Advanced Topics in the Science and Technology of Concrete
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Sulphate attack of concrete

Hello everyone, in the last lecture we were talking about different aspects of durability and the fact that the control of the water tightness of the concrete is absolutely critical as far as achieving the right long term durability is concerned, one aspect that we all must identify is that in the field very often the durability problems are because of a mixture of different transport mechanisms, you do not always have the same transport mechanism operating everywhere, usually it is a mixture of different transport mechanisms which leads to overall deterioration of the concrete.

Among the principle problems of durability you will be learning later about corrosion of steel and reinforce concrete that is probably the most critical problem but apart from that there are also lot of other problems which deal with the local environment around the concrete which affect the quality of the concrete, one such environment is the presence of sulphates either in the ground water or in the soil or in sea water in some cases, okay. So we are talking in this class about sulphate attack of concrete.

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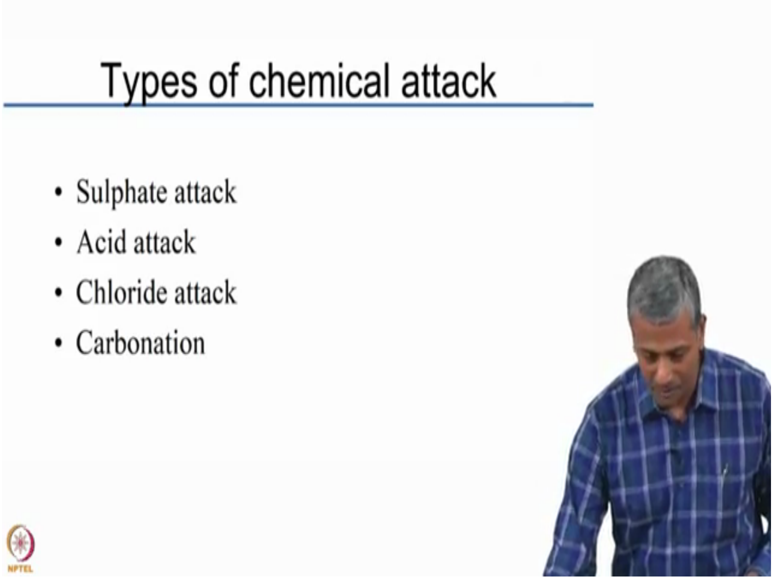

Types of chemical attack

- Sulphate attack
- Acid attack
- Chloride attack
- Carbonation

Now there are generally several other type of chemical attacks apart from sulphate attack also. For example you may have acids attacking concrete, you may have chlorides directly attacking concrete as in the case of sea water, and sometimes even in ground water there might be the sources of chlorides and the other chemical attack is carbonation that is attack of concrete by atmospheric carbon dioxide.

Now why are we calling these specifically differently because mechanisms involved and the kind of reactions that are involved in these chemical attacks may be different, but again one thing still stands in common between these classes of chemical attack is that they still require the presence of water because these chemicals are present in the chemical environment for them to be carried into the concrete a liquid medium or an aqueous medium is obviously necessary so that is what transports the material into the concrete.

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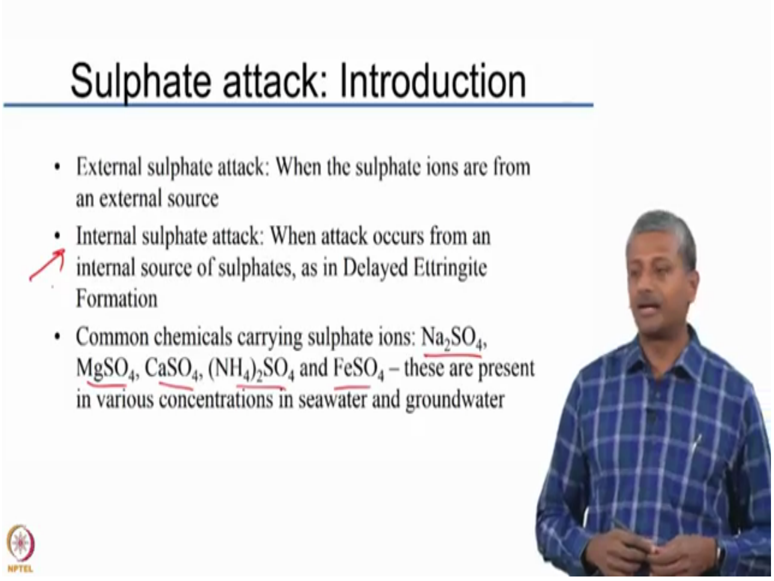

Sulphate attack: Introduction

- 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: Na_2SO_4, $MgSO_4$, $CaSO_4$, $(NH_4)_2SO_4$ and $FeSO_4$ – these are present in various concentrations in seawater and groundwater

So let us talk in a little bit more detail about sulphate attack which is the main topic of this lecture. Sulphate attack is classified into external and internal the external is when you have sulphates coming from an external source, okay. So for example if you have an agriculturally polluted soil lot of fertilizers they may be bringing in lot of sulphates, you may have soils which have a rich deposit of gypsum and that gypsum may slowly contribute the sulphate there into the concrete or sometimes even in sea water there is mixed chloride in sulphate, so sulphate can also attack the concrete from sea water.

So because of these multiple types of pollutants the concrete quality gets degraded, but then there may be some variations in the type of sulphates that are actually attacking the concrete you may have for example sodium sulphate, magnesium, calcium, ammonium, ion sulphate these are all species of sulphates that may enter the concrete. Now what is interesting is you also needs to understand which species is present in the local environment because that dictates the solubility of the material which dictates how much of it will actually get into the concrete because again please remember if it is a solid sulphate in the external environment there is no way it can find a way inside apart from some minor mechanisms like osmosis for example yeah like osmosis.

But in reality when there is ground water present it can actually dissolves from these sulphates and carry it into the concrete through the porous structure or the permeable structure of the concrete network. So again presence of water is absolutely necessary and the amount of dissolved sulphates is what is very important to consider. You may also have another type of sulphate attack or internal sulphate attack, here the source of sulphates does not come in from the outside, there is already a source which is built in in the concrete which somehow creates a deleterious reaction later on in the lifecycle of the concrete, okay we will talk about this also, this is also known as delayed ettringite formation.

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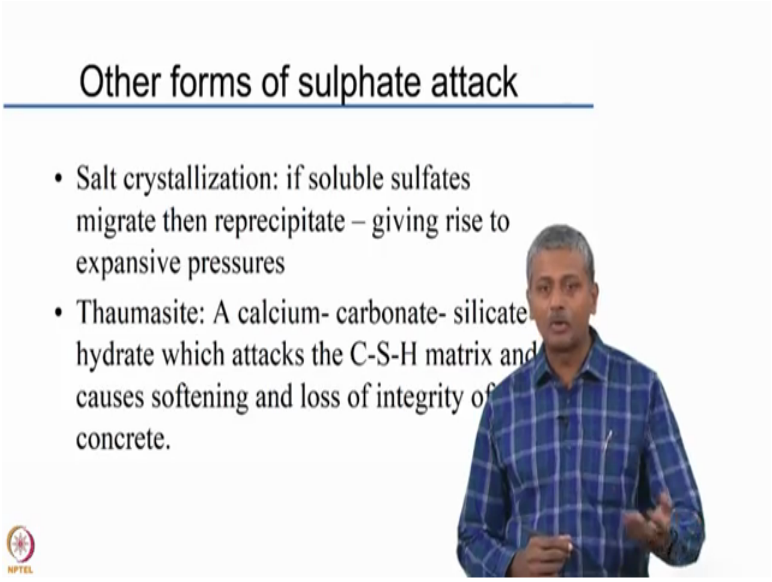
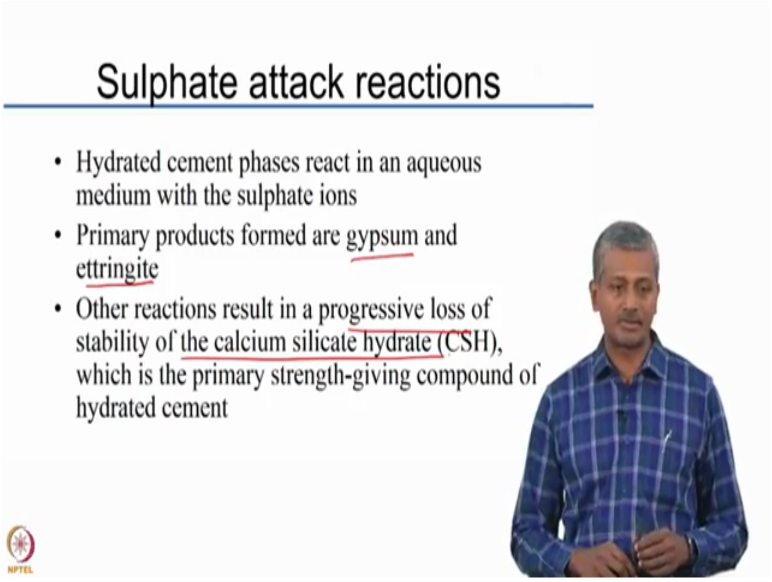


Other forms of sulphate attack

- 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 concrete.



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

Alright, so apart from these chemical attacks we may also get other forms of sulphate attack of course there is nothing purely physical or purely chemical, there is always an interpolate of physical and chemical aspects happening but for the ease of understanding people have generally divided sulphate attack into the chemical mechanisms and the physical mechanisms.

Salt crystallization is basically a physical mechanism, so we have the sulphates which are entering the pores of the concrete and crystallizing when there is sufficient concentration of the sulphate building up inside, there is super saturation and crystal growth will happen form that point onwards, when the crystal grows within a confined space of the pore the resultant stress can lead to cracking of the concrete that is called salt crystallization, okay.

You may also have a special form of chemical sulphate attack called Thaumasite attack and this happens whenever there is a source of carbonates present. For example your concrete may have used cement that is having limestone blended in it, limestone is calcium carbonate, you may have a soil or a ground water that has got lot of carbonates in it, hard water for instance.

In the presence of carbonates, sulphate chemical reactions involved in sulphate attack can take a new course is that you can actually lead to the destruction of your C-S-H directly by an attack on C-S-H and this leads to the formation of a very much like absolutely without any structural integrity the kind of product that forms is much like it is called Thaumasite. So that is a form of attack that can be quite deleterious especially in conditions which are below 15 degree Celsius, so the optimal range for formation of Thaumasite is between 5 and 15 degree

Celsius. So you do not see this everywhere but you see it in a great amount of detail when the temperature of the surrounding environment is less than 15 degree Celsius.

Okay, so what are these reactions that lead to the formation of products that are causing harm to the concrete? So again we are talking about hydrated cement phases such as calcium hydroxide, calcium silicate hydrate, calcium aluminates that can react with the sulphate ions coming from the external environment in an aqueous medium. So again water is absolutely essential.

The primary products that form as a result of this reaction are gypsum and ettringite. Now you are familiar with cement chemistry, so you know that cement originally has gypsum, the product cement itself has some gypsum in it and its formulation because gypsum is intended to control the reaction of the aluminates and bring about a controlled setting of the cement, okay.

On the other hand ettringite is a compound that forms in the early stages of cement hydration, in the long term this ettringite because of the availability of access aluminates in your system converts to mono sulphate. So when external sulphate attack occurs the external sulphate gets into the concrete, reacts with the mono sulphate and recrystallizes ettringite and this formation of ettringite is now happening in a harden concrete and from our understanding about the structure of the ettringite which I will also explore in some level of detail in the fourth coming slides ettringite has an expensive nature. So if it is forming in a harden concrete the expansion associated with ettringite formation can lead to cracking.

