

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

**Lecture - 38**  
**Durability Issues in Concrete – Part 2**

So we were talking about different methods of measurement of migration and we saw that some of these measure parameters which basically relate to the conductivity or the resistivity of the concrete.

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**Wenner 4 Probe Resistivity Test**

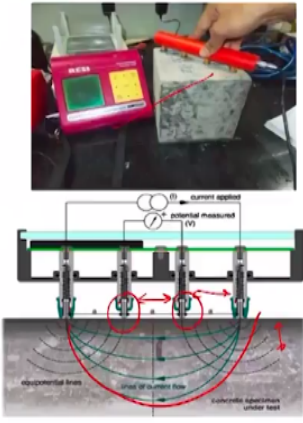
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- Not truly a migration test
- Consists of four probes
- Through two outer probes current is applied while the inner two probes measure the potential

Classification Criteria  
(Andrade et al., 2004)

Resistivity, k $\Omega$ -cm	Concrete quality
> 100	Good
50 - 100	Normal
10 - 50	Poor
< 10	Very poor

$\rho = \frac{2\pi sV}{I}$



So there is a simple test called 4 probe resistivity test, which has the advantage of being portable enough to be carried out in site directly.

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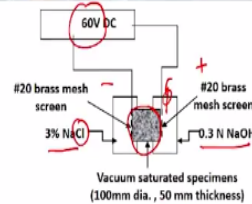
## Rapid Chloride Permeability Test (ASTM C 1202)

- Specimen subjected to a 60V potential, for 6 hours
- -ve side filled with 3% NaCl solution and +ve side with 0.3M NaOH solution
- Current is measured in each half hour, from which the total charge passed is calculated



Classification Criteria  
(ASTM C 1202)

Charge passed (Coulombs)	Chloride ion penetrability
> 4000	High
2000 - 4000	Moderate
1000 - 2000	Low
100 - 1000	Very Low
< 100	Negligible



We also looked at the most common test which is used for durability considerations that is the rapid chloride permeability test which is based on the ASTM standard and is widely adapted in most countries. Again the basic emphasis that you need to give on this is that most of the parameters that you get out of these durability tests are not quantitative parameters, they are qualitative. So they need to be characterized qualitatively.

You do not really get a quantitative estimate of the ability of chlorides to pass through the concrete you get a qualitative estimate of whether the concrete is good or not.

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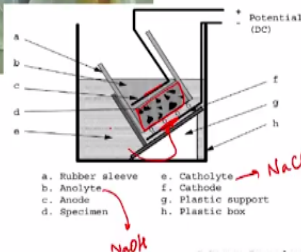
## Accelerated Chloride Migration Test (NT Build 492)

- 30 V potential is applied initially and after measuring the initial current, voltage is adjusted.
- After specified duration the specimen is split and silver nitrate solution is sprayed
- Depth of chloride penetration is used to calculate the non-steady state migration coefficient



Classification Criteria  
(RILEM TC PSC - 230 Report)

Nordtest Method BUILD 492, Migration coefficient (m <sup>2</sup> /s)	Concrete quality
< 2 × 10 <sup>-12</sup>	Very good
2 - 8 × 10 <sup>-12</sup>	Good
8 - 16 × 10 <sup>-12</sup>	Normal
> 16 × 10 <sup>-12</sup>	Poor



*Duracrete*

Now there is another test which is more widely being accepted nowadays. It is called the accelerated chloride migration test or rapid migration test sometimes it is called an RMT, rapid migration test. Now here the principle is still similar to what you have with the rapid chloride permeability test RCPT except the difference is here you have the specimen which is sitting inside this big container.

There is a big water bath as you see in this picture here and this water bath is filled up with the catholyte solution. What is the catholyte solution? Sodium hydroxide or chloride. Cathodic electrode has sodium chloride solution. Because, the chloride has to move towards the anode, the positively charged electrode. So this is the sodium chloride solution. The reason that you place your entire sample container inside sodium chloride solution of such a large volume is that.

When you have a large volume of the solution, the heating of the specimen is almost negligible. In the previous case you saw that this solution amount was equal on both sides, chloride and hydroxide were almost equal on both sides, but in the case of migration test the chloride solution is available in a very large volume. So because of that you have less chance of heating up of the specimen. So what you do here is again the same.

You apply a potential difference between the electrodes and you make the chlorides drive through the concrete to the other side where you have your anolyte which is sodium hydroxide. So anolyte is your sodium hydroxide, catholyte is sodium chloride. The one difference here is that for different types of concrete, you choose different voltages at which the test is to be conducted. So if you choose a concrete which is poor in quality so how do you choose that?

You basically do an initial test to determine the amount of charge that is passing through the concrete. Measure the current passing through the concrete and base your voltage for this test based on how much current is passing through. So if a concrete is poor it passes a lot of current through it. So then you choose a lower starting voltage. So the starting voltage can vary between 15 and 60 volts. You can apply different voltages to the concrete.

Now of course what you need to do is apply it for a certain period of time to ensure that the same amount of charge is passing through. So if you apply a lower voltage need to conduct the test for a longer duration of time. If you apply a higher voltage you need to conduct the test for the shorter duration of time. Nevertheless, at the end of the test what you do is you split the specimen.

You have cylindrical slices, the same type as you had in RCPT 100 mm diameter and 50 mm thick slice and this is split open and then you spray silver nitrate on the split surface. So what does silver nitrate do? It reacts with chlorides to form silver chloride which is white in colour. So you actually get to see the depth of chloride penetration directly from your specimen. So you can actually measure the depth of chloride penetration directly from your specimen.

So that is the advantage here that we actually get some inclining of how much chloride can actually go through, but still please remember this chloride is still getting driven through because of potential difference. It is not driving because of diffusion. Diffusion can never happen so quickly. It takes months to happen. So this is a case of chloride getting migrated, but nevertheless you are actually measuring the chloride migration by looking at the depth of chloride penetration.

