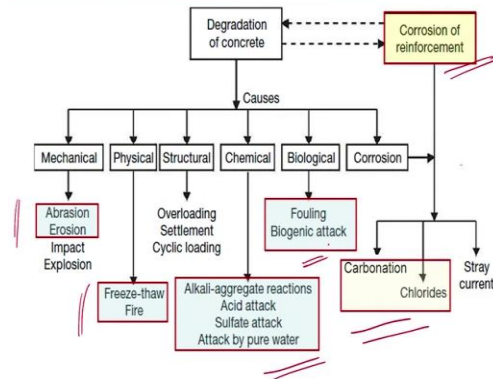


Before getting into the various deterioration mechanisms, I would like to tell you about other courses which are offered through NPTEL from our group. *Modern construction materials* by Prof. Ravindra Gettu, *Advanced concrete technology* by Prof. Manu Santhanam

And then *Advanced topics in science and technology of concrete* where we have collected lectures from multiple experts from all over the world who have visited us or we requested them to give couple of hours of lectures in their topic of expertise. All those lectures are collated and are nice topics especially for research scholars and researchers, this course is very useful and then another course on *Characterization of construction materials* by Prof. Manu Santhanam and Dr. Piyush Chaunsali.

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## Various deterioration/damage mechanisms in reinforced concrete systems



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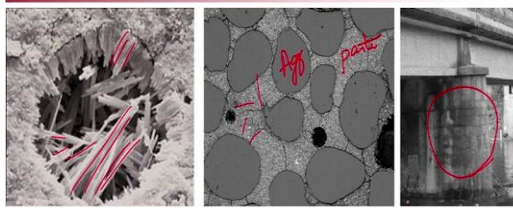


Looking at various deterioration or damage mechanisms in concrete systems, main thing why we are worried about is, if the concrete gets damaged eventually it affects the steel inside the concrete and then it influences the structural capacity of the system. So, we already talked about how corrosion happens mainly due to carbonation and chloride attack.

And when we talk about the concrete, we are going to talk about abrasion, erosion very briefly. Freeze-thaw attack, fire, alkali-aggregate reaction or alkali-silica reaction, acid attack, sulphate attack and fouling. So, all these we will be discussing.

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## Sulphate attack (External and Internal)



Ettringite needles and cracking

Mehta and Monteiro



First we are going to talk about sulphate attack. There are 2 types of sulphate attack depending on the source of the sulphate. They are external and internal sulphate attack. The major mechanism I am just showing 3 pictures here on the left side, you will see what happens at the microscopic level, you have this formation of these needle shaped Ettringite crystals wherever there is a little bit of space available and the volume of the Ettringite needles are actually more than that of reactants which eventually leads to expansive stresses.

This expansive stress induces cracks like this as you see on the second picture, you can see this is an aggregate and then this is the cement paste and you can see significant cracking all along the cement paste and along the boundary between the aggregate and cement paste or ITZ. So, the system is not really an integral system when you have significant cracking like this on a larger scale.

Third one is a picture of a bridge where you can very clearly see a lot of cracking in that column or the pier which you are seeing. So, from micro structure to macro level, cracking really leads to significant distress of the structure.

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## 1a. External sulphate attack



P. Paramasivam, PCA, <https://civilblog.org/2015/02/27/how-to-protect-concrete-from-sulphate-attack/>



So, it is a major deterioration mechanism which we all need to know and worry about, so that we can design our structures to prevent them. Now, I am showing some examples of how this external sulphate attack, not the internal. This picture mainly shows about external sulphate attack where over here you can see this is a concrete element which has degraded exactly where it is coming out of the soil.

And here also you can see where it is in touch with the water, you have degradation. Here also you can see when the region, where it is in contact with water, it is almost completely gone. I mean, there is no more concrete left in that element. And one thing to note here, you can see this close up of that concrete element with the small pen to give you an idea about what is the size, you can very clearly see that the aggregates which are basically river gravel, I think, it looks like.

So, the rounded aggregates they are not damaged, they are intact. However, the cement which is in between the aggregates which is supposed to glue the aggregates together is almost lost or completely degraded. It's a clear indication that it is the harden cement paste which is getting attacked and not the aggregate.

So, if you reduce the amount of cement again it is going to be easier to resist sulphate attack. Now here on the bottom image you can see the water cement ratio of 0.65 and water cement ratio of 0.39 or let us say 0.4. So, the one with 0.4 or 0.39 is highly resistant against

sulphate attack as compared to the one with 0.65 on the left side. And you can also see that both are using type v cement and also you can see this on the left side that much degradation happened in 12 years whereas on the right side that much degradation happened in a longer time, which is 16 years. So, even after exposing the concrete for a longer period of time when you have a lower water cement ratio definitely the amount of sulphate attack is going to be less.