Now of course beyond all this there is a much more deleterious reaction which is a progressive loss of stability of C-S-H, now C-S-H you know very well is the adhesive phase inside your cement. So cement paste basically binds the aggregate together primarily because of C-S-H, okay of course all the other hydrate products like calcium hydroxide, ettringite, mono sulphate they are also filling a porosity which leads to an enhancement of the structural characteristics but the primary binding capacity is provided by C-S-H so progressive loss of the structure of C-S-H can lead to a major deterioration in the characteristics of the concrete.

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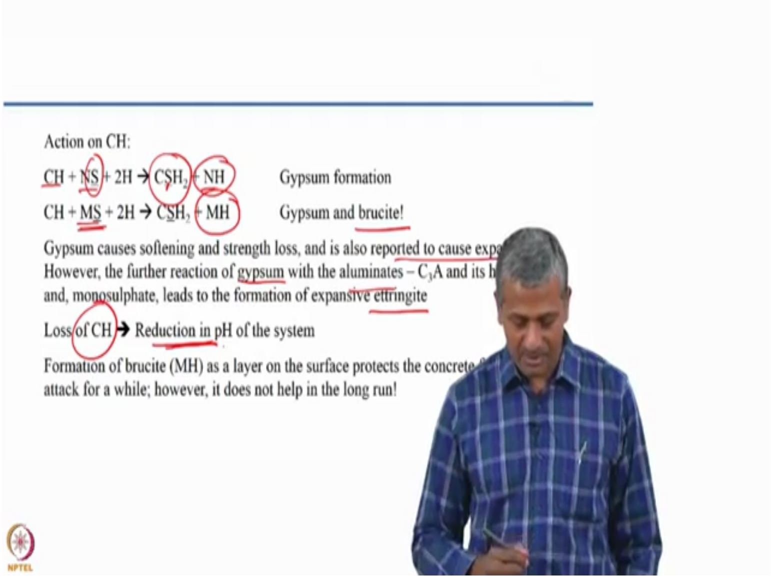

Action on CH:

$CH + N\underline{S} + 2H \rightarrow C\underline{S}H_2 + NH$ Gypsum formation

$CH + M\underline{S} + 2H \rightarrow C\underline{S}H_2 + MH$ Gypsum and brucite!

Gypsum causes softening and strength loss, and is also reported to cause exp

However, the further reaction of gypsum with the aluminates – C_3A and its h

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

attack for a while; however, it does not help in the long run!

Now just to put in simple terms the reaction which is represented in cement chemistry notation between calcium hydroxide and sodium sulphate leads to the formation of gypsum and sodium hydroxide, if you have magnesium sulphate as the attacking solution, now you may find that in literature people have looked at lot of sodium and magnesium sulphate based attack and this is because these sulphates are highly soluble and you can accelerate the process significantly in a laboratory environment that leads you to get your results much faster.

So lot of the literature are published about sulphates involving sodium and magnesium, but in reality you can have a mixture of different type of sulphates in your soil or ground water which may be ammonium, which may be ion whatever it may be, but the fact is that your sulphate goes into reaction first with your calcium hydroxide to produce gypsum and gypsum itself is not a very hard material, you are transforming your calcium hydroxide which is a hard product into something softer because of which there obviously be some softening and strength loss.

But there is also some literature which says gypsum formation causes expansion especially when you have very high concentration of sulphates that is some controversy regarding that. So again gypsum itself just like what happens in fresh cement paste this gypsum can go into (hydration) reaction with the aluminates involving C 3 A or hydrated forms of C 3 A like mono sulphate or calcium aluminate hydrate and reform expansive ettringite and that is probably the most deleterious stage of this reaction as observed in laboratory experiments but in the field there is something different that happens I will talk about that later.

One major issue is that you are losing calcium hydroxide so you are causing a reduction in the alkalinity of the system, okay. Now in the case of sodium sulphate attack you are also producing sodium hydroxide, so the alkalinity loss is not that great because your surrounding environment still has a fairly alkaline medium. But if you have magnesium sulphate as the attacking solution you form an insoluble solid called magnesium hydroxide or brucite and this brucite because of its nature of insolubility keeps promoting the dissolution of calcium hydroxide this forward reaction involving magnesium sulphate in calcium hydroxide is promoted to such an extent that you can actually lead to a complete removal of calcium hydroxide.

So that means you are going to cause more and more reduction in pH and when a lot of reduction in pH happens your C-S-H calcium silicate hydrate can start getting decalcified in other words it will start losing some calcium from within. In any acidic condition this is a very common phenomenon that happens is that the calcium to silicon ratio of C-S-H keeps progressively reducing because calcium wants to come out and provide a high pH environment, okay. So the decalcification of C-S-H happens in this.

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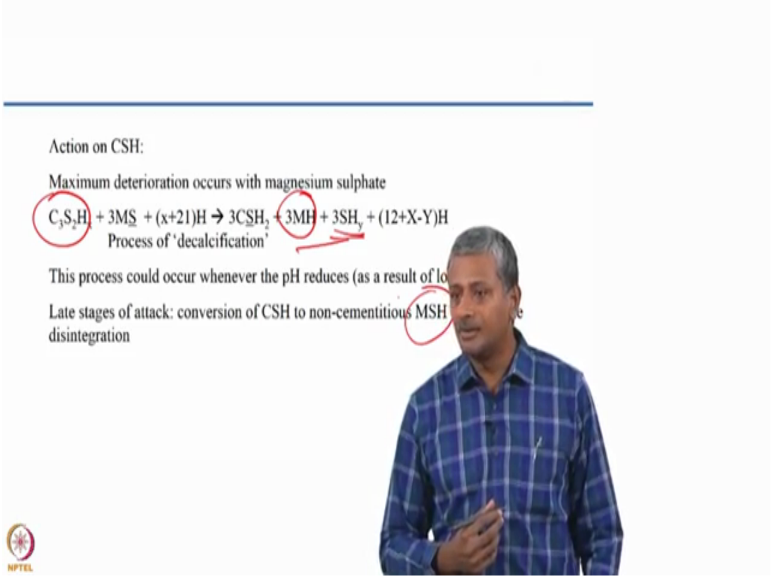

Action on CSH:

Maximum deterioration occurs with magnesium sulphate

$C_3S_2H_x + 3M\underline{S} + (x+21)H \rightarrow 3C\underline{S}H_2 + 3MH + 3SH_y + (12+X-Y)H$

Process of 'decalcification'

This process could occur whenever the pH reduces (as a result of lo

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

disintegration

So what happens ultimately is your C-S-H can decalcify and lead to the formation of something like a silica hydrate. Now silica hydrate does not have the same binding characteristic as your C-S-H, okay and soon this magnesium which is present as a magnesium hydroxide can combine with the silica hydrate to form what is called magnesium silicate hydrate MSH magnesium silicate hydrate then absolutely that is absolutely got no binding characteristic just like your C-S-H. So this means that you are getting a complete loss of your cementitious structure at this stage.

So you have several stages one is formation of gypsum, then you have formation of ettringite but slowly but surely you will also get the decalcification of the calcium silicate hydrate whenever any acidic condition is created around the C-S-H. So in this study if I used instead of (cal) sodium or magnesium sulphate if I use sulphuric acid the reaction will be all that much more faster you will form some gypsum, you may or may not form ettringite I will talk later about the fact that ettringite is not very stable in a low pH environment.

But because of low pH conditions your C-S-H will very soon start getting decalcified and you will lose your cementitious structure very fast. So you can very quickly dissolve your cement paste in acid of course we use that as a means of determining the amount of cement paste in concrete the acid dissolution test provided obviously that your aggregates are siliceous aggregates they do not dissolve in acid whereas cement paste being a calcium silicate hydrate it dissolves easily in acid.

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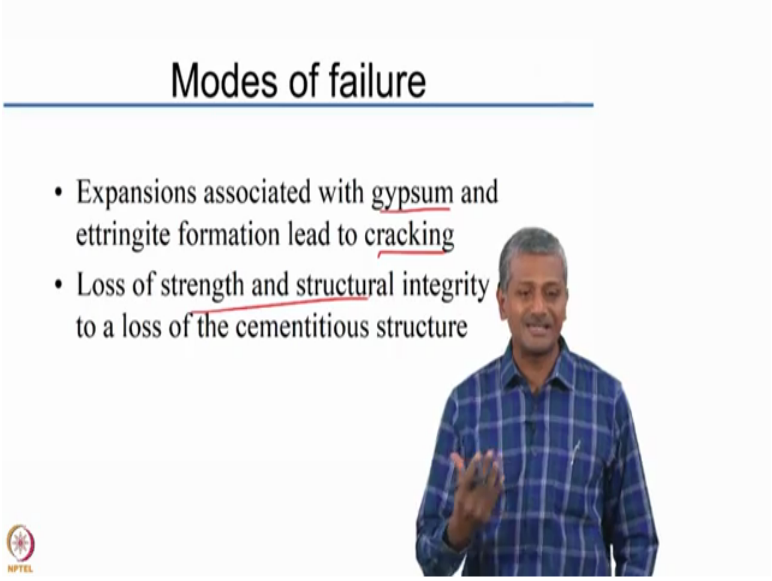

Modes of failure

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

Photos courtesy Prof. P. Paramasivam

Okay, so what are the modes of failure, how does failure manifest itself? You have the expansions, maybe because of gypsum but mostly because of ettringite that lead to cracking, so when expansion is happening inside a harden concrete system there is obviously a chance of extensive cracking to happen because concrete does not have the (())(12:18) to take the pressures related to the expansion.

In a fresh state concrete is still pliable, it has got a low modulus, it does not resist expansion or contraction much so it does not crack. But in a harden concrete it has got a high modulus, it is rigid if you are causing any volume changes obviously there will be cracking, okay. Then the other aspect is a loss of strength and structural integrity because you are losing your C-S-H structure. So these are the modes of failure and you can see from this classical picture of this concrete column which is standing in a sulphate rich soil that a lot of deterioration is seen at the interface between the soil and the air, okay.

Now this is because you have multiple transport mechanisms that are actually acting, under the soil there is obviously going to be a sulphate rich solution which is permeating into the concrete, but because of the air interface at this location there is substantial drying which is pulling up the surface further into the concrete and because of drying the water is going away enriching the sulphate in this region.

So we got more higher concentration of sulphates at this interface region as compared to what is under the soil, okay. So we get very high deteriorations whenever you have multiple transport mechanisms involved. For example even in the lab environment instead of continuous emergent if you do wetting and drying you will ultimately get a larger level of attack, we will talk about that later also.

So again another picture, you can see the surface deterioration which is happening in the case of sulphate attack. Now surface deterioration is a common phenomenon in most chemical attack, okay most chemicals are attacked from an external source will lead to a slow but steady deterioration from the surface inverts.

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Bridge columns in North Dakota in sulfate soils

Hooton, 2009

Again this is a example provided by Professor Doug Hooton from the US where these columns are standing in North Dakota in sulphate soils and you can see that almost all of the concrete in the cover zone is completely spalled you can see the pieces of concrete lying around, so much expansive stresses have been generated that you are spalling is tremendous in these columns.