And using the Nernst Planck equation that we talked about earlier, you can convert this chloride depth into the migration coefficient, which is basically an equivalent of the diffusion coefficient, not the same, but an equivalent to the diffusion coefficient that is called migration coefficient and that again people have suggested researchers have suggested classifications based on the values of the migration coefficient for the qualitative classification of the concrete.

Now one thing you need to understand is in RCPT we got an idea about the charge that is passing and I told you that that is not really a quantitative parameter that can be linked to the design of the concrete. However, in this case, you get actually a migration coefficient if you utilize the relationships that they are similar to the Fick's second law where we look at the non-steady state diffusion.

You can relate this migration to the diffusion coefficient that you find in Fick's second law and then try to model this process. So you can actually this migration coefficient as a quantitative parameter in models that predict the service life of the concrete. In deed the European model which is called Duracrete looks at the use of this migration coefficient value to determine the service life of your concrete structures.

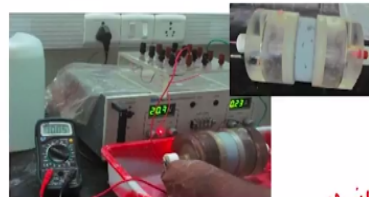
So this is probably a more useful test as suppose to the RCPT test to obtain the result which can be quantitatively utilized. The only problem is this test takes much longer than the RCPT depending upon the type of your concrete so you may actually have to wait a much longer time to get a reasonable result. RCPT again because of familiarity because of the way the people have been expose to it again remember I told you that the silica fume manufacturers were one of the primary reasons that RCPT got promoted in a big way.

Because silica fume concretes were showing really excellent results with RCPT. So for a long time that was the only durability test that was actually being conducted. Only in the last 10 to 15 years, the debate on use of appropriate durability tests has been rekindled and people have started talking about additional test that can actually be done along with RCPT to really get a better estimate of concrete durability.

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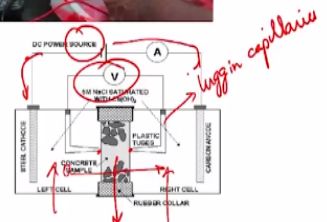
### Chloride Conductivity Test (DI Manual, SA)

- Consists of a two cell conduction rig in which concrete core specimens are exposed on either side to a 5M NaCl solution
- Chloride conductivity is determined by measuring the current flowing through the specimen due to the application of 10V potential difference



Classification Criteria:  
Alexander et al., 1999

Chloride conductivity (μS/cm)	Concrete quality
< 0.75	Very good
0.75 – 1.50	Good
1.50 – 2.50	Poor
> 2.50	Very poor



The other variant of this migration test is called a chloride conductivity test. Now what was happening in the previous 2 investigations that is the chloride permeability as well as chloride migration test was the fact that your chloride and hydroxide presented 2 different media on each side of your concrete specimen. So that means there are multiple reaction mechanisms that are involved or transport mechanisms that are involved.

Not only is the migration causing the chloride ions to move there is also possibility of chloride diffusion, there is a possibility of movement of other ionic species and so on and so forth. So what the South Africans did was they took the test for what it intended to convey? What does it convey primarily? the conductivity of the concrete. That is what is being conveyed in most of these experiments. The higher the conductivity, the less the durability of the concrete.

So the South Africans modified this test to simply measure the conductivity and to ensure that this conductivity was not being driven by either migration or by diffusion of the chloride ions what it did was both the anolyte and the catholyte solutions were made to be sodium chloride and on top of that the specimen itself was vacuum saturated in a sodium chloride solution. So what happens here?

When you vacuum saturate specimen in sodium chloride solution it is already filled up with chloride. All the pores are filled with chloride again. So there is no way that the chloride from here would like to move to the other side because first of all concentrations are equal and the sample is also saturated with the chloride solution. So what you are doing is simply applying a current across the outer electrodes and measuring the voltage across the concrete specimen.

The inner electrodes are connected directly to the concrete specimen by the help of these capillaries called Luggin capillaries. So you apply this power source, is applying a current on the outer electrode and you are simply measuring the voltage across the concrete and you convert this voltage to the conductivity of the concrete. So you find inverse of resistivity and call it conductivity and based on the concrete conductivity you can again qualify the concrete in terms of being very good or good or poor or very poor.

Again qualitative classification. Conductivity does not have any significance in directly associating itself with any service life parameter. We are talking all about service life but we will actually look at it only we get to corrosion, but right now what I am just trying to tell you is these values are not directly utilized in any service life prediction model. So they are just qualitative classifications of the type of concrete that you have in your system.

So again I was talking about this South African national roads agency so they are implementing durability specification in their projects by calling upon the contractor to actually build mock up panels or mock up slabs along with the other regular concrete specimens or not specimens along with regular concrete structure which are subjected to the same curing conditions and site conditions as the actual concrete structure.

Then from time to time we need to pull out core specimens from these slabs or mock-up panels, test the durability of that and the durability is tested by 3 methods, 1 is chloride conductivity, the other is oxygen permeability and the third is water sorptivity. So in all 3 methods the concrete has to satisfy certain minimum characteristics. So what they are doing is using these durability parameters to tightly control the quality of concrete that has been achieved in their projects.

And the roads agencies have been implementing this for nearly 10 years now or more than 10 years now and they have had very good success with it. The only difficulty lies in actually establishing where they can do the test because the laboratories where the test can be done, has to have a proper working system for example the oxygen permeability cell has to be properly calibrated.

The chloride conductivity apparatus has to be properly done and so on. What is softivity you do not really need anything other than a balance so it is not that difficult anyway, but vacuum saturation has to be done for the specimen so that is something different. So when all these tests are done you need to ascertain you need to ascertain that the labs which are doing the tests have they required equipment as well as our calibrated to do these tests accurately.