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### External sources of sulphates



- Soil ✓
  - Most soils contain sulfate in the form of gypsum (say, 0.01 to 0.05 % expressed as  $\text{SO}_4$ ). This amount is harmless to the concrete.
- Groundwater ✓
  - Higher concentrations of sulfates in groundwaters are generally due to the presence of magnesium and alkali sulfates
- Other sources
  - Ammonium sulfate is frequently present in agricultural soil and water
  - Effluents from furnaces that use high-sulphur fuels and from the chemical industry may contain sulphuric acid
  - Decay of organic matter in marshes, shallow lakes, mining pits, and sewer pipes often leads to the formation of  $\text{H}_2\text{S}$ , which can be transformed into sulfuric acid by bacterial action
- It is common to find deleterious concentrations of sulfate in natural and industrial waters

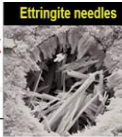


Now, let us look at what are the different sources of sulphates. As we saw in the previous slide definitely there are sulphate rich soils and sulphate rich groundwater or water bodies, present next to the concrete structures or in contact with the concrete structures and also depending on the type of structure, we have to see whether there is any agricultural soil or water adjacent to the concrete elements and also effluents of furnaces and effluents from the chemical industry.

These are all other sources where you will have significant amount of sulphates present and if they are coming in contact with the concrete element then that element is vulnerable to sulphate attack and further deterioration. Now, the bottom line of this slide is that it is not that difficult to find high concentrations of sulphates in either soil or water body which is in contact with the concrete structures. So, you have to really think about this and make sure that the type of concrete which you are using is sufficiently resistant against the sulphate attack for that desired life which we are talking about.

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## Mechanisms of external sulphate attack



Reaction Step	Chemical Reaction	Relevant Factor in Concrete	Control Strategy
1	$\text{SO}_4^{2-}(\text{external}) \rightarrow \text{SO}_4^{2-}(\text{internal})$	Permeability	Low w/c, pozzolan addition, slag addition <i>SCM</i>
2	$\text{Ca}(\text{OH})_2 + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{OH}^-$ <small>monosulphate</small> $\text{C}_3\text{AS}_2 + \text{gypsum} \rightarrow \text{C}_4\text{A}_3\text{H}_{12}$ (ettringite)	$\text{Ca}(\text{OH})_2$ content	Pozzolan addition, slag addition <i>SCM</i>
3	$\text{C}_3\text{AS}_2 + \text{gypsum} \rightarrow \text{C}_4\text{A}_3\text{H}_{12}$ (ettringite)	$\text{C}_3\text{A}$ content of cement	Type II or V cement

(Type II ≤ 7%  $\text{C}_3\text{A}$ ; Type V ≤ 5%  $\text{C}_3\text{A}$ )

- In addition, attack by magnesium sulphate is more damaging since the magnesium hydroxide that is formed in the reaction with the C-S-H replaces the  $\text{Ca}^{2+}$  ions with  $\text{Mg}^{2+}$ , which destroys the cementing effect.

(oung et al. (2003))



As we mentioned earlier, there are 2 types of sulphate attack one is external and one is internal. In the external sulphate attack, first step is the sulphates from either water or soil body will enter the concrete so now they become internal to the concrete. And then second step is once they enter the concrete it reacts with the calcium hydroxide which is present and forms gypsum.

Now, in step 3 that gypsum will react with mono sulphate which is present and this conversion of this mono sulphate into Ettringite will happen. This conversion is the dangerous part, because there is a volumetric expansion, because Ettringite will consume more space or will need more space than the combined volume of mono sulphate and gypsum and it leads to cracking of the concrete because of the expansive stresses.

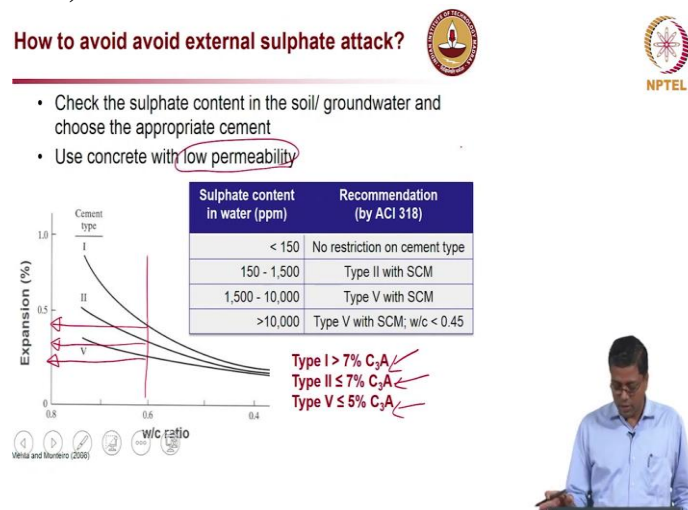
So, here you have a product which is having more volume than the reactants, definitely that will induce stresses in the entire matrix of the concrete and eventually leading to cracking. So, how we can actually control this is on the right side of this table, the first step we can control by reducing the permeability of the concrete cover either by using low water cement ratio or by using SCMs.