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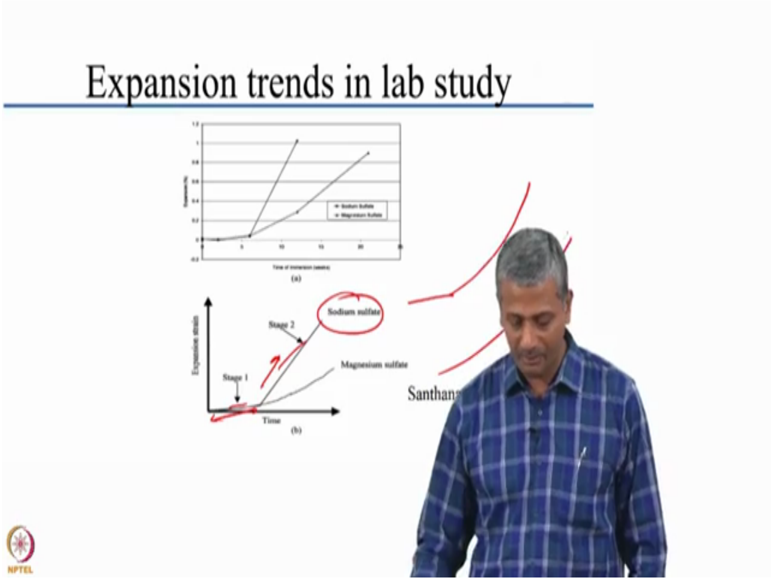

Expansion trends in lab study

Now in the lab studies generally if you look at lab studies done across the world these are based on continuous emergent of mortar bars inside sulphate solutions, why mortar? Because it is much faster to make then concrete and generally the reactions also can be studied in a much smaller size scale that leads to a quicker interpretation of the results, okay. In general what you see is when you look at chemicals like sodium sulphate there is a two stage mechanism that is typically observed in the expansion process.

So you have a stage 1 where the expansion is quite small and it is almost like an initiation process like what you see in corrosion, beyond this point there is a rapid rise in the rate of expansion of course this need not be perfectly a straight line you could have something like this also, okay. So this is just an idealization of some experimental data and magnesium sulphate you actually see this kind of a slow but steady rise of expansion which is almost a curve type behaviour, okay.

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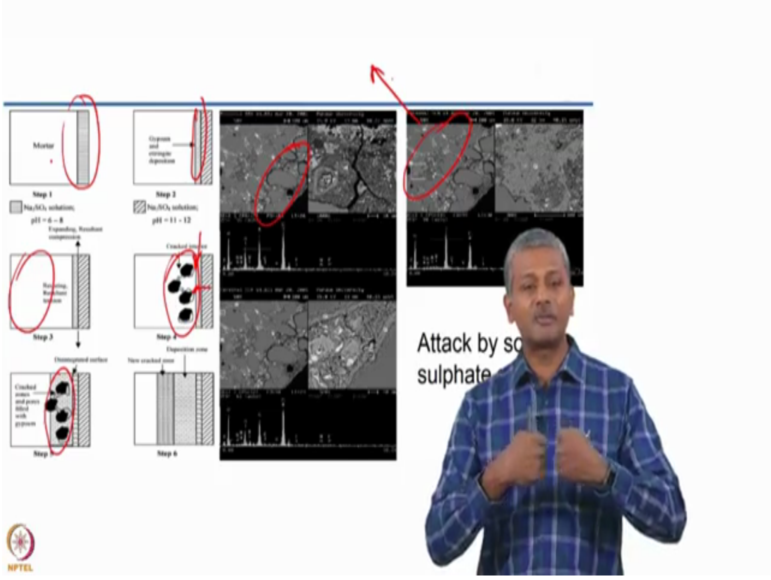

Now if you look at how this can be related to what microstructural changes actually happen in the system, you can see that in a mortar that is immersed in sulphate solution there is sulphate solution just surrounding the mortar at the beginning of the experiment, slowly you start forming a layer of gypsum and ettringite just below the surface or just at the surface, this gypsum and ettringite layer will start causing expansions so this layer would like to expand but the bulk material that is inside is going to resist this expansion, right because the bulk material does not want to change its volume because of this there will be a bulk compression in the expanding layer and a tension inside the bulk layer, okay because of that the interior starts getting cracked.

Now with time gypsum ettringite which are in the outer layers start getting unstable, more and more sulphate penetrates and then starts depositing gypsum and ettringite in this cracked interior, okay. Now further again this cracked interior will be having the ettringite in gypsum deposition which will lead to again expansion and then further crack the zone right under that, okay.

So there will be a progressive deposition, expansion and cracking inside and further propogation of your sulphate solution itself. So this is like a three stage mechanism that actually is prevailing here and this on the right you see several images that are sort of supporting this evidence. So for example you have a surface zone which seems to be cracked here which seems we have already undergone this problem and you can see that just under the surface zone there is a layer which is full of attack products, okay and I have not shown a picture of what happens still further in when you go towards the interior of the system is that there is more cracking in the interior that is because of the resulted tension which is caused by restricting the expansion of this surface zone.

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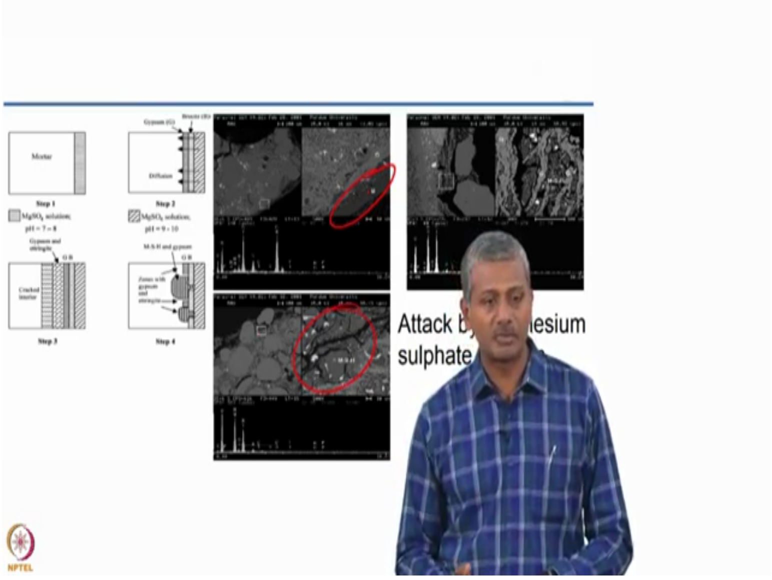

In the case of magnesium sulphate as I said brucite layer forms on the surface, so you have this brucite layer which is forming on the surface at very early stages of the attack and it somehow acts like a protective skin for some time, it prevents further penetration of sulphate for some time, but then because of its propensity to keep on removing calcium hydroxide it is going to lead to something like this where ultimately your C-S-H completely goes away and it is transformed into what is called magnesium silicate hydrate which is not having any significant binding characteristics, okay.

So the attack depends a lot on the cationic species that is involved, in most other cases calcium, ion, sodium you have primarily an effect of the sulphate itself which is attack in concrete, but when you talk about magnesium the cationic role is also very important and again with ammonium sulphate also because of extremely high solubility you can actually get a lot more dangerous attack in the case of ammonium sulphate solutions also.

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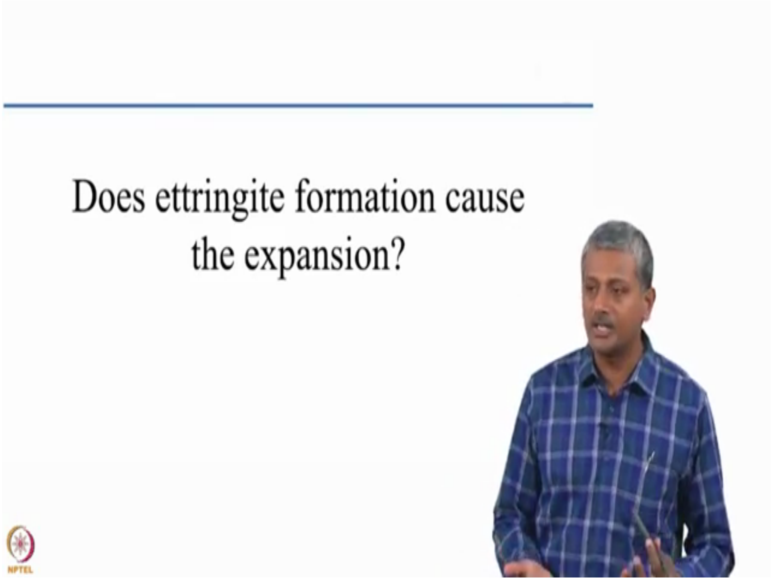

Does ettringite formation cause the expansion?

Okay, so let us try and look at this question whether ettringite formation actually leads to expansion? Now there have been several theories proposed as to how ettringite formation causes expansion and in what conditions does it cause expansion?

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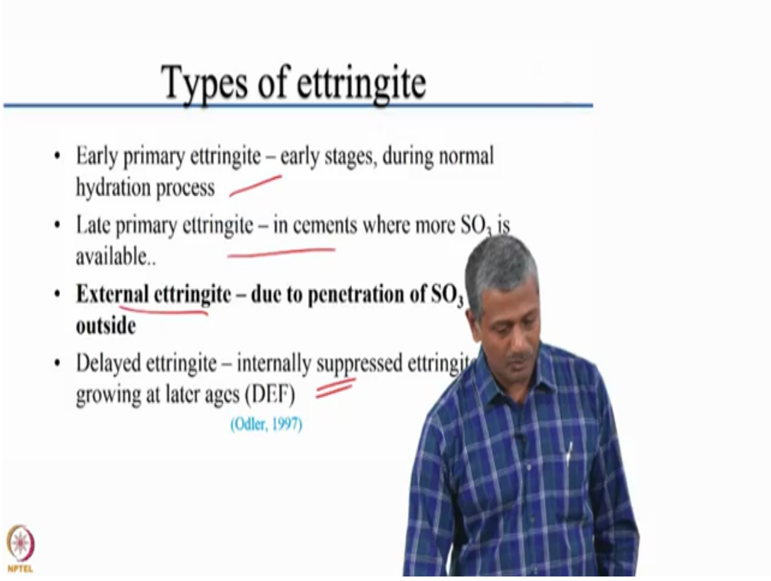

Types of ettringite

- Early primary ettringite – early stages, during normal hydration process
- Late primary ettringite – in cements where more SO_3 is available..
- **External ettringite – due to penetration of SO_3 outside**
- Delayed ettringite – internally suppressed ettringit growing at later ages (DEF)

(Odler, 1997)

So there are different types of ettringite which we must consider before we answer that question, one is early primary ettringite which forms at early stages of the hydration process which is normal, then you have late primary ettringite in cements where more sulphate is available, if you have a lot of sulphate in your system you will continue to form ettringite over a long period of time, all the eliminates will start getting utilized to form the ettringite.

Then you have external ettringite which forms because of penetration of sulphate from the external environment, okay this is what we are trying to consider in the case of sulphate attack and there is of course delayed ettringite formation about which we will talk a little bit in the last few slides of this lecture.

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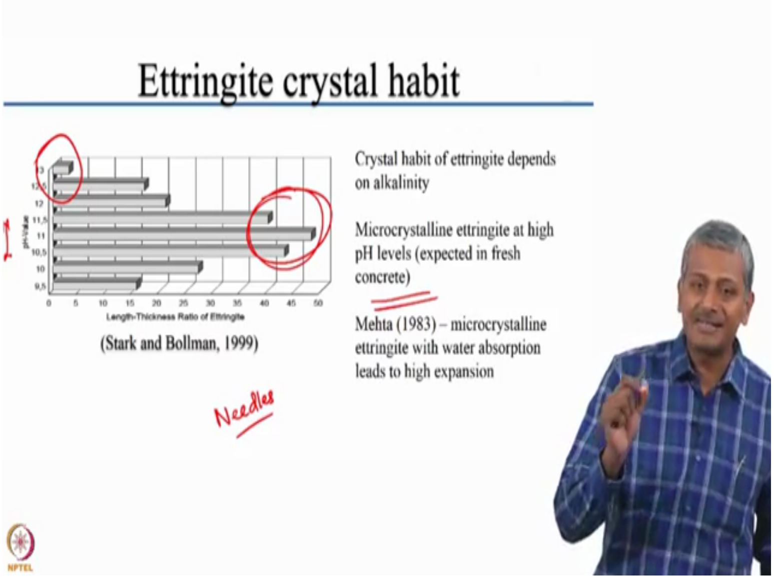

Ettringite crystal habit

(Stark and Bollman, 1999)

Needles

Crystal habit of ettringite depends on alkalinity

Microcrystalline ettringite at high pH levels (expected in fresh concrete)

Mehta (1983) – microcrystalline ettringite with water absorption leads to high expansion

Now if you look at the literature on the crystal form of ettringite generally if you look at most classical literature there you will see their ettringite deposits in the form of needles, okay and this needle like structure of ettringite can have a very different aspect ratio that is length to cross sectional area ratio depending upon the pH conditions that are prevailing at the system. So you see here that the length to thickness ratio of the ettringite is maximum when you have a pH range between 10 and 12, what does this mean? That when your conditions become more acidic as compared to your regularly highly alkaline cementitious paste system you have a chance of seeing a larger length to thickness ratio of ettringite.