So they actually have an audit team from the South African International Roads Agency limited which goes in audits the lab to check whether all these systems are well in place. Only if they are qualified they can take up the testing of these specimens. So this is a very good example of how the state authorities have actually been influenced by the academic research to implement the durability specifications directly in their construction and they have been quite successful with it.

Now there was a study that was done there by one of the research scholars at university of Cape Town and that found that using these projects they were able to bring down the variability and concrete tremendously and the variability was almost non-existent especially in the case of a precast concrete production. Now in precast obviously we know the quality is much better controlled.

So they actually could see the difference very clearly from regular concrete construction to precast concrete construction. The quality difference clearly manifested itself in the durability values that were obtained. So again this is an example that can be emulated in our country also we also have several highway projects which are being currently executed we have lot of metro specifications that are currently been written.

And it all requires a little bit of willingness on the part of the owners to try out these systems because ultimately they are guaranteed a much better quality of the construction if they implement these systems properly, but for that they need to go the whole hog, they need to understand that all this has to be preplanned, the concrete mix design also has to be done with sufficient amount of time and to ensure that they get the kind of quantity that they have.

Because first of all the awareness of durability testing in our country is quite limited not many people know much more about durability tests. Increasingly as more number of consultants from abroad are taking part in joint ventures in India and different construction projects. There is a lot more awareness of durability testing that is slowly creeping in, but if you go to any major project for example most of the airports that were expanded.



They were done not by just an Indian company but they had to have a joint venture with a company that had executed airports of similar types abroad. So in most of these projects you had people from external conditions who had actually been exposed to durability related specifications previously in the construction projects. So these days you are increasingly seeing an infiltration of more and more durability tests in our construction projects.

But it will only increase in the near future, but for that to be ready for that we also need to understand what these durability tests are actually telling us. What kind of what are these results conveying with respect to the quality of the concrete? Are we accurately testing what we want to test in that given environment or not? So for that the basic background knowledge that I talked about in this entire chapter is very essential.

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Summary - Durability test methods and parameters

Category	Test method	Parameter
Test methods to assess chloride penetration	Rapid Chloride Permeability	Total charge passed
	Accelerated Chloride Migration	Non-steady state diffusion coefficient
	Chloride Conductivity	Chloride Conductivity
	Bulk diffusion	Chloride concentration profile
Test methods to assess gas penetrability	Oxygen Permeability	Oxygen Permeability Index
	Torrent Air Permeability	Coefficient of Permeability
	Accelerated Carbonation	Carbonation depth
Test methods to assess water penetrability	Sorptivity	Sorptivity index
	Germann water Permeability	Surface Permeability
	German water Permeability	Water penetration depth
Test method to assess concrete resistivity	Wenner 4 Probe Resistivity	Surface Resistivity

So just to summarize the durability test methods and parameters there are set of durability test methods that address chloride penetration and here we are looking at migration based test so diffusion based test, so you have the RCPT, accelerated chloride migration, chloride conductivity and bulk diffusion and again the parameters that they are giving could be quite different in this case it is a total charge passed.

In this case it is actually a diffusion coefficient, non-steady state diffusion coefficient or migration coefficient and chloride conductivity test. You actually get simply the conductivity of

the specimen and here you get the concentration profile that can again be fitted into a model to obtain the diffusion coefficient, the apparent diffusion coefficient. So if you look at the models they make use of this.

The duracrete model from Europe makes use of chloride migration coefficient and the life 365 model about which we will talk about in the corrosion chapter makes use of the apparent diffusion coefficient from chloride diffusion tests directly into the prediction of service life. Now added to this you have gas penetrability measurements using oxygen permeability, air permeability or accelerated carbonation.

And then you also have water permeability test that look at sorptivity or surface permeability or penetration depth of the water itself and then there is an indirect method that measures the concrete resistivity directly that is called the concrete resistivity method. Resistivity is not really giving you an indication of any of these 3 characteristics. It is a combination of all the factors. It basically reflects the interconnectivity of the porosity of that you have in your system.

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Summary - Transport mechanisms in concrete and test methods

Mechanism	Definition	Test method
Sorption	Capillary action	Sorptivity
Permeation	Flow under pressure	Oxygen permeability, Torrent air permeability ( <b>Gas permeability</b> ) Germann water Permeability, DIN 1048 water penetration ( <b>Water permeability</b> )
Diffusion	Flow under concentration gradient	Bulk diffusion, Rapid Chloride Permeability, Accelerated Chloride Migration, Accelerated carbonation
Migration/Conduction	Movement due to applied electric field	Rapid Chloride Permeability, Accelerated Chloride Migration, Chloride conductivity, Wenner resistivity
Wick action	Transport of ions or water from a face in contact with water to drying face	Sorptivity
Absorption	Bulk intake of water	Sorptivity <i>Water absorption</i>

This table simply again summarizes all the transport mechanisms and concrete and the relevant test methods and this is the very good guideline to have to think about what test methods you need to prescribe for a specific service environment. So you have this option which is basically

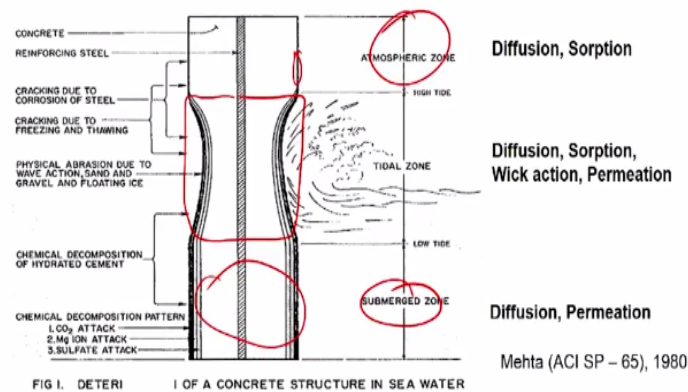
capillary action so this is represented by the sorptivity test method. Again another example wick action is transfer of ions.