And if you are in the second step that can be controlled by controlling the amount of calcium hydroxide, if you have lower calcium hydroxide content, then definitely the amount of reactants is less or the amount of gypsum formed is also going to be less. So again, that can be

achieved by using pozzolana or SCMs. And in the third step, as you see here in the mono sulphate phase you have  $C_4A$ . So definitely, if you have less amount of  $C_3A$  in your cement, again we are controlling the amount of reactants.

So, the amount of this mono sulphate phase which is available is going to be less if you have low  $C_3A$  contained cement, which is type 2 or 5 cement. But essentially it is the  $C_3A$  content which we are trying to reduce. So, type 2 is the cement with about less than 7%  $C_3A$  and type 5 is cement with less than 5%  $C_3A$ .

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Now, this is a graph showing how this amount of  $C_3A$  or the  $C_3A$  content is going to influence. It is just a demonstration of that, let us say you are talking about concrete with 0.5 water cement ratio or let us pick 0.6 water cement ratio here. As you see, if it is type 1 cement you have this much expansion, if it is type 2 cement you have this much expansion and if it is type 5, you have this. So, definitely there is a reduction. Type 1 is more than 7%, type 2 is more than 5 to 7% and type 3 is less than 5%. So, as the amount of  $C_3A$  is reduced, definitely the amount of expansion is less.

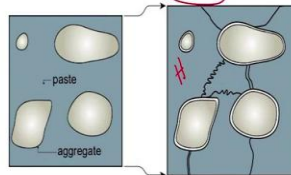
So, definitely if you are talking about sulphate resistant concrete systems, we have to go for cement, which are having low  $C_3A$  content. Lower the water cement ratio entire pore structure is better refined. I mean, fewer amounts of pores are available. So effectively you use low permeability concrete.

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## 1b. Internal sulphate attack



- In the 1980s, German researchers reported internal sulfate attack in heat-cured concrete products.
- DEF is a result of high early temperature ( $> 70^{\circ}\text{C}$ ) in concrete, which prevents the normal formation of ettringite.
- Typical manifestation of distress is the presence of voids around the coarse aggregate, indicating expansion of the cement paste.
- Often these voids are filled with ettringite crystals, which also often fill other voids and cracks in the matrix. Because of the late precipitation of ettringite, this phenomenon is called delayed ettringite formation (DEF).



Volumetric expansion and cracking

<https://theconstructor.org/concrete/types-sulphate-attack-concrete/5286/>; [https://www.nptel.net/learn/ndcm2015/app/content/slides/18\\_Livingston.pdf](https://www.nptel.net/learn/ndcm2015/app/content/slides/18_Livingston.pdf)



Now, internal sulphate attack, where we are talking about some issues related to the time at which these Ettringites are formed. So for example, what happens especially in terms of hot weather concreting or mass concreting where the heat generated is significantly high which leads to curing temperature or early temperature of more than  $70^{\circ}\text{C}$ . If that happens, then the normal formation of Ettringite will not happen. I am going to the next slide to show you what this normal formation of Ettringite is.

(Refer Slide Time: 32:17)

## Evolution and volumes of hydration products of Portland cement

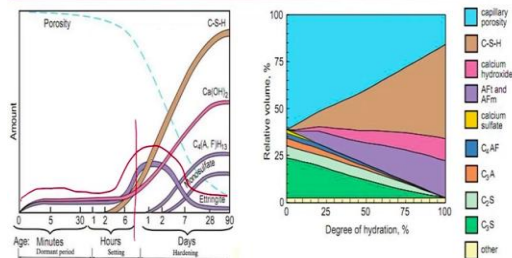


Fig. 2-28. Relative volumes of the major compounds in the microstructure of hydrating portland cement pastes (left) as a function of time (adapted from Locher, Richartz, and Spring 1976) and (right) as a function of the degree of hydration as estimated by a computer model for a water to cement ratio of 0.50 (adapted from Tinnis and Jennings 2008). Values are given for an average Type I cement composition (Gebhardt 1995):  $\text{C}_3\text{S}=55\%$ ,  $\text{C}_2\text{S}=18\%$ ,  $\text{C}_3\text{A}=10\%$  and  $\text{C}_4\text{AF}=8\%$ . "AFi and AFm" includes ettringite (AFi) and calcium monosulfaluminate (AFm) and other hydrated calcium aluminates compounds. See Table 2-5 for compound transformations.