Now in some cases you may form microcrystalline ettringite of very high pH levels. Now what is going to happen is such large needles of ettringite will need a lot of space to actually grow, so if the space is available in your system like pores and voids this kind of ettringite can actually start forming there, okay. Now what type of formation should cause expansion? The expansion should be caused by ettringite that is actually growing within very small pores such large ettringite probably will not be able to grow in very small pores.

Now this ettringite which is forming at high pH levels and that level it is microcrystalline and that size can start forming in small pores and because of the tubular structure that ettringite has such ettringite in smaller porosity when it imbibes more water can lead to a lot more expansive stresses in the system. So now the general agreement in literature is that the expansion due to ettringite formation primarily happens because of the smallest scale ettringite that is present in the small pores of C-S-H, not the ettringite that is present in voids or cracks, okay when ettringite deposits in voids or cracks it is a recrystallization that is actually happening because it has got a lot of space now to move (and break) and grow, but the expansion is not really at that stage, the expansion is really is caused when you form this microcrystalline ettringite inside the C-S-H.

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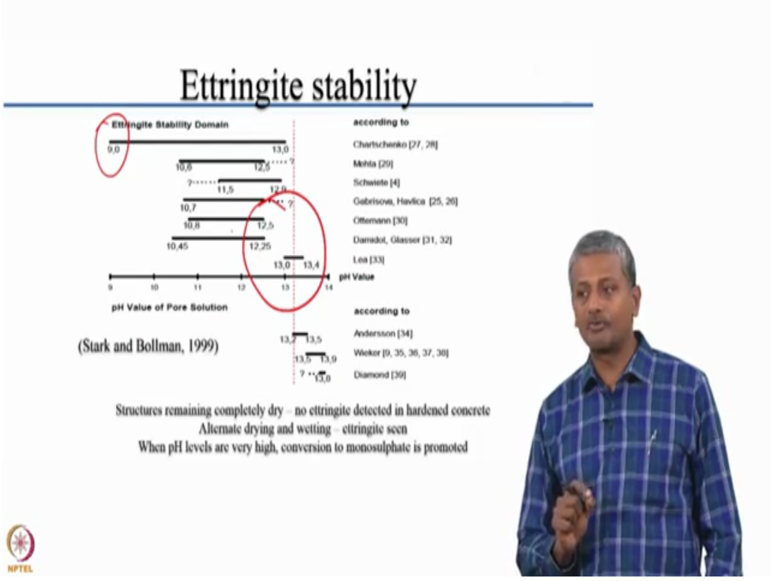

Ettringite stability

(Stark and Bollman, 1999)

Structures remaining completely dry – no ettringite detected in hardened concrete
Alternate drying and wetting – ettringite seen
When pH levels are very high, conversion to monosulphate is promoted

Again as far as stability of ettringite is concerned the stability domain is restricted to certain pH. So for example in highly acidic solutions like sulphuric acid for example you will probably will not have any ettringite unless you go deep into the structure of the concrete, in the surface zones where the acid has already penetrated you will probably not be able to crystallize ettringite because it is not stable in that domain.

So very few literature is actually reported observing ettringite at pH levels are below 9, okay. So in most acidic cases obviously your pH's are going to be dropping much further. Just like for example when you have carbonation, okay one of the common phenomena in carbonation or because of the lowering of the alkalinity of the system the ettringite that is present in the concrete will dissociate and form other products like aluminium hydroxide, gypsum and so on, it is not going to be remaining stable as ettringite because of the low pH conditions.

So again what you need to understand is the formation of ettringite can happen in specific circumstances, the stability of ettringite can also happen only in specific circumstances and whether this ettringite leads to expansion or not depends on where this ettringite is actually growing, okay. So we are mostly worried about the high pH ranges of ettringite formation where it is actually growing in the extremely minute pores of your cementitious system.

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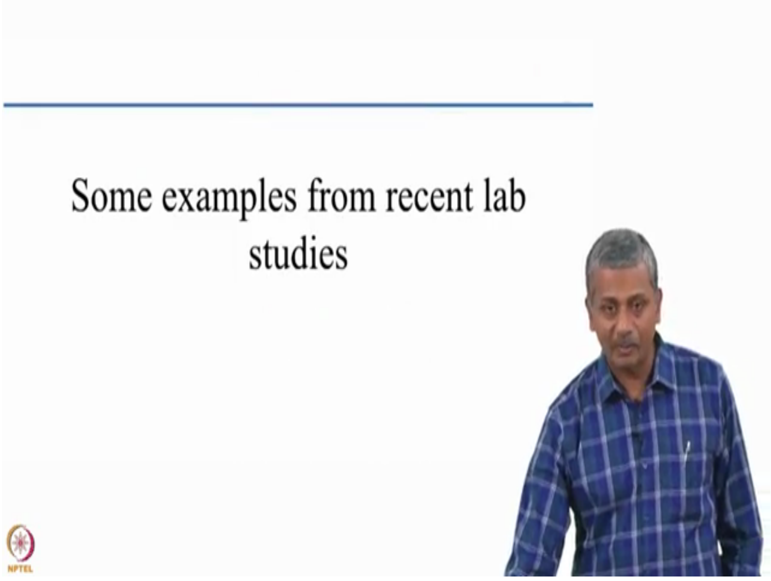
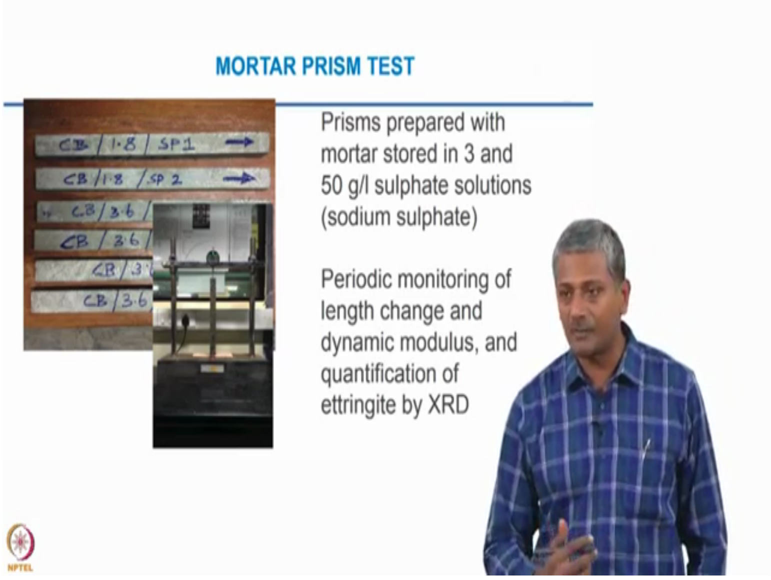


Some examples from recent lab studies



MORTAR PRISM TEST

Prisms prepared with mortar stored in 3 and 50 g/l sulphate solutions (sodium sulphate)

Periodic monitoring of length change and dynamic modulus, and quantification of ettringite by XRD

Some examples from recent laboratory studies just to put this in perspective so here these are mortar bars which are stored in different concentration of sulphate solutions 3 gram per litre and 50 gram per litre of sodium sulphate solution and periodic monitoring of the length change was done, also dynamic modulus by resonant frequency was determined for this mortar bars.

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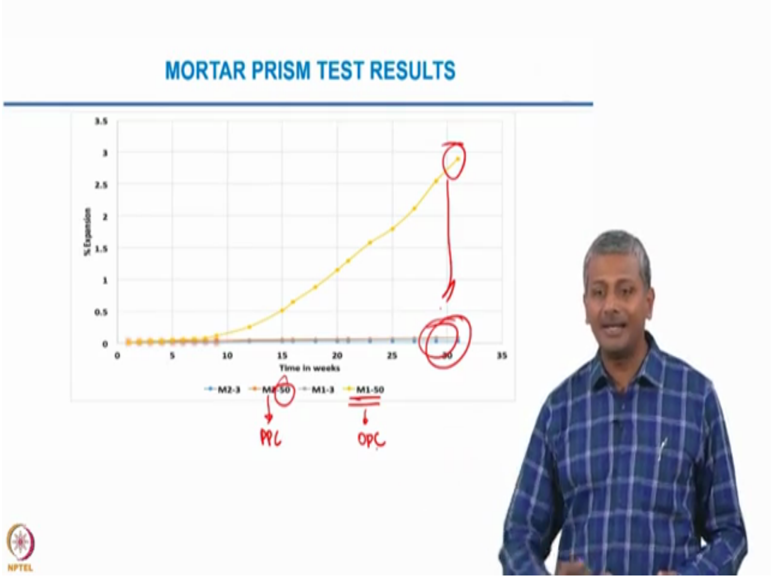
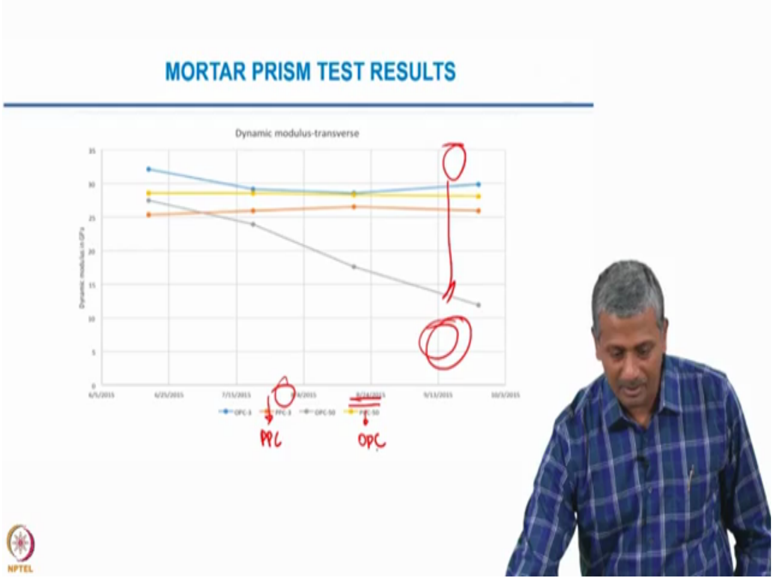


MORTAR PRISM TEST RESULTS



MORTAR PRISM TEST RESULTS

You can see the expansion results here in terms of this M1 basically relates to Ordinary Portland Cement and M2 relates to portland pozzolana cement so that has got fly ash in it 30 percent fly ash in it, okay. So M1 at 50 gram per litre is showing a significantly high expansion close to 3 percent after about 32 weeks of exposure, okay these are weeks of exposure.

And then all the other systems seem to have expansions which are much lower than 0.1 percent, generally tendency for us to classify concrete as being sulphate resistant is when we do this mortar bar test and find an expansion of less than 0.1 or 0.2 percent that is typically taken as a criteria of a sulphate resistance. So obviously when you are changing OPC to PPC even at the 50 gram per litre solution you have a very low expansion, so the obviously using fly ash leads to sulphate resistance there is no question about that.