Or water from a face in contact with water to a drying face that again is reflected quite nicely with a sorptivity test. Now bulk intake of water by absorption is not necessarily related to sorptivity you could also do water absorption test directly, but the sorptivity test if you look at the details of the sorptivity test the last step in the test is to actually completely vacuum saturate the concrete.

So actually measure the actual absorption also apart from the sorptivity rate. So, but if you want to directly measure water absorption that is also possible. So based upon the type of environmental condition you have you establish first what are the mechanisms that are likely to be acting in that region and what are the test methods that you need to look at?

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### Example - Concrete column in a marine environment



Give you an example I have picked up the example of a concrete column in a marine environment. You know that the concrete column in a marine environment is probably the most difficult condition for concrete to perform itself, to perform service in. so you have 3 different zones within a marine environment. You have a zone which is completely submerged where the water level is always above that level so that you have a complete submersion.

The concrete here in this region is subjected primarily to chemical attack because of the chemicals present in the sea water and there is also water pressure so there will be driving water inside by permeation. So you have permeation and then what is the second mechanism you will have. Since there are chemicals outside ionic species outside will start diffusing into the system. So you have permeation and diffusion as the primary mechanisms that are driving the performance of concrete in a submerged condition.

Now you have the atmospheric zone which is on top, which is not really subjected to a direct influence of the water, but there will still be some salt spray that will be spraying on to that. So it is not directly in touch with the water, but there will be salt spray. So there will be drying and wetting. So what sort of mechanism will act there, sorption there will be sorption. Definitely sorption will be there.

What else will happen? There will be wick action because there is extreme drying happening on top and to some extent there will also be diffusion. To some extent there will also be diffusion if the chlorides are deposited on the surface slowly then diffuse into the concrete only thing that will depend entirely on whether the concrete is in a saturated condition or unsaturated. If it is unsaturated, there is no question of diffusion.

Only when it is saturated you get diffusion. Now the main zone to worry about in sea water is this zone which is directly exposed to the splashing of the waves as well as the zone which is exposed to the tidal action. So in high tide, there is wetting and in low tide. There is going to be drying. So again all the mechanisms that we talked about whether in the submerged condition or atmospheric zone all of those come together in this splash zone, in the tidal zone.

So you have diffusion, you have water permeation, you have wick action, you have sorption, you also have physical degradation because your waves are splashing against the concrete so there is physical degradation. So that is probably the most extreme condition that you want to design for. So based on that you can then list out the mechanisms that are actually acting in these regions and for that you need to actually specify the test methods.

Now, we will connect this again with the actual classification how you can use different test methods to specifically address these issues in a later chapter, but right now this is what I wanted to tell you that for a particular service environment you need to work out the kind of transport mechanisms that will be prevalent and then address that by suitable durability test that we saw in the previous slide. So that is how you do a durability design for a concrete structure.

Assess the environment first, identify transport mechanisms, prescribe test methods, but there is one very important step that we have not covered here is for those test methods what are the limiting values of the durability parameters. I showed you some examples previously from performance specifications where people said 600 coulombs, 100 coulombs and so on, but is that reflecting anything about the service life of the concrete probably not. It is more a way of controlling the quality of concrete.

And indeed researching around the world is shown that if you specify a durability test in addition to strength test the quality of the concrete ends up being much better in the long term. So right now durability tests are being used for qualitatively characterizing the concrete to ensure the quality is maintained during the construction project, but what we want to do further is to utilize these durability parameters to actually predict how long it will take for corrosion to initiate in the system. So we will look at how this can be done to some extent in a later chapter.

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## Suggested reading

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- Alexander, M., Ballim, Y., and Santhanam, M., "Performance Specifications for Concrete Using the Durability Index Approach," *Indian Concrete Journal* Vol. 79, No. 12, **2005**, pp. 41 – 46.
- Mark G. Alexander, Manu Santhanam, and Yunus Ballim, "Durability Design and Specification for Concrete Structures – The Way Forward," *International Journal of Advances in Engineering Science and Applied Mathematics*, Vol. 2, No. 3, **2010**, pp. 95 – 105.
- Santhosh G Cheriyan and M. Santhanam, "Demystifying durability testing for Indian concrete construction industry," *Indian Concrete Journal*, Vol. 87, No. 7, **2013**, pp. 18 – 34.
- B S Dhanya and M. Santhanam, "Performance Specifications for Concrete Construction in India – Are We Ready," *Indian Concrete Journal*, Vol. 87, No. 9, **2013**, pp. 36 – 43.

With that we come to the end of the chapter on durability. There are lots of papers in this subject. I have only selected a few where we have directly provided our inputs also. So lot of research in this has happened in our laboratory primarily with the research project that we were involved in this Lafarge which is one of the largest construction material manufacturing companies.

And we did this research over the period of 4 to 5 years and we produced a lot data based on this research which talks about how these tests can be utilized and what we can do with the values we get the kind of durability parameters that we obtained from these tests. What do they signify for the performance of the concrete?

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## Durability – Chemical attack

### Chapter 5 in textbook

So this chapter is on chemical attack which is one of the primary causes of durability related issues and concrete. There are many types of chemicals that can attack concrete and in the last chapter we saw how different kinds of transport mechanisms can drive these chemicals into the concrete system, but 1 factor that is controlling all the chemical attacks or any durability problem in concrete as we saw in the last chapter is the interconnectivity of the porosity.

And concrete or the permeability of the concrete. So the primary factor that controls most durability problems is permeability. So you will see in this chapter and in the chapter that follows that the primary mechanism of protection of concrete will still be based on production of

concrete with low permeability and that is how you will obtain a better quality concrete that will resist most of the durability problems.