PCA: Kosmatka (2005)



So, here you can see this curve here, which is this one, which goes like this, that is the curve for ettringite formation and you notice that after few hours of concrete is mixed, there is a increase in the amount of ettringites which are formed and they occupy their space because at

that stage, the concrete is still somewhat plastic, so that they can occupy that space and it is not completely hardened or not completely set also.

So at that time it occupies the space without creating any damage to the concrete. But when you have this high temperature of greater than  $70^{\circ}\text{C}$  and then this Ettringite is not stable and it does not form. And what happens is, it does not form at that time and does not occupy the space required. But after several years or decades, when sufficient amount of the reactants which we were talking about earlier, moisture is available, this mono sulfates might get converted to ettringite at a later stage.

So, we call it delayed ettringite formation just because it is not happening during the early curing period, but it is happening at a much later stage. When it is happening at a delayed time or at a later stage this concrete is already hardened concrete and there is no reserved space for this ettringite in that concrete because it was not reserved in the early stage.

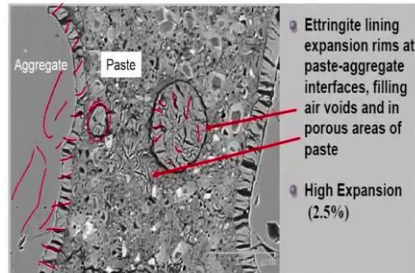
So, it generates a tremendous expansive stresses, which leads to cracking., First it will occupy all the space between the aggregate and the cement paste and then eventually try to exert tensile stresses or expansive stresses which lead to significant cracking. So, this is the problem with delayed ettringite formation because that space required is not originally reserved and when it forms at a later stage, it does not have that space thus exerts significant expansive stresses which lead to cracking.

**(Refer Slide Time: 34:52)**

## Mechanism of DEF-induced cracking



- Expansion in the paste caused by DEF originates cracks in the paste and at the aggregate-cement paste interface
- Subsequently, ettringite recrystallises in the cracks from sub-microscopic crystals dispersed through the paste



Mansu Santhanam



Now, this already we discussed. You can see here significant cracking in the aggregate phase also and these are all the needle shape ettringite which are occupying the voids available within the concrete system.

**(Refer Slide Time: 35:15)**

## Delayed ettringite formation (DEF)



<https://theconstructor.org/concrete/types-sulphate-attack-concrete/#266/>, Godart and Dixel (2013)



Now, this is some demonstrations of sulphate attack, you can see these are very large bridge piers. So, definitely these are mass concrete elements. Probably the curing temperature might have reached a level which is beyond 70 degrees Celsius. And after a long period of time they started degrading or deteriorating due to sulphate. You can see a significant cracking here on these concrete elements. So, significant cracking, especially for mass concrete elements, we have to really think about this.

(Refer Slide Time: 35:57)

### Delayed ettringite formation (DEF)



<https://theconstructor.org/concrete/types-sulphate-attack-concrete/5266/>



Now, here are some more examples where you can see map cracking, there is no particular shape for these cracks which are formed due to sulphate attack and here also you can see random cracking on all these elements. Again all these are mass concrete elements and that is where we see maximum delayed ettringite formation internal sulphate attack.

(Refer Slide Time: 36:22)

### French bridges undergoing DEF



	Ondes	Bourgogne	Lodève	Bellevue	Beynost	Chevîrè
Date of construction	1955	1990	1980	1988	1982	1988/89
Casting of concrete	August	August/September	August/September	August/September	August	July/August
Structural part	Cap beam	Base of pylon	Cap beam	Pier	Cap beam	Base of pier
Delay in occurrence of damage	27 yrs	6 yrs	9 yrs	10 yrs	10 yrs	8 yrs
Environment	Waterproofing Problem	Immersed & variable immersion	Lack of drainage	Immersed & variable immersion	Exposure to rains	Rains and capillarity
T max (°C)	80	79	80	80	69	75
W/C ratio	0.50	0.45	0.47	0.54	0.49	0.48
Nature of cement	CEM I	CEM I	CEM I	CEM II/A	CEM I	CEM II/A
Cement content (kg/m <sup>3</sup> )	430	400	400	380	350	385
SO <sub>3</sub> cement (%)	2,5	2,8	2,6	2,5	3,4	2,5
C <sub>3</sub> A cement (%)	11,2	8,2	9,8	7,0	10,4	7,0

Godard and Divil (2013)



This is a table which shows study done on various bridges in France. Main point to notice here is the maximum temperature which is in this one, the blue box you can see that they are all actually above 70 °C except one which is 69 °C. But we can say for all practical purposes they are high temperatures which is probably not good. And also the amount of C<sub>3</sub>A, which is in the



cement which was used, is very high more than 7%  $C_3A$ . So, these are all leading to significant internal sulphate attack.