What happens when you lower the concentration? Again when you lower the concentration your attack mechanism is such that the there is a significant delay in the process itself, okay this is just the result in dynamic modulus.

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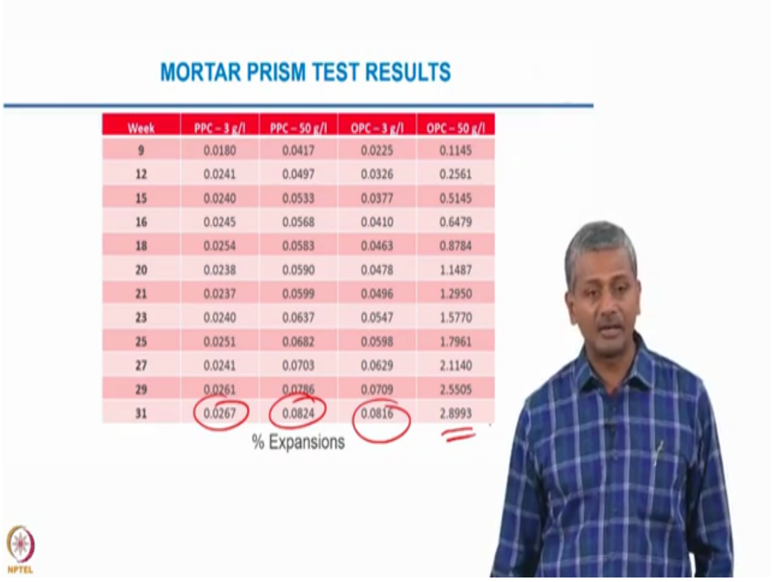
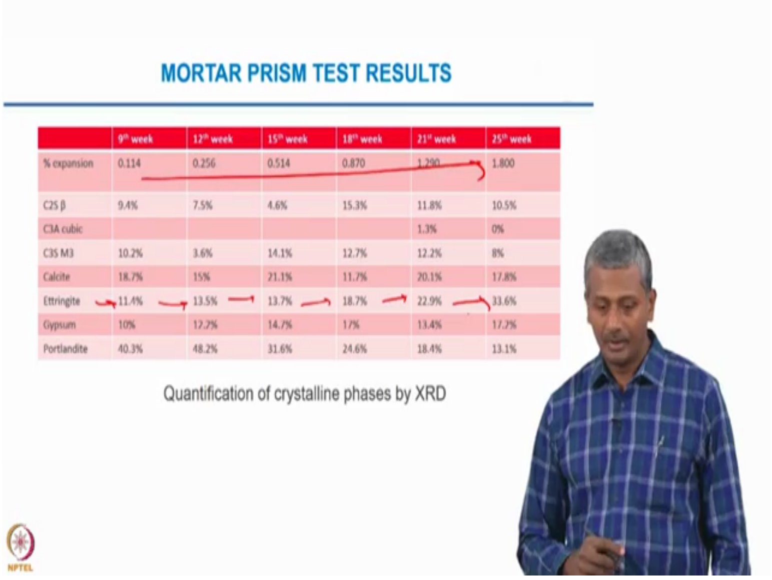


MORTAR PRISM TEST RESULTS

Week	PPC – 3 g/l	PPC – 50 g/l	OPC – 3 g/l	OPC – 50 g/l
9	0.0180	0.0417	0.0225	0.1145
12	0.0241	0.0497	0.0326	0.2561
15	0.0240	0.0533	0.0377	0.5145
16	0.0245	0.0568	0.0410	0.6479
18	0.0254	0.0583	0.0463	0.8784
20	0.0238	0.0590	0.0478	1.1487
21	0.0237	0.0599	0.0496	1.2950
23	0.0240	0.0637	0.0547	1.5770
25	0.0251	0.0682	0.0598	1.7961
27	0.0241	0.0703	0.0629	2.1140
29	0.0261	0.0786	0.0709	2.5505
31	0.0267	0.0824	0.0816	2.8993

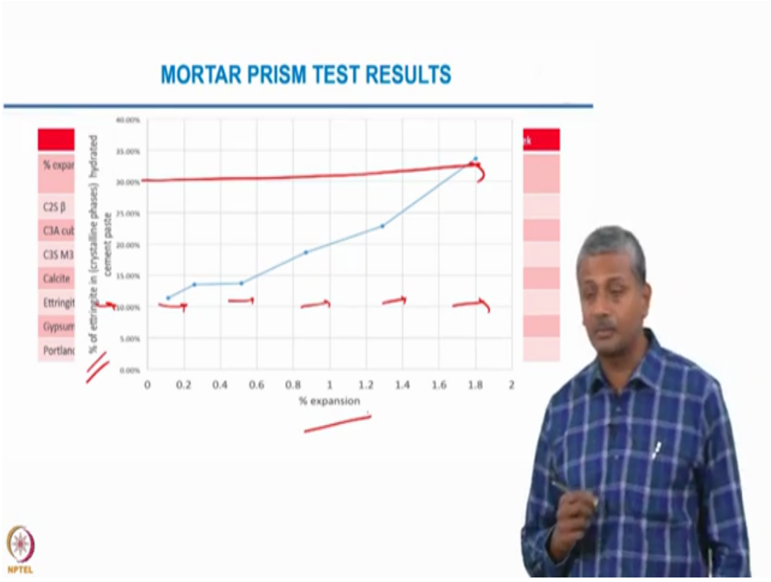
% Expansions

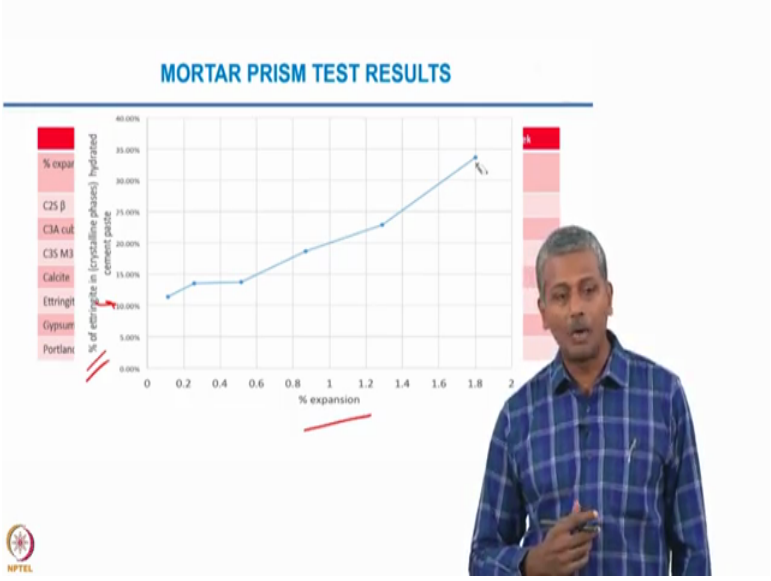


MORTAR PRISM TEST RESULTS

	9th week	12th week	15th week	18th week	21st week	25th week
% expansion	0.114	0.256	0.514	0.870	1.290	1.800
C2S β	9.4%	7.5%	4.6%	15.3%	11.8%	10.5%
C3A cubic					1.3%	0%
C3S M3	10.2%	3.6%	14.1%	12.7%	12.2%	8%
Calcite	18.7%	15%	21.1%	11.7%	20.1%	17.8%
Ettringite	11.4%	13.5%	13.7%	18.7%	22.9%	33.6%
Gypsum	10%	12.2%	14.7%	17%	13.4%	17.2%
Portlandite	40.3%	48.2%	31.6%	24.6%	18.4%	13.1%

Quantification of crystalline phases by XRD


MORTAR PRISM TEST RESULTS


MORTAR PRISM TEST RESULTS

For mortar prism test of course these are the just the results of percentage expansions in the actual numbers just to show that at 31 weeks the extent of expansion is less than 0.1 percent in other three cases where it is close to 3 percent in the case of 50 gram per litre sulphate solution. Again this is just showing you the rate at which it is the growth is happening, so this is the rate of expansion from 9th to 25th week in the same time period what we also did was we took the mortar from the expanding prisms and then analyse the cementitious materials or the crystalline phases that are in the system using quantitative x-ray diffraction.

And what you can also see is that in this process there is a steady growth in the amount of ettringite that seems to be forming in the system, okay and if you do a plot between the ettringite content versus the of course this is not the 100 percent correct quantitative estimation because we are only looking at ettringite as a function of the amount of crystalline phases, whereas you know that in cementitious systems there is going to be (())(24:50) phases also. So this is a semi quantitative approach to look at whether ettringite formation can be related to expansion or not and the trends do indicate that yes you are getting a fairly significant dependence of expansion on the amount of ettringite that is there in your system.

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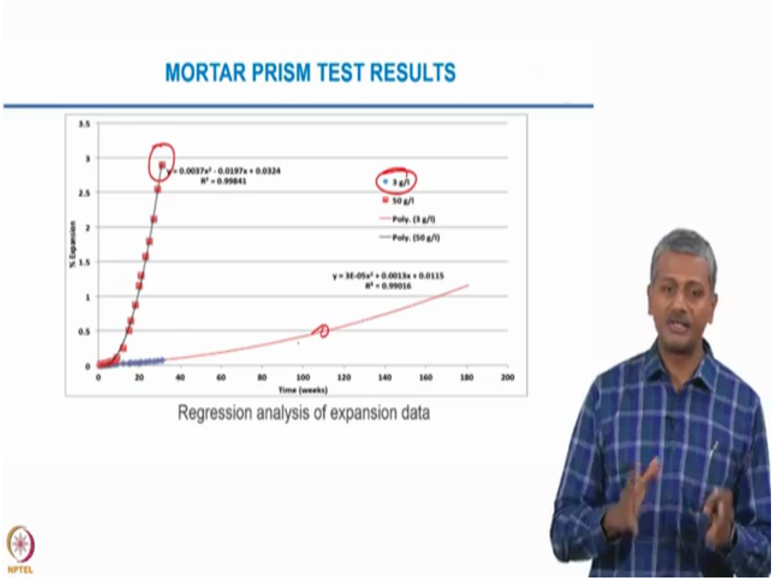

MORTAR PRISM TEST RESULTS

Regression analysis of expansion data

Now you can also look at your data and sort of forecast what is going to be the behaviour in the long term. So if you look at the 50 gram per litre solution already had 31 weeks has reached nearly 3 percent so there is no forecasting here, you have already crossed any possible limit of expansion to this case, but when you do the 3 gram per litre solution you can forecast that your significant expansion of even more than 0.5 will only happen after 100 weeks of exposure.

And please remember these are dealing with small scale prisms in laboratory conditions, in real life you have much larger cross sections of your concrete so there the role of your surface can expanding and resulting in such high levels of expansion is going to be minimal, okay in real life you are actual expansions that you see in the field are going to be much lower as compared to what you see in laboratory conditions.