But in this chapter we will try to look at what are the mechanism of different types of chemical attack and how we can actually device strategies for protection other than the fact that we can produce concrete with low permeability that is something which will be a common strain in all the durability investigations that we talk about.

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## Types of chemical attack

- Sulphate attack
- Acid attack
- Chloride attack
- Carbonation

So there are different types of chemical attack. The most common ones being sulphate attack, acid attack, chloride attack, and carbonation. So let us look at these in more detail.

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# Sulphate attack: Introduction

- External sulphate attack: When the sulphate ions are from an external source
- Internal sulphate attack: When attack occurs from an internal source of sulphates, as in Delayed Ettringite Formation
- Common chemicals carrying sulphate ions ( $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{CaSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{FeSO}_4$ ) – these are present in various concentrations in seawater and groundwater

$\text{SO}_4$   
Cation

First Sulphate attack happens whenever there are sources of sulphates present in the ground water or in the soil and generally when the sulphates are getting driven from an external environment into the concrete we call it external sulphate attack, but there are some conditions under which we can actually have the kind of symptoms that are shown by external sulphate attack happening from within the concrete.

That means the source of the sulphate which is leading to deterioration is within the concrete and that is called internal sulphate attack or delayed ettringite formation. So we know that ettringite forms in the early stages of cement hydration and slowly converts to the monosulphate phase. If there is more sulphate available towards the end this ettringite will reform because the monosulphate is combining with sulphate to form trisulphate which is ettringite.

So this reformation of ettringite is what causes the problems because we have discussed earlier that ettringite can be expansive based on the type of crystal habit that has actually forms and in normal sulphuric attack also this ettringite formation happens in the harden concrete and to protect against that we use what? What type of cement do you use to protect against the ettringite formation? Sulphate resistant cement.

We use sulphate resistant cement which is low in C3A, tricalcium aluminate because if you have more C3A the tendency is to stabilize the formation of monosulphate. So that monosulphate can



reconvert to ettringite in the hardened concrete, but when you have low C3A the tendency is to stabilize the ettringite in the early stages so you do not have formation of later ettringite. So although we call this internal sulphate attack is DEF, delayed ettringite formation.

Even in external sulphate attack the primary cause of failure is the expansion caused because of secondary ettringite formation that means the ettringite that is not forming at the early stages I mean that is forming at the later stages. Early stage ettringite is called primary ettringite; the ettringite that forms later is called secondary ettringite. The common chemicals that carry sulphate ions include; sodium sulphate, magnesium sulphate, calcium sulphate, ammonium sulphate, iron sulphate.

What are some sources of pollutants which carry sulphates? Soil has obviously; agricultural soil can have sulphates from the fertilizers. So these are active sulphate based chemicals which are there in the soil, but what you need to understand is not all of them are soluble to the same extent. For example, if you look at sodium or magnesium sulphate the extent of solubility is much greater as compared to calcium sulphate.

The most abundant sulphate in the soil is calcium sulphate, but the solubility of calcium sulphate is limited whereas you have much greater solubility for all the other types of sulphates including sodium magnesium, ammonium or iron. Now why is that important? Why is the solubility important only if they are soluble they can actually penetrate the concrete either by diffusion or by permeation?

So getting into the concrete by the sulphate is only possible when you have soluble sulphates present in the soil so the ground water will dissolve these sulphates and bring it to the concrete surface and then the sulphates will penetrate either based on diffusion or a combined diffusion permeation mechanism. So now what you need to worry about is not just the amount of sulphate in the soil, but how much of this is present in a soluble form.

But I will also tell you one more thing that you need to be very careful about is the cation that is associated with the sulphate primarily we need to worry about magnesium and ammonium as

cations. We will discuss why that happens later because mostly the cationic species which are associated with the sulphates if they are of a type that lead to an acidic reaction in the cement paste then they are highly disastrous.

For example, magnesium and ammonium can really cause a lot more problems in your cement paste as suppose to sodium or iron or calcium. So when you are looking magnesium particularly a magnesium attack we need to be extremely careful about the role of the magnesium ion in the solution also. So not only we need to worry about sulphate we also need to worry about the cation. So cationic damage with magnesium especially is very important we will talk about how that happens in just a minute.

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## Other forms of sulphate attack

- Salt crystallization: if soluble sulfates migrate then reprecipitate – giving rise to expansive pressures
- Thaumasite: A calcium- carbonate- silicate hydrate which attacks the C-S-H matrix and causes softening and loss of integrity of the concrete.



Now there are other forms of sulphate attack also. We have talked about external sulphate attack in turn sulphate attack primarily related to ettringite formation, but then you can also get salt crystallization if you have drying and wetting the salts that are getting deposited by the water in the porosity after the water dries out the salt starts crystallizing again this can happen because sorption, wick action, all those kinds of things can make this problem even worse.

Because of which you have salt crystallization and this crystallization happening in fine porosity of concrete can create crystallization pressures and that pressure will break open the concrete. So again you have salt crystallization damage. The other damage which is getting more and more

important these days is called thaumasite attack. Now thaumasite is a phase that forms when apart from sulphate you also have a source of carbonate inside the system.

So you form a calcium silicate, sulphate, carbonate it is a very complicated product that actually forms because there is source of carbonate available in system where is this carbonate coming from limestone, lot of limestone is being used in the concrete these days so especially when you have low temperature conditions  $< 15$  degree you can have a lot of chances of thaumasite forming and this thaumasite attack actually happens directly on the CSH.

So you convert CSH into thaumasite which is your calcium, silicate, sulphate, carbonate. Complicated formula, but essentially the CSH is getting converted into thaumasite and this thaumasite is absolutely no binding strength whatsoever and it turns your concrete completely to mush. So there have been instances where this has been detected as a cause of damage. In the early day's people were not able to distinguish thaumasite from ettringite.