**(Refer Slide Time: 37:03)**

#### How to prevent sulphate attack?



- Low curing temperature ( $< 70^{\circ}\text{C}$ )
- Concrete with low permeability
- Cement with low  $C_3A$  content
- Less availability of water



This is a nutshell on how to prevent sulphate attack. We have to use low curing temperature or make sure that the temperature during the curing period is less than  $70^{\circ}\text{C}$  and concrete should have low permeability by using SCMs or good mix design and curing practices we can achieve low permeable concrete. Also the cement which we use should have low  $C_3A$  content and definitely less availability of water. So, if we are able to achieve these, then we can definitely prevent sulphate attack.

**(Refer Slide Time: 37:39)**

## 2. Biofouling in concrete structures



- Unwanted growth of microorganisms, plants, algae, or animals on wet concrete surfaces
  - Bacteria, fungi and algae
  - Aqueous medium or damp environment
- Microorganisms can cause mineralogical, chemical and microstructural damage to the concrete (biodegradation).
  - Acidic excretion by microorganisms
  - Sulphuric acid, Nitric acid



An Octopus nest on the soffit of concrete anchor

Betron (2014)



Now, the next damage mechanism or deterioration mechanism we are talking about is bio fouling in concrete structures. Not really given much importance to it but we thought to include and give some light on this type of deterioration which happens on concrete structures. So, as you see here on the picture, you can see a nest of an octopus on the soffit of concrete anchor.

So, these are the nice resting place for these microorganisms. So, what is there in concrete which is attracting these microorganisms to get attracted to the concrete elements? So, we will see on the next slide.

**(Refer Slide Time: 38:34)**

## Cases of biofouling on outdoor concretes



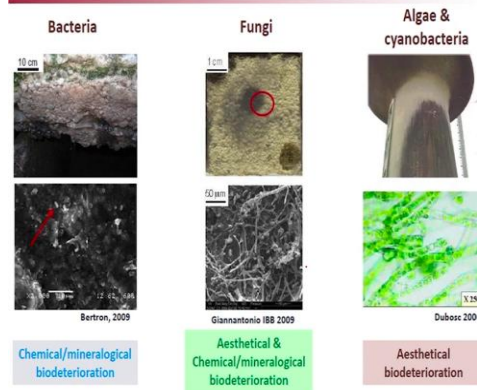
Giannantonio et al. (2009); Coalle, PhD thesis (2015)



These are some more pictures or photographs showing different types of bio fouling. So, the first picture is a repetition actually here anyway, you can see here it is a bridge column. I had another nice picture of bridge in a port where again significant fouling was there. Also this picture is giving similar message and you can see here significant surface damage on these concrete elements. Here all these are actually concrete surfaces getting damaged because of bio fouling.

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## Microorganisms interacting with building materials



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This is again microorganisms, how they interact with various building materials. I am not going to much detail into this, but as a civil engineer, we should know that these microorganisms can also actually damage concrete elements in the long run and we should keep away these

microorganisms from the concrete surfaces and how do we do that? We will see towards the end of this lecture.

**(Refer Slide Time: 39:48)**

### Deterioration of concrete due to algal growth



- Algae consume different elements (e.g. calcium, aluminum, silicon, iron etc.) for their metabolism
- These are available in hardened concrete
  - Portlandite (calcium hydroxide)
  - Yeelimite (form of calcium sulfoaluminate)
  - Gismondine (hydrated alumino-silicate)
- Involves production and release (excreta) of organic acids onto concrete surface



Jayakumar and Saravanan (2006)



This is again another picture showing again this. So, the main damage mechanism here is few minutes ago I said why are they attracted to these concrete structures? So, all algae or this microorganisms they consume calcium, aluminum, silicon, iron etc., for their metabolism. In concrete we have all these available for example, in your cement, you have calcium, you have aluminum, you have silicon and you have iron in oxides of these are available in our cement or hardened concrete systems.

What happens is, these metabolic actions involve production and release of organic acids. So, essentially these lead to acid attack of concrete surfaces that is a key message here.

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## Deterioration of concrete due to effluents from the agricultural and agrofood industries



- Agricultural effluents
  - Liquid manure, molasses, silage juices
- Effluents from biogas systems
  - organic matter (including organic acids)
  - microorganisms (bacteria, yeast)
- Bacteria and yeast can
  - degrade the organic compounds and produce organic acids
- Fungi can
  - damage concrete and stone by slow penetration into the surface



Betron (2014)



Now, other examples where similar acid attack is witnessed or observed are effluents from the agriculture and agro food industries, where all the effluents might have significant amount of acids which is actually thrown into or the concrete structures nearby will get exposed to these acids and what do they do? These bacteria and yeast they can degrade the organic compounds and produce organic acids and fungi can also damage concrete and even stone by slow penetration into the surface. If you Google you will see a lot of pictures showing these kind of long term deterioration mechanisms.