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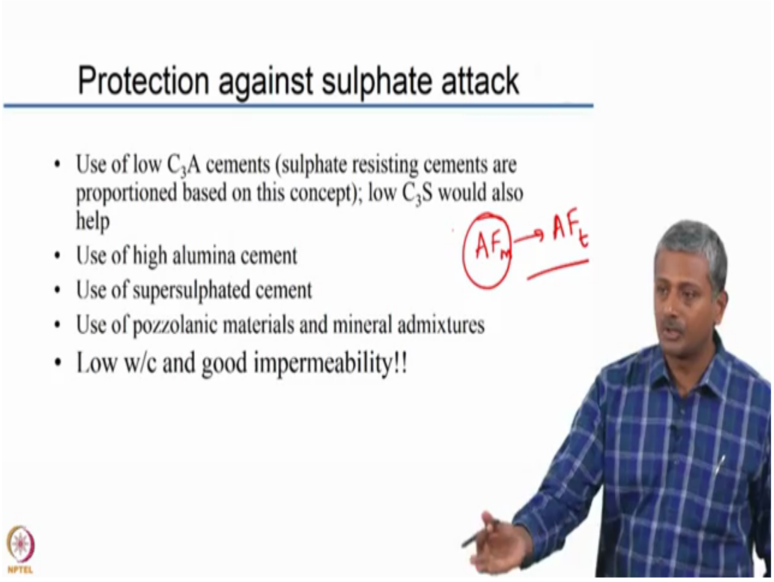
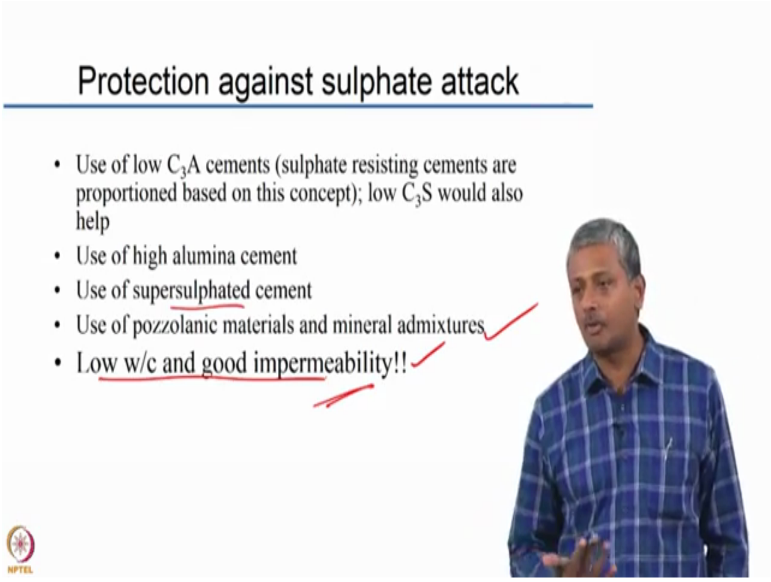


Protection against sulphate attack

- Use of low C_3A cements (sulphate resisting cements are proportioned based on this concept); low C_3S would also help
- Use of high alumina cement
- Use of supersulphated cement
- Use of pozzolanic materials and mineral admixtures
- Low w/c and good impermeability!!

$\boxed{AF_M} \rightarrow AF_t$



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- Low w/c and good impermeability!!

So I will come back to that in just couple of slides but before that just to put in perspective what really leads to a improved performance against sulphate attack one is obviously the use of low C 3 A cements your sulphate resistant cements or type 5 cements as far as ASTM is concerned are primarily based on this approach that you lower the C 3 A because of which at the early stages of hydration you keep the ettringite stable, the primary formed ettringite if you keep it stable without its conversion into mono sulphate that leads to a long term resistance to sulphate attack because this mono sulphate is the one which later converts to ettringite.

If you remember mono sulphate is AF M and that converts to ettringite which is called AF t, t is tri sulphate, ettringite is 3 molecules of sulphate and that structure whereas mono sulphate is one molecular sulphate. So in a regular portland cement system it is sulphate deficient there is lot more aluminate than sulphate because of which it leads to the formation of mono sulphate in the long run but this mono sulphate has a tendency to convert to ettringite.

Now there are other special cements that could be used like high alumina cement which is not really a portland cement system and really it is moved to discusses because it is only used in very specific applications it is not a general purpose cement. Similarly super sulphated cement is not something that is in use today because it has shown lot of problems in long term stability.

Now the one most important character or two most important characteristics as far as sulphate resistance are concerned is the use of pozzolanic materials and mineral admixtures. Now what happens when you use pozzolanic materials? You are lowering your calcium hydroxide content, okay so what happens because of that? When you lower calcium hydroxide what is going to happen? The first mechanism of reaction involves the formation of gypsum, right from calcium hydroxide. So if you have lesser calcium hydroxide there will be lesser gypsum formation.

Secondly when you are taking up calcium hydroxide you are going to be slightly reducing your alkalinity in the system also. So your circumstances favouring ettringite formation will be formation and subsequent expansion will again be reduced significantly, okay because calcium hydroxide forms gypsum, gypsum forms ettringite, right lesser gypsum automatically lesser ettringite at the same time smaller reduction small reduction in the alkalinity means that ettringite is no longer as expansive as it was in a regular portland cement system that is why in a sodium sulphate attack based research you will obviously see a 100 percent or major improvement as far as even 20, 30 percent (())(28:28) cement is concerned.

But when you shift to magnesium sulphate or any other attack that leads to acidic conditions acid attack, carbonation, and any of the acidic conditions mineral admixtures and pozzolanic materials do not really act very well because of the consumption of calcium hydroxide because calcium hydroxide is a very good buffer to have against an acidic medium, if you do not have this calcium hydroxide you will not be able to resist this as acidity of the medium and your C-S-H is going to be starting to deteriorate much faster when you do not have enough calcium hydroxide in the system, right.

So whenever you have acidic medium like magnesium sulphate or acids you will ultimately end up deteriorating a concrete much faster when you have pozzolanic materials and admixtures, but all this again come from laboratory studies. Now how does it actually relate to the experience in the field? In the field you have larger structures, the role of permeability will be much greater in field, right and we know for a fact that when you use mineral additives the permeability of concrete gets reduced significantly.

So that aspect you are not able to somehow capture in the laboratory studies because of that you do not really see the same effect that you see in the lab studies in the field conditions, although technically or theoretically we expect that the resistance should be lowered in acidic conditions when you use pozzolanic materials. In regular conditions like sodium sulphate you generally have much better performance with pozzolanic and mineral admixtures and obviously when you use low water cement ratio and result in a good concrete of less permeability you obviously have a much higher resistance to sulphate attack or any other form of chemical attack also.

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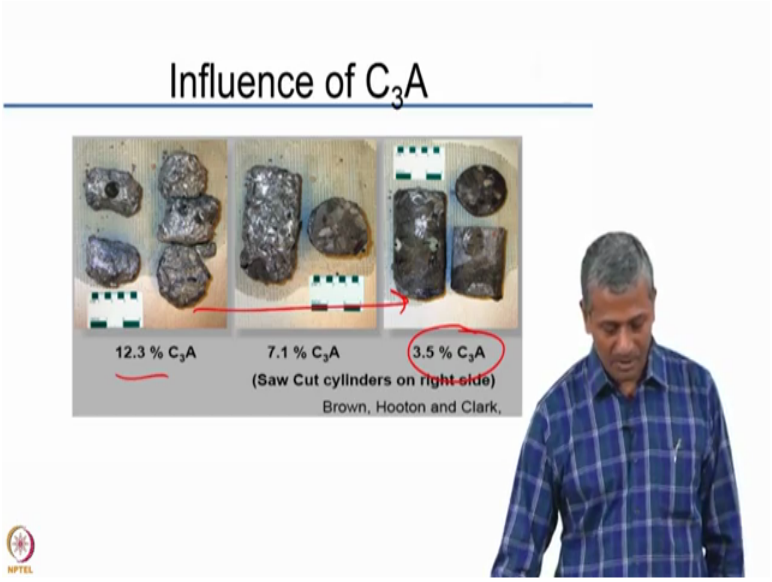
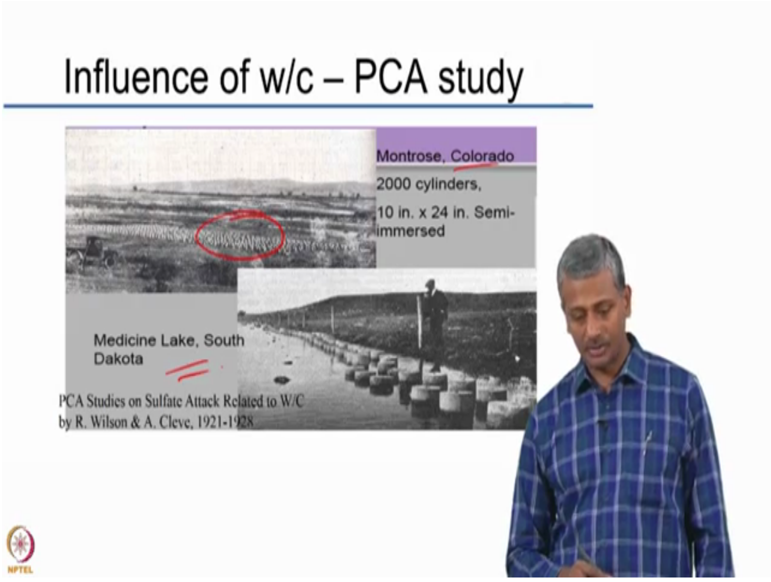


Influence of C_3A

12.3 % C_3A 7.1 % C_3A 3.5 % C_3A

(Saw Cut cylinders on right side)

Brown, Hooton and Clark,

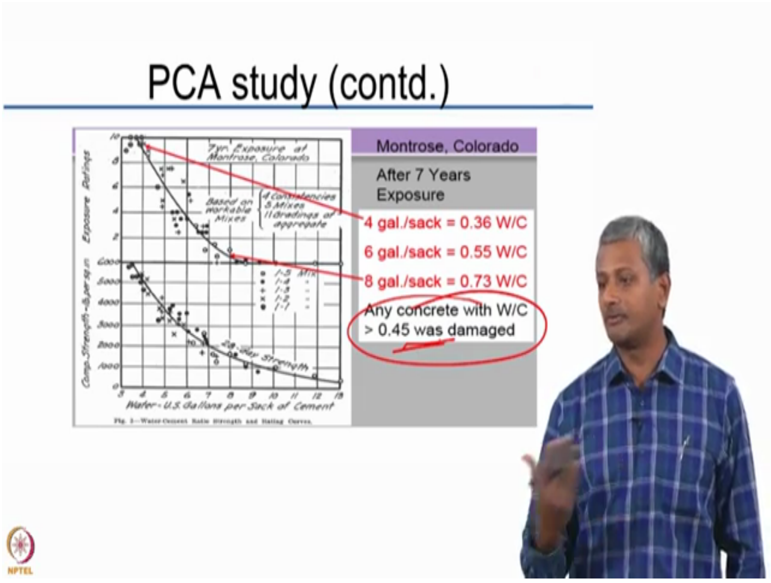


Influence of w/c – PCA study

Montrose, Colorado
2000 cylinders,
10 in. x 24 in. Semi-immersed

Medicine Lake, South Dakota

PCA Studies on Sulfate Attack Related to W/C by R. Wilson & A. Cleve, 1921-1928



PCA study (contd.)

Fig. 1—Water-Cement Ratio Strength and Rating Curves.

Montrose, Colorado

After 7 Years Exposure

4 gal./sack = 0.36 W/C

6 gal./sack = 0.55 W/C

8 gal./sack = 0.73 W/C

Any concrete with W/C > 0.45 was damaged

Again this is some classical work done in Canada rich shows the influence of the C 3 A you can see when you have very high C 3 A and when you transform the concrete with very low C 3 A you see much greater resistance you can see that the specimens are still intact even after storage in sulphate for a long time, there is a very important study done by the portland cement association where they actually semi immersed these 10 by 24 inch cylinders in a sulphate rich soil in Montrose, Colorado and also in Medicine Lake in South Dakota which is highly sulphate rich.

What they ultimately found out from this is that any concrete with water cement ratio more than 0.45 was damaged. Now this goes to show that the primary characteristic that is controlling sulphate attack is permeability and not really C 3 A, so here they have different forms of cement, different types of cement, whatever. The cement chemistry is probably not as important in this case as is the permeability because again permeability obviously depends on the water to cement ratio, if you have lesser water cement ratio you have lower permeability.