Because both of them look quite similar as far as the x-ray peaks are concerned, but later people started looking at these mechanisms and looking at the influence of carbonate in these mechanisms. So when you have carbonate sources available you do have a chance of forming this material thaumasite which leads to a lot more destruction as appose to simple sulphate attack. I won't say this reaction does not happen at higher temperature there had been evidences of thaumasite formation even at higher temperature.

When we are talking about 20 to 25 degree Celsius, but the chances are less that thaumasite would form in that temperature and sometimes they have formed without any carbonate sources in your aggregate also. Why does that happen because there is some amount of CO<sub>2</sub> dissolved in water especially from outside if you have sea water especially will have lot more carbon dioxide dissolved so you can get thaumasite formation in those conditions.

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## Sulphate attack reactions

- Hydrated cement phases react in an aqueous medium with the sulphate ions
- Primary products formed are gypsum and ettringite
- Other reactions result in a progressive loss of stability of the calcium silicate hydrate (CSH) which is the primary strength-giving compound of hydrated cement

CH ↓  
pH ↓  
role of carbon

Now what are the reactions of sulphate attack? Let us look at these a little bit more detail. We have hydrated cement phases that react in aqueous phase with sulphate ions. So what are the hydrated cement phases that will react? Monosulphate. What about calcium hydroxide? Will it not? Calcium hydroxide also will react. When calcium hydroxide reacts with sulphate? What is the product they should form? Calcium sulphate or gypsum.

Start precipitating gypsum and remember the original cement reactions. The gypsum goes into reaction with C3A to form ettringite. So you have the remnants of C3A and tricalcium aluminate hydrates along with monosulphate that can then react with this gypsum to reform ettringite. So gypsum forms first and then combine with the aluminate sources to form. So again gypsum formation itself has been associated with some level of damage primarily because gypsum is much softer than CSH or calcium hydroxide for that matter.

An ettringite formation primarily causes expansion that leads to damage in the matrix. Once these reactions almost near completion you have another type of reaction that may happen is the progressive loss of stability of CSH. Now why do you think CSH becomes unstable? When would CSH become unstable? When the pH of the surrounding system reduces. So if you are consuming calcium hydroxide.

When your calcium hydroxide goes down your resultant pH will also go down and this is where the role of the cation is very important. Certain cations for example like sodium; if you have a sodium sulphate reacting with calcium hydroxide what you will get? Gypsum plus sodium sulphate + calcium hydroxide should give gypsum + sodium hydroxide. So we are not really changing the basicity of the system much because we are again forming a highly alkaline material.

You are depositing a salt, but you are also forming an alkaline system around it. So the CSH does not get really unstable in sodium sulphate solution. Now when you have magnesium sulphate attack,  $MgSO_4 + Ca(OH)_2$  will give you  $CaSO_4$  gypsum + magnesium hydroxide. Now this magnesium hydroxide is an insoluble solid and when that forms it drives more and more of the calcium hydroxide to get removed from the system.

I will show you the example of how that happens and that leads to a major reduction in pH and where that pH reduction happens this will become a reality and that is when your concrete will get really broken down tremendously. It is not because of gypsum and ettringite that concrete fails in a major way primarily it is because of this fact that your CSH is losing its stability in an acidic system or not acidic less alkaline system.

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Action on CH:

$$CH + NS + 2H \rightarrow CSH_2 + NH$$

Gypsum formation

$$CH + MS + 2H \rightarrow CSH_2 + MH$$

Gypsum and brucite

*Insoluble solid*

Gypsum causes softening and strength loss, and is also reported to cause expansion. However, the further reaction of gypsum with the aluminates –  $C_3A$  and its hydrates, and, monosulphate, leads to the formation of expansive ettringite

Loss of CH → Reduction in pH of the system

Formation of brucite (MH) as a layer on the surface protects the concrete from further attack for a while; however, it does not help in the long run!

So let us look at the reactions in more detail. Again please remember this sulphate should be written with a bar on top for convenience i have used bar at the bottom or underlined letters at the bottom. I did not have an equation editor at that time so I just prepare it like this. So your calcium hydroxide + sodium sulphate of course there is water associated in this reaction without water this reaction does not happen. You have gypsum,  $\text{CSH}_2$  and sodium hydroxide.

In second case you get gypsum and magnesium hydroxide which is also known as brucite. Now this brucite is the insoluble solid that actually forms the layer on the surface of the concrete. Now you may wonder that if you are forming a layer insoluble layer in the surface it must be protecting your concrete from further damage. In deed that is what happens in the early stages of magnesium sulphate attack.

Then after this layer actually forms in the surface you get some respite from the further penetration of the sulphate solution, but please remember when you form this layer you are causing this reaction to keep on happening. So there has been more and more of calcium hydroxide will keep getting consumed and at a given stage the sulphate reactions just underneath this layer may be creating expansions that are large enough to break this layer.

This is only forming a surface skin right and this layer will eventually break and when it breaks already the concrete has very poor insight more sulphate gets in you start re-precipitating other phases. So this layer will afford protection only to a certain period of time. Unfortunately, we do not have a clear measure as to what is the time frame up to which it will afford protection.

It is a very complicated mechanism still debated by several people as to whether we can look at mineral mixtures positively or not we will look at that in just a minute. I will show you the results. So the formation of brucite protects the concrete from further attack in the initial stages, but it does not help in the longer.

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Action on CSH:

Maximum deterioration occurs with magnesium sulphate



This process could occur whenever the pH reduces (as a result of loss of CH)

Late stages of attack: conversion of CSH to non-cementitious MSH → complete disintegration



Ca leaching

The CSH especially when you have cations like magnesium present can react directly with your magnesium sulphate and lead to the precipitation of gypsum again magnesium hydroxide or brucite and silica hydrate that means your calcium from CSH is getting removed. Now why is this happening? I told you that calcium hydroxide is getting consumed that means the quantity of CSH is going down.