(Refer Slide Time: 41:38)

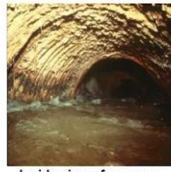
## Deterioration of concrete due to inorganic acids



- Household and certain industrial wastes
  - contain organic matter that, if not kept cold, will start to breakdown or biodegrade (bacteria will eat and digest the organic matter)
  - Based on the oxygen availability, they either produce sulphate ( $\text{SO}_4$ ) or hydrogen sulphide ( $\text{H}_2\text{S}$ ) as waste



Inside view of a concrete manhole



Inside view of a sewer pipeline

[http://xpx.com/docs/default-source/mailchimp-technotes/technotes\\_microbial.pdf?sfvrsn=0](http://xpx.com/docs/default-source/mailchimp-technotes/technotes_microbial.pdf?sfvrsn=0)



Deterioration of concrete due to inorganic acids. Here you can see household and certain industrial waste. You know, they contain organic matter that if not kept cold because the

temperature also matters a lot, will start to break down or biodegrade. So bacteria will eat and digest the organic matter and then throwing away their excreta which might be acidic in nature.

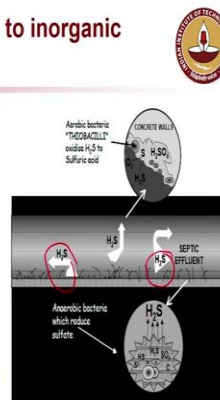
You also have formation of hydrogen sulfide mainly depending on the amount of oxygen available. So, depends whether it is a closed system or an open system, depending on that the amount of  $H_2S$  or the type of  $H_2S$  also matters. Now, here you see that picture on the left side it is an inside view of a concrete manhole on the right side, inside view of a sewer pipeline.

So, why I am showing these pictures are, these are major infrastructure systems where we tend to repair these systems very frequently mainly because of this acid attack or  $H_2S$ .

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### Deterioration of concrete due to inorganic acids (in sewer pipes)

- Being heavier than air,  $H_2S$  will settle on the surface of the sewage water
- Then, they will be circulated around the structure's air-filled cavities through convective currents
- Then, they re-dissolve in the water or slime that adheres to the concrete walls
- Hydrogen sulfide ( $H_2S$ ) forms weak sulfuric acid
- Weak  $H_2SO_4$ 
  - attacks the concrete directly
  - lowers the pH of concrete from to about 9 → corrosion of steel



[https://www.researchgate.net/publication/280941785\\_Biogenic\\_corrosion\\_of\\_rebar\\_reinforcement\\_rebars\\_with\\_different\\_bending\\_angle](https://www.researchgate.net/publication/280941785_Biogenic_corrosion_of_rebar_reinforcement_rebars_with_different_bending_angle)  
<http://kypex.com/>, Scriver K. (2003)



So, let us see how the deterioration of concrete happens mainly because of the inorganic acids especially in sewer pipeline. So, we will look at that mechanism alone here. So, think about the sewer pipeline.  $H_2S$  is produced and then what will happen is this  $H_2S$  because it is heavier than air, it will try to settle right above the water body and then because of the convective currents, it will actually get circulated inside the air space available or air fill cavities, which are present on the concrete surfaces.

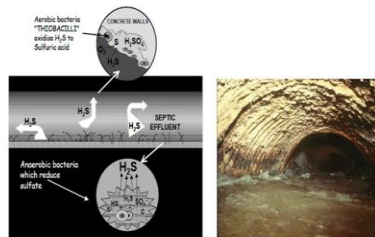
And then they eventually redissolve in the water or slime. If I draw a picture here, so if this is the water body and then you will see a lot of slime formation in this right here and then they get to the concrete walls then hydrogen sulfide forms a weak sulphuric acid and this weak

sulphuric acid attacks the concrete directly, especially that happens right here at the crown of the pipeline, it will directly attack the concrete and then lower the pH of the concrete from about 12 + to about 9.

And now we all know that when the pH is about 9 or at that low pH, the steel is very vulnerable to corrosion. So that is why we have this significant problem of corrosion of this pipelines or sewer pipelines and their life is not really very long, even though we desire it to have.

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### Deterioration of concrete due to inorganic acids (in sewer pipes)



- Poor quality sewer pipelines usually gets deteriorated in about 5 years – where as the desired service life (or design life) is longer.