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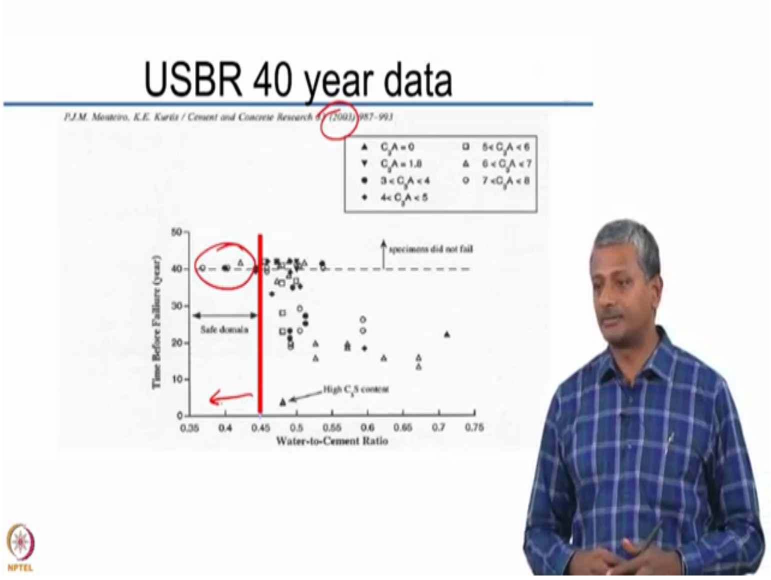

USBR 40 year data

P.J.M. Monteiro, K.E. Kurtis / Cement and Concrete Research (2003) 987–993

Again the same data was again further analysed statistically by researchers not too far back in 2003 and they again found that irrespective of the C 3 A content of your cement irrespective of C 3 A content of your cement if your water cement ratio is less than 0.45 all your concretes were safe, they did not fail at all even after 40 years of exposure.

So this is not something which we are talking about as done in the lab like 40 weeks of exposure this is 40 years, so the significant amount of work and this clearly shows that the influence of water cement ratio is paramount which is why if you pick up any standard or guideline which talks about sulphate resistance the first thing they point out that is that you must choose your concrete with the water cement ratio lower than 0.45 this 0.45 is not something which is picked out of thin air, it is coming out of all these long term studies, okay.

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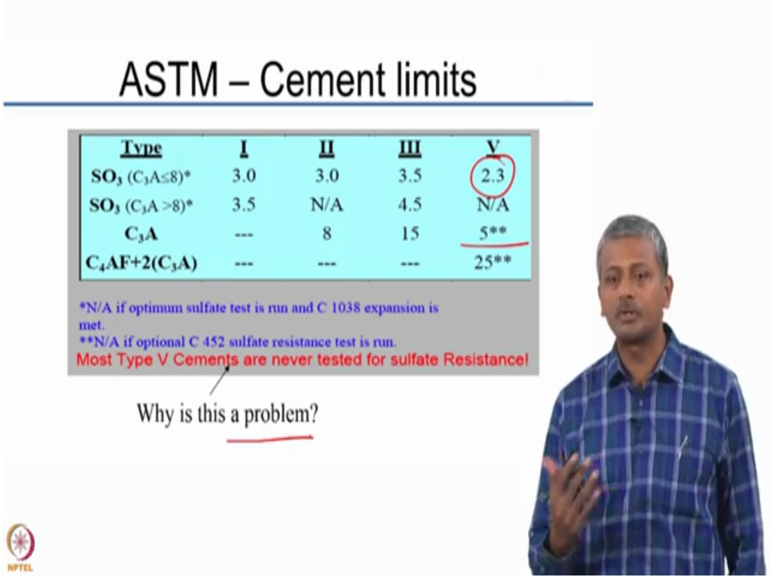

ASTM – Cement limits

Type	I	II	III	V
SO_3 ($C_3A \leq 8$)*	3.0	3.0	3.5	2.3
SO_3 ($C_3A > 8$)*	3.5	N/A	4.5	N/A
C_3A	---	8	15	5**
$C_4AF+2(C_3A)$	---	---	---	25**

*N/A if optimum sulfate test is run and C 1038 expansion is met.

**N/A if optional C 452 sulfate resistance test is run.

Most Type V Cements are never tested for sulfate Resistance!

Why is this a problem?

Again there are cement limits obviously given in various standards this is ASTM for example if you look at sulphate resistance cement it gives a limit of C 3 A as 5 percent, if you look at IS codes the limit of C 3 A for sulphate resistance cement is 4 percent, okay but often times what we do is we say that okay let us use sulphate resistance cement and let us forget about it, but there is a problem that we do not test the sulphate resistance cement against sulphate attack because we are not paying attention to the kind of sulphate that is actually there.

For example in the case of magnesium sulphate where the dominant mechanism is not ettringite formation, it is actually the C-S-H attack in the long run, sulphate resistance cements are known to perform poorly in that circumstance. So we need to understand the kind of sulphate that is present, test for the sulphates by using whatever cement we are or combination of the cement we are trying to us and ensure we are providing the best solution for the particular case or particular scenario.

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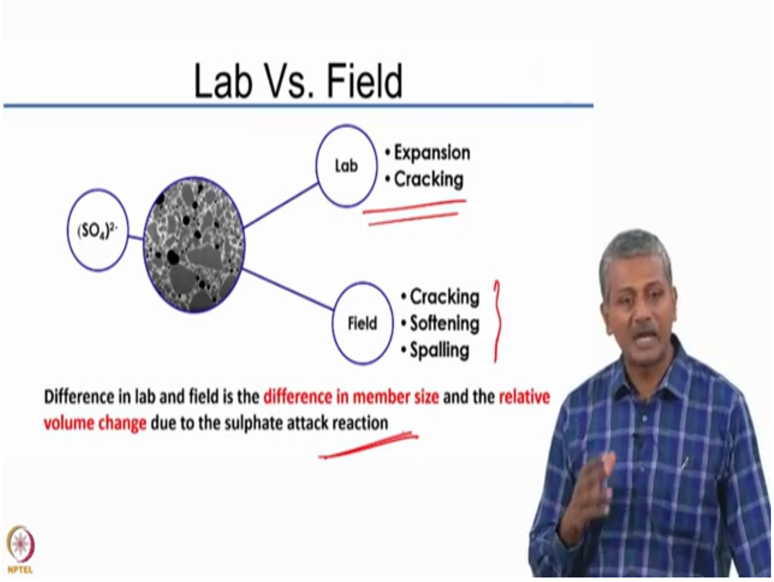

Lab Vs. Field

$(SO_4)^{2-}$

Lab
- Expansion
- Cracking

Field
- Cracking
- Softening
- Spalling

Difference in lab and field is the difference in member size and the relative volume change due to the sulphate attack reaction

Now again let us look at lab and field for a minute again, I talked about the fact that in the lab we have smaller scale specimens they are usually continuously immersed or sometimes we may introduce variations like wetting and drying, okay but there is no way that you are ever going to able to simulate real life environment in the laboratory, okay. So let us look at something little bit in more detail.

In the lab typically what you see is expansion and cracking that happens in your specimens, whereas in the fields the dominant manifestations of your failure involved crackings, softening and spalling, this softening and spalling you do not often see in the lab studies but in the field you see this all the time, this mainly is because of the difference in member size and the relative volume change during the sulphate attack reaction, what do you mean by relative volume change?

Again I am talking about sulphate attack being a surface phenomenon. So we have a very small layer in the surface that is causing the expansion, on the bulk of the concrete it is going to resist that. In a laboratory scale the bulk is not that big as compared to the expanding skin in the real life the expanding skin is too small as compared to the bulk. So obviously you are going to cause differences in the way that the attack manifests itself in the field.

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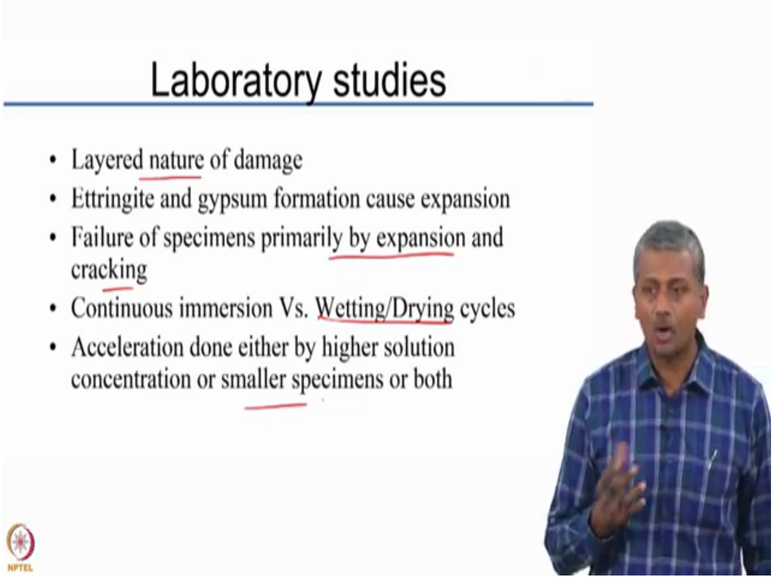

Laboratory studies

- Layered nature of damage
- Ettringite and gypsum formation cause expansion
- Failure of specimens primarily by expansion and cracking
- Continuous immersion Vs. Wetting/Drying cycles
- Acceleration done either by higher solution concentration or smaller specimens or both

Now again just to summarize the lab studies you have layered nature of damage, you have ettringite and gypsum formation that cause expansion, failure happens primarily because expansion and cracking, you may sometimes introduce variations of the system by introducing wetting drying cycles that may lead to salt crystallization which I will touch up on briefly later and acceleration is done either by using higher solution concentration, we saw earlier results between 3 gram per litre and 50 gram per litre, there is major acceleration that happens when you use 50 gram per litre solution, at 3 gram you are not even able to see the expansion in the time period of the study or sometimes we use smaller specimens or a combination of high concentration in small specimens.

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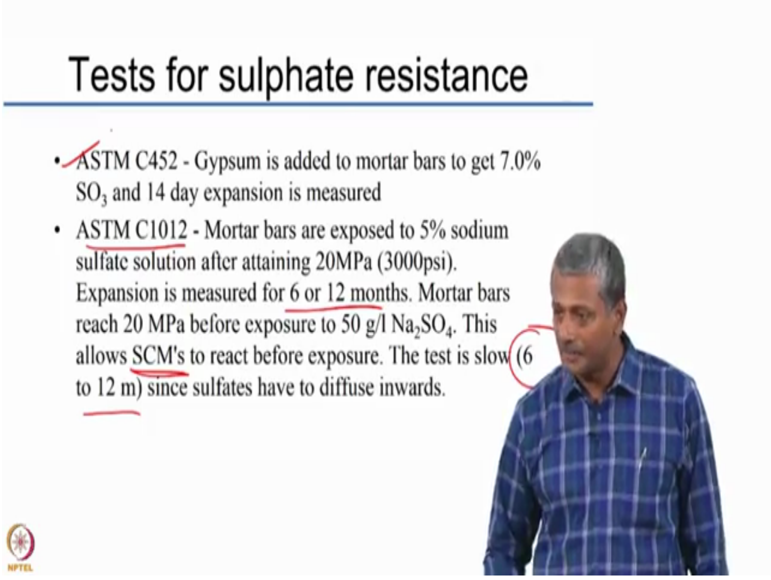

Tests for sulphate resistance

- ASTM C452 - Gypsum is added to mortar bars to get 7.0% SO_3 and 14 day expansion is measured
- ASTM C1012 - Mortar bars are exposed to 5% sodium sulfate solution after attaining 20MPa (3000psi). Expansion is measured for 6 or 12 months. Mortar bars reach 20 MPa before exposure to 50 g/l Na_2SO_4. This allows SCM's to react before exposure. The test is slow (6 to 12 m) since sulfates have to diffuse inwards.