To maintain a balance or to maintain a pH balance what the CSH does is it gives out calcium to the surrounding system to maintain the valence to maintain its stability. So what is happening to the calcium to silica ratio? It is progressively going down in the CSH. At a given point the amount of attack is so much that all the calcium is actually gone out of the system and you form a silica hydrate.

If you look at any acid attack this silica hydrate formation is quite similar. So this is what is called leaching, calcium leaching. Now what I have not told you about is even if you have a pure source of water, pure water, distilled water it can actually lead to calcium leaching in your system, but of course the effect is not going to be as disastrous as magnesium sulphate attack, but it is slowly but surely going to cause calcium leaching from your system.

That is why when we cure concrete in the laboratory if you cure it underwater in just plain water tank we are going to have calcium leaching in the system, but if you cure it in a moist room

where there is fog bringing moisture to the system, it is not going to happen like that or alternatively for laboratory purposes if you want to store underwater it is better to store in a solution which is saturated with lime so that there is no external diffusion of the calcium.

So calcium leaching needs to be avoid in those cases. Now in magnesium sulphate attack this calcium leaching happens to a large degree. You form silica hydrate and then this magnesium silica hydrate can combine to form what is called magnesium silicate hydrate MSH which is quite different from CSH, it does not have the kind of characteristics as CSH has.

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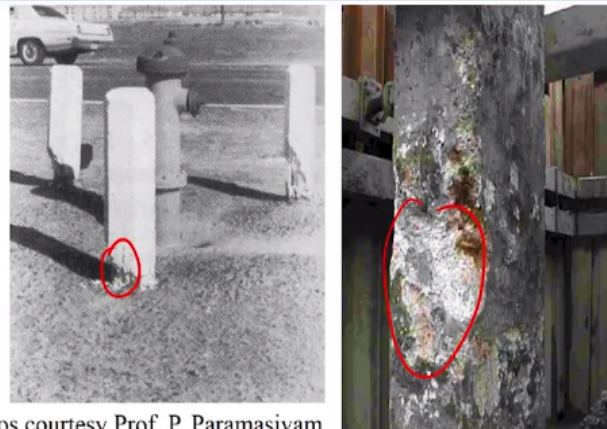
## Modes of failure

- Expansions associated with gypsum and ettringite formation lead to cracking
- Loss of strength and structural integrity due to a loss of the cementitious structure

I will show you some images from the thing before that of course of modes of failure are associated with expansion forms because of gypsum and ettringite formation that lead to cracking and then because CSH itself is losing its stability, you have a loss of strength and integrity of the system.

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Photos courtesy Prof. P. Paramasivam

So this is the picture from a column exposed to a sulphate soil and this is exactly what we are talking about in the last class where you have the major part of the damage at the soil air interface and that is because not only have a chemical effect here you also have the wick action, sorption all those are forming a large part of what has happened to this system. So, most of the sulphate attack is characterized by damage to the surface of the concrete. Obviously, sulphates are penetrating from the surface inwards so most damage will be at the cover zone of the concrete.

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Bridge columns in North Dakota in sulfate soils

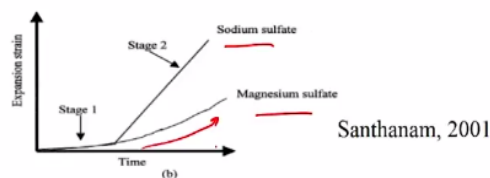
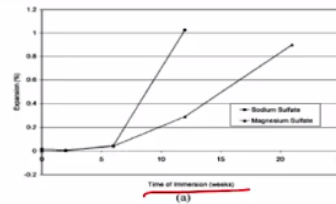
Hooton, 2009

This is a case where the concrete at the cover has been almost completely removed from the system. So you can see the rebar underneath and the concrete has basically fallen away

completely. The aggregates are intact, obviously aggregates are not participating in the attack, but the cement paste has been transformed into basically a non cementitious system.

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## Expansion trends in lab study

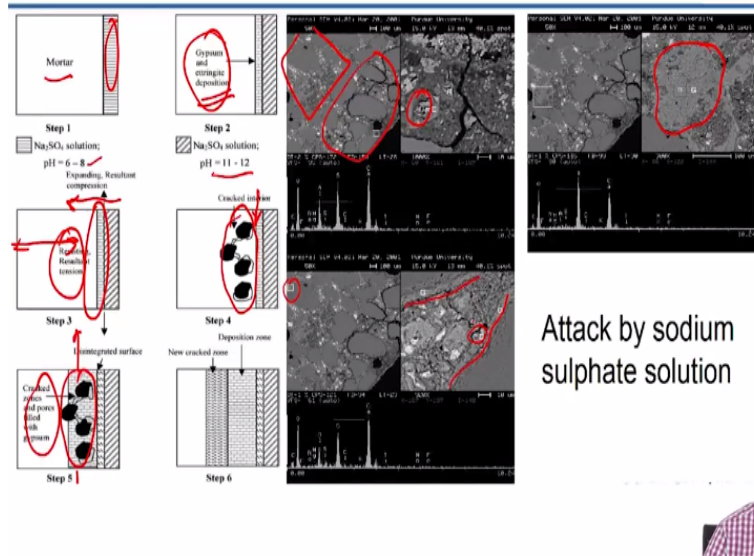


When you look at lab studies, from my own PHD works, so I have some slides from that. So if you look at lab studies general trend seems to indicate the there is some stage wise attack that is taking place and most research that you find in sulphate attack will be related to sodium or magnesium sulphate. Primarily from the view point, that these sulphates have the maximum solubility.