<http://vipes.com/>; Schinner K. (2003)



So, this picture on the left side actually shows how this entire sulphate attack mechanism is in a pipeline and the point here is poor quality sewer pipeline usually get deteriorated in about 5 years. This is data obtained by talking to various people in the industry, they say mostly sewer pipelines get damaged in about 5 years, whereas the design life is about 20 years.

So, how do we ensure that these infrastructure systems are free from deterioration in the design life? Main thing is this deterioration happens below ground so we do not really see them happening on a regular basis. So, that is the main major challenge in identifying what is happening and then really making sure that they do not really fail. And before that we are either replacing or repairing the structure.

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## Remedial measures for existing concrete systems



- Repair strategies
  - Power washing ✓
  - Repair materials ✓
  - Surface coatings ✓



Different repair strategies for existing concrete systems, especially when we talk about this biological attack. Now, one is power wash, basically clean and then use good quality repair material and then use good quality surface coating. On the picture on the bottom left you can see power washing, but of course, you have to really think about what is a pressure to be used for and also it is good when you are talking about large surface area, otherwise it may not be really economical.

On top right image you can see, good quality repair materials and then the surface coating and nice coating with smooth finish will definitely help in preventing this biological attack.

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## Power washing



- Primarily done to avoid slip hazard
- It can start a devastating vicious cycle
  - High pressure and a high velocity
  - Can dislodge not only dirt and debris, but also create flakes, popouts, and concrete spalls



Now, power washing you can see here on the picture on the left side, it is nicely cleaned. Power washing is primarily done to avoid slip hazard. And it can start devastating vicious cycle because if you are actually going for very high pressure and high velocity, it may actually dislodge the aggregate particles also or the cement particles at the near surface. So, you have to really think about what is that pressure which we need to use. So, an optimal pressure is very important to decide before we go for power washing.

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## Repair materials



- Bio-deteriorated concrete can be repaired using suitable repair materials
- Protective coatings may be applied over the repaired concrete to prevent further deterioration



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And repair materials and again selection of the repair materials is very important.

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## Chemical resistance of some common coating materials



Chemical resistance against	Coating materials									
	Acrylic Emulsion Coating	Polyester	Vinyl Ester	Bis A Epoxy	Bis F Epoxy	Norolac Epoxy	Reactive Acrylic (MMAs)*	Elastomer Polyurethane Polyurea	Furan	
Inorganic Acids	low	med-high	med-high	low-med	medium	high	low-med	low-med	high	
Organic Acids	low	high	high	low-med	medium	high	low-med	low-med	med-high	
Alkalis	low	medium	high	med-high	high	high	medium	low-med	med-high	
Chlorinated Solvents	low	low-high	med-high	low	medium	medium	low	low-med	high	
Drypenated Solvents	low	low-high	med-high	low-med	medium	med-high	low	low-med	med-high	
Hydrocarbon Solvents	low	med-high	med-high	low-med	medium	med-high	low	med-high	high	
Salts	medium	high	high	med-high	high	high	med-high	high	high	
Water	medium	med-high	med-high	medium	med-high	high	high	med-high	med-high	

\* MMAs = methylmethacrylate acrylics

[http://www.paintsquare.com/library/articles/Coating\\_Selection\\_and\\_Important\\_Properties\\_of\\_Coatings\\_for\\_Concrete.pdf](http://www.paintsquare.com/library/articles/Coating_Selection_and_Important_Properties_of_Coatings_for_Concrete.pdf)



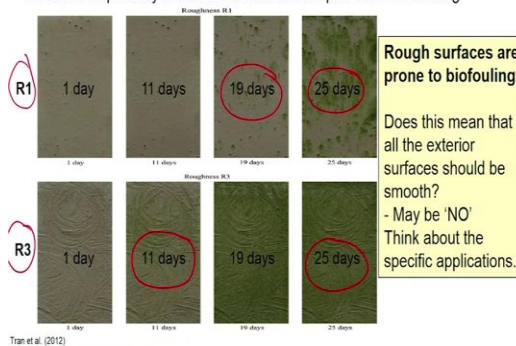
Here are the different materials available, this is just a simple table which I got from the internet, and you can see the resistance of these different coating materials. So, all these are different coating materials. And these are the chemical resistance against what type of material. So, you can see that, the resistance is varying from coating material to material behaves in a different way. So, you have to really think depending on the type of exposure conditions you might have, which type of coating material have to be picked.

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## Precautions to be taken while repairing



- Choose the right material for the right environment
- Prepare the substrate carefully before applying the repair material
- Ensure compatibility between substrate and repair material/ coating



Tran et al. (2012)



Now, another thing is, how smooth the surface of the repaired surface should be. So here it is a picture showing R 1 is the roughness 1 and R 2 is a third level or rougher surface and if you look closely on these 8 photographs, which you have on screen. You can see that on the first

row, surface with less roughness, the amount of green spots which you see is much less as compared to that on the second row, which is R 3 or more rough surface.

So, see in 19 days, in the row 1 you have some spots forming, but in row 2 you have more green spots on 11 days itself or even before but when you look at 25 days, you can see that on the second row it is completely green and in the first row, you still have significant region which is not attacked. So definitely roughness of the surface plays a role on resistance against bio fouling.

Now, the question is, does this mean that all the exterior surfaces should be smooth, maybe no. If it is smooth for a wall element, it may be ok but if you are talking about a floor where you also walk, you may not want it to be very smooth, because people will slip it will be a slipping hazard. So, all these techniques, whatever we talk, you have to really think about where you are applying for what specific conditions or specific applications.

And you have to also think about multiple damage mechanisms and it is not like you look at only one thing and then forget about the other damage mechanisms. So you have to think holistically when we decide about.

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**Calcium Aluminate Cements (CAC) can have good resistance against acids**



Good resistance by CAC cement      Poor resistance by Portland cement

Comparative performance may vary as the type of acid changes

<http://www.calucem.com/index.php?id=42&type=98>

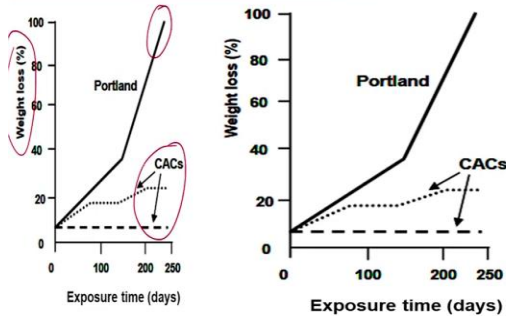


What type of deterioration and how to prevent? Now again, one last thing to talk about is acid attack. Calcium aluminate cement has been proven to be highly resistant against acids. However, I am showing this picture here, the one on the left side is showing a calcium aluminate cements and the one on the right side is showing Portland cement very clearly the one on the right side is more degraded.

So, we can conclude that CAC cements are more resistant against acids. However, there are publications which say in some cases you might have different or the resistance might vary from case to case or from acid to acid. So, you have to really look at what type of acid or acidic conditions you will have and then accordingly decide on the type of cement used.

**(Refer Slide Time: 51:08)**

## Calcium Aluminate Cements (CAC) can have good resistance against acids



Comparative performance may vary as the type of acid changes

Schinner K. (2003)



From the same literature this is another case showing that the Portland cement system will have much more weight loss or more degradation as compared to CAC systems when it is exposed to acids.

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## Interior coating for pipes



- Resistance of the coating for specific applications must be considered.



<http://www.calucem.com/index.php?id=62&type=98>



Nowadays, you have a lot of these pipes, which are coming with interior coatings, which are very highly resistant against the various types of acids. So, the products are available, you have to really make sure that the tender specifications which we make are actually looking for some measurable parameters which will really give you long life as decided and if you do a good homework in framing the tender specifications, I think most of our constructed facilities will last really long.

But most of the time we fail there, we do not really put in enough time in planning or in making these tender specifications thinking about what could go wrong and if how do I prevent that from happening. I think towards the end of the course, we will have one lecture exclusively on designing tender specifications. So, by the end of the course, you will be better prepared to handle certain situations and really be able to construct durable systems.

**(Refer Slide Time: 52:42)**

### Summary



- Mineral and chemical admixtures can be used to get a good quality covercrete
- Susceptibility and effect of sulphate attack, biofouling and biogenic acid attack can be reduced by understanding the mechanisms and addressing the factors affecting the degradation during the design of concrete
- Most often, prevention is better than cure!
  - Make good concrete in the beginning itself.
  - Select good materials, have good mix design and cure the concrete adequately



So, as a summary, mineral and chemical admixtures can be used to get a good quality concrete, especially cover concrete, and then susceptibility and effect of sulphate attack, acid attack etcetera can be reduced by understanding the mechanisms, how they really happen and understanding what type of exposure conditions you have, and then addressing those factors. Then coming up with good tender specifications or good measurable parameters for the type of system which you are designing mainly to prevent such deteriorations from happening during the design life.

As we always say, prevention is better than cure. So, the idea should be, make good concrete at the beginning itself and then for that we have to select good materials, have good mix design, good placing procedures, compaction and then cure the concrete adequately. All these are very much necessary and if we do all this, we will definitely have long lasting beautiful concrete structures.

**(Refer Slide Time: 53:58)**

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Now, next this is the list of references.

**(Refer Slide Time: 54:02)**

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Which have been used to make this particular presentation. Thank You.