So if you want to do research on sulphates you want to do it in a reasonable period of time. If you use calcium sulphate or gypsum or calcium sulphate to do your attack, then you have to wait for a long time because you cannot really put so much calcium sulphate into the water. In sodium and magnesium sulphate you can make highly concentrated solutions. So the typical study involves preparation of mortar prisms and immersion inside a sulphate solution.

And from time to time we measure the change in length of mortar prisms and this change in length is recorded with respect to the time of immersion and in general what this tends to tells us is some sort of a stage wise process is happening in the case of sodium sulphate attack. In magnesium sulphate it is a more gradual increase of the expansion.

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Now what I looked at further when I combine these physical deterioration characteristics with the actual micro structural images from the system, what I was able to work out was some sort of a mechanism by which this damage actually occurs. Now here this is your Mortar which is immersed in a sulphate solution. The sulphate solution initially has a pH of 6 to 8. So as soon as you put your mortar inside this 6 to 8 pH sulphate solution.

There will be an outward diffusion of calcium hydroxide that leads to a increase in the pH of the surrounding environment to 11 to 12. And as calcium hydroxide is going out there is some sodium sulphate that is coming in which is going to start depositing gypsum and ettringite, at the skin of your specimen. Now what is happening is the skin where gypsum and ettringite are formed is now starting to expand.

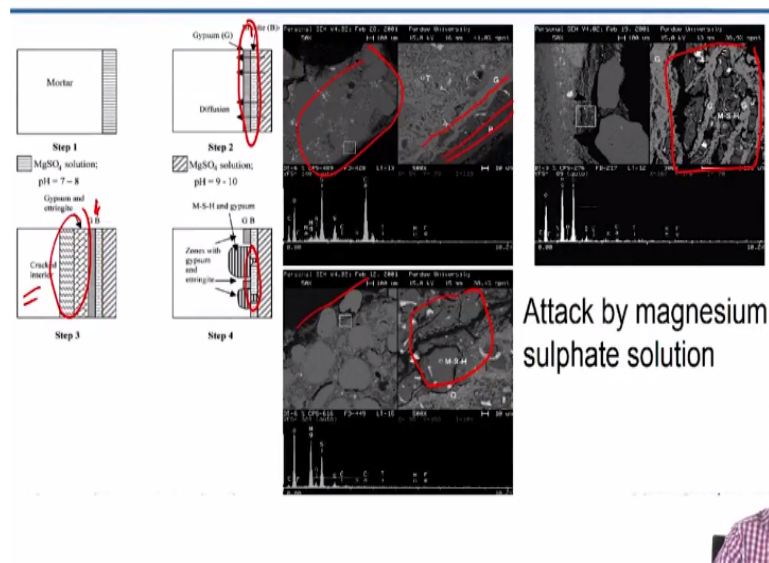
It wants to expand, but there is an interior which is not attacked and it is restraining this expansion from taking place. So what is happening as a result of that is that this resultant restraint to the expansion is leading to tension being created just underneath the skin and the interior starts getting cracked with time this part which is having lot of gypsum and ettringite starts becoming soft.

Sulphates penetrate further in, and start depositing gypsum and ettringite in this cracked zone which is at the interior. Then what happens next, this zone starts to expand and then you have a

cracking further interior to it and so on. So this is a stage wise process. So with this actually we were able to explain how mineral admixtures could be effective in this system because when you form lesser gypsum and ettringite.

When you replace cement for the mineral admixtures there is lesser tendency for gypsum and ettringite formation because you are lowering the amount of calcium hydroxide in a system. When you do that you are obviously causing a positive effect so the rate at which this progression actually happens to the inside of the concrete is reduced significantly when you substitute cement with mineral additives.

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Now when you use magnesium sulphate solution the effect is quite different. Of course the same sort of thing happens in this case also you have invert diffusion of your magnesium sulphate and outward movement of your calcium hydroxide that leads to the formation of this double layer on the system, you have a gypsum and brucite or magnesium hydroxide layer forming. The brucite may be stable for some time, but then all the inside reaction are still happening, gypsum.

And ettringite formation is happening which may again lead to cracking in the interior because their surface expansion leads to cracking the interior eventually this surface expansion will also fail the brucite layer may lead to cracking in the brucite layer and your system, your sulphate will

further penetrate into the system again start depositing your magnesium related products and gypsum and this is the kind of scenario you will get.

So in the previous one you can see the surface zone it is quite extensively cracked after certain period of exposure it is about 32 weeks of exposure to the concentrated sulphate solution and if you look at the microstructure within that you see a lot of ettringite in the pockets. If you look at this zone here which looks like it has not been attacked and if you look at the details, there you will see massive deposits of gypsum that means there is lot of attacks product have got deposited.

There and especially if you go in a region around the aggregate you will see a complete layer of gypsum forming around the aggregate and you have ettringite also which is there in inside the concrete. So although it looks like the zone is un-attacked there is a lot of deposition of attack products that is happening that so. So, based on micro structural evidences, and the way that the length change happened in the system.

I worked out this mechanism which would explain the role of different kinds of chemical and mineral additive in the system. In magnesium sulphate you can see very clearly at the early stage after about 12 weeks of attack you do not really see that much damage here in the surface zone because you have a very stable here of brucite and just underneath that you have a layer of gypsum forming inside.

But at a late state of attack you do not see that brucite layer any more if you see the entire surface has been converted into magnesium silicate hydrate MSH and this is another case where the entire surface seems to be a mixture of MSH and gypsum which is arising directly from this reaction I showed you earlier. You get magnesium silicate hydrate and gypsum. So this is almost forming a bands here you can see in the micro structural study here.

And that is what makes micro structural analysis of sulphate attack very interesting because you get to see these features if you look at regular concrete under the microstructure it always looks the same. So trying to figure out differences between 2 sets of concrete can be quite different and

frustrating at times. In sulphate attacks or any chemical deteriorate you will see a lot of alteration for the structure increase in porosity, deposition of attack products which makes it very interesting to do this.