Now if you look at test methods that are there in the standards for sulphate resistance most people use this test methods called C1012 which is you make Mortar bars with the certain cement to aggregate ratio and expose them to 5 percent sodium sulphate solution after retaining 20 mega pascal of strength, why you wait till they attain 20 mega pascal strength is that you have sufficient degree of curing provided to your system before you expose it to a sulphate condition, okay.

Expansion is generally measured for 6 to 12 months, generally motor bars reach 20 mega pascal before exposure to 50 gram per litre sodium sulphate, now this also allows supplementary cementing materials to react significantly before it is exposed to sulphate. Test is slow takes 6 to 12 months, okay because sulphates have to slowly diffuse inwards. There was an older method ASTM C452 where they talked about mixing sulphates within the concrete to increase the rate of ettringite formation but then that is not really reflecting anything about the concretes behaviour to resist the penetration of the sulphates so 1012 obviously is a better method.

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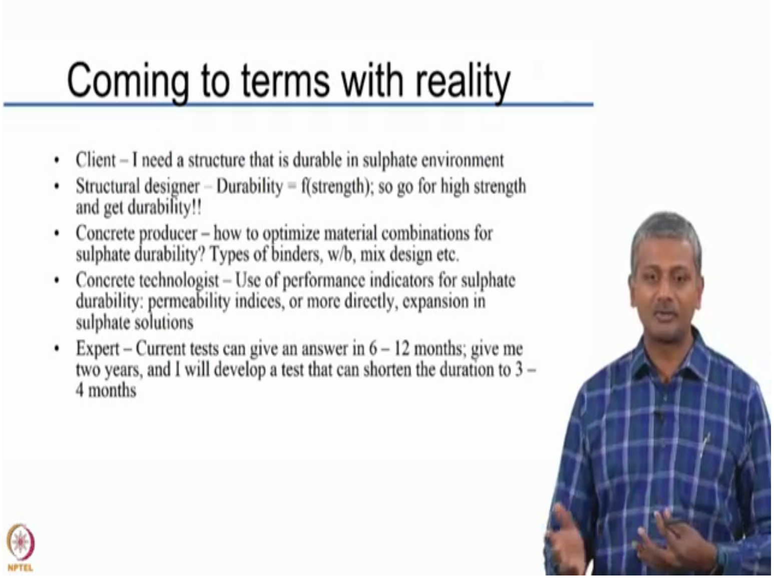

Coming to terms with reality

- Client – I need a structure that is durable in sulphate environment
- Structural designer – Durability = f(strength); so go for high strength and get durability!!
- Concrete producer – how to optimize material combinations for sulphate durability? Types of binders, w/b, mix design etc.
- Concrete technologist – Use of performance indicators for sulphate durability: permeability indices, or more directly, expansion in sulphate solutions
- Expert – Current tests can give an answer in 6 – 12 months; give me two years, and I will develop a test that can shorten the duration to 3 – 4 months

However, in reality what happens is you have a client who says that he needs structure that is durable in sulphate environment, the structural designer says okay durability is related to strength, we talked about this in the last lecture, designer is design everything in terms of the compressive strength of the concrete, okay they think that durability also is related directly to the strength so let us go for high strength and get durability but that is not really economical because if you need M20 in a particular location you do not want to shoot for M60 just because you have higher durability, you need to ensure that you are getting the same strength but with an enhanced durability characteristic by appropriate choice of materials.

The concrete producer says okay let us look at how to optimize material combinations for sulphate durability choosing the right type of binders, water binder ratio, choice of mixed design and so on. The concrete technologists now says that use of performance indicators for sulphate durability is necessary. For example we can define permeability indices that need to be satisfied by the concrete or more directly we can say that we measure the system as it expands in the sulphate solution and use that as a predictor for the damage.

The upshot of all this is that once the data is analysed when exploded it takes 6 to 12 months to provide an answer because again if you are looking waiting for this concrete to expand in the sulphate solution it is a slow process, how do you simulate this or how do you simulate other conditions of the field in the lab? Impossible, so experts will say okay now give me 2 years and I will develop a test that can shorten the duration to 3 to 4 months, still for the people who are actually practicing concrete technology on the field this is too longer time period to wait, they want answers immediately.

So what can we do? We need to somehow look at how we can simulate field conditions in the lab and that has been a subjective a lot of research over the current years and people have not really found the right answer for that.

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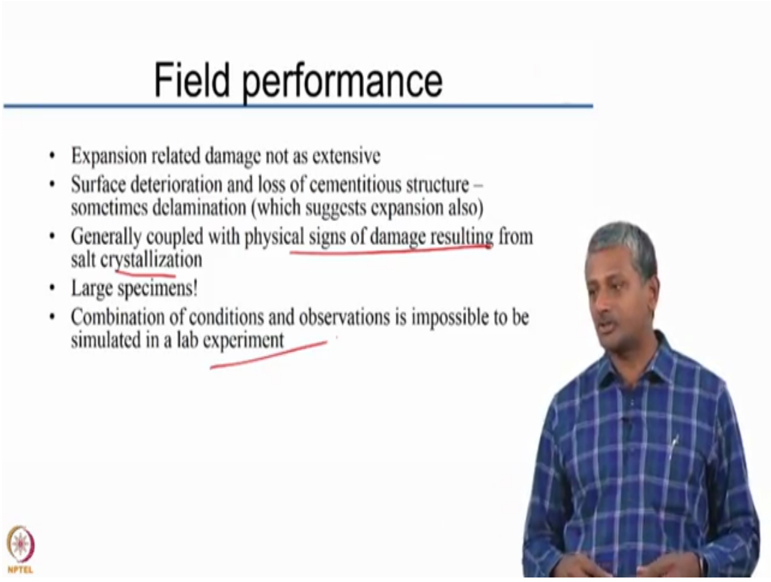

Field performance

- Expansion related damage not as extensive
- Surface deterioration and loss of cementitious structure – sometimes delamination (which suggests expansion also)
- Generally coupled with physical signs of damage resulting from salt crystallization
- Large specimens!
- Combination of conditions and observations is impossible to be simulated in a lab experiment

So in field you see that expansion related damage is not extensive because small skin expanding on the surface will not result in a major cracking of the system. Surface deterioration, loss of cementitious structure or sometimes delamination can actually happen in the systems on the field and generally it is coupled with physical science of damage from salt crystallization.

Again this happens because of large specimens please remember there is a specimen size difference and relative volume of the available material that can actually react with your sulphate system. So combination of conditions and observations is impossible to simulate in lab environment. So we are actually not really going to be getting towards it (())(38:39) because that is absolutely not possible to simulate things in the laboratory. However, we can come up with estimates by doing some assessment of how does the size effect change the extent of expansion or deterioration and sulphate solution.

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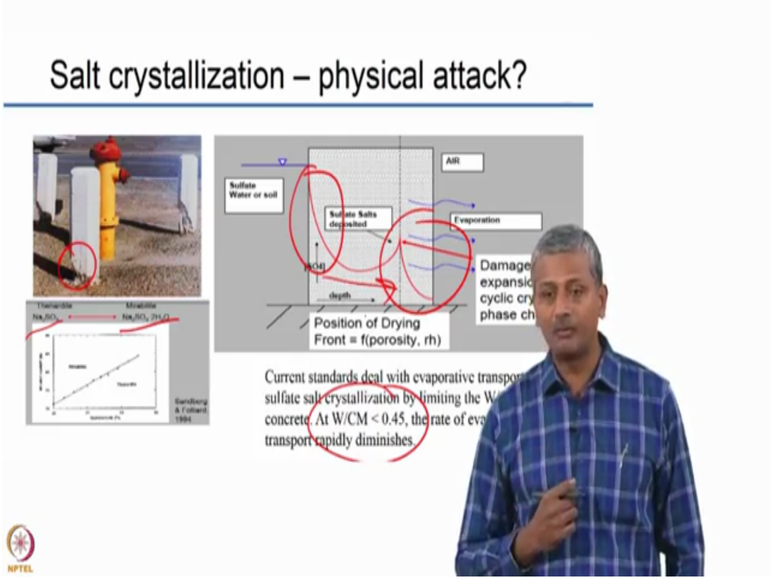

Salt crystallization – physical attack?

Current standards deal with evaporative transpo
sulfate salt crystallization by limiting the W
concrete. At W/CM < 0.45, the rate of eva
transport rapidly diminishes.

Now one aspect that you see in the field often is salt crystallization, which exerts a bits or deteriorates a concrete much further, okay and again this example of the soil air interface was primarily because of the salt crystallization problem, certain forms of sulphate like sodium sulphate can transform into hydrated forms like (mirabilite) thenardite to mirabilite transformation and this happens within these restricted pores spaces of your system, okay.

So there are cycles of wetting and drying which actually in reality happen and because of the cycles of wetting and drying the wetting phase deposits the sulphate inside, the drying phase removes the water and slowly leads to salt crystallization. Now further you can also have the effects of drying out on a structure that is dry on one side and wet on the other side, so you are pulling the salts to the other side by wick action, okay. So that again increases the sulphate levels in the system.

So there are lot of aspects of physical attack, but interestingly literature says that if you go for water cement ratios less than 0.45 the rate of evaporative transport actually diminishes. So this issue of wick action and increase in the sulphate concentration inside seizes to be a major problem when you have (more than 0.45 water to cement) less than 0.45 water to cement ratio.

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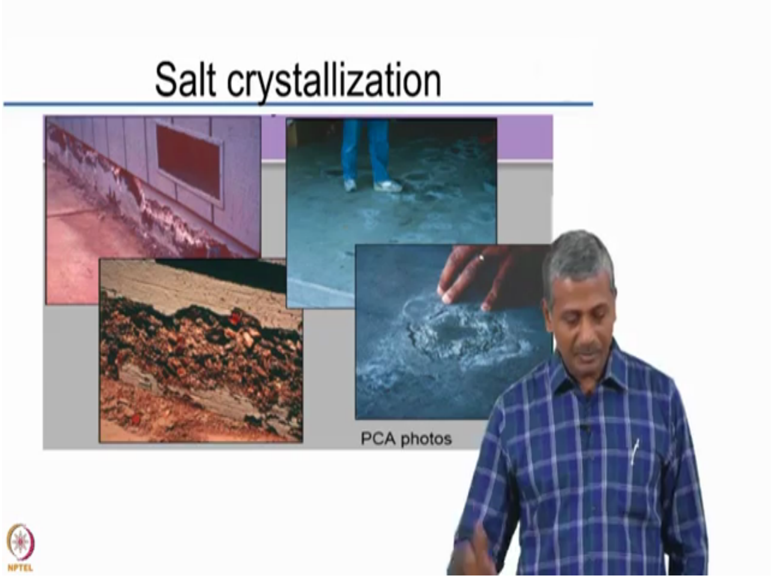

Salt crystallization

PCA photos

Role of w/c

Rating of Concrete: 5 @ 12 yrs
Type V Cement
W/C = 0.65

Rating of Concrete: 2 @ 16 yrs
Type V Cement
W/C = 0.39

PCA, Sacramento Site

So interestingly this is still something which we observe this is examples of salt crystallization and again data from portland cement association which clearly show that compared to a high water cement ratio system a low water cement ratio system even after 16 years had a very high visual rating after being exposed to very aggressive sulphate solutions, okay. So again the control of water cement ratio happens to be the most critical aspect as far as sulphate is concerned, okay.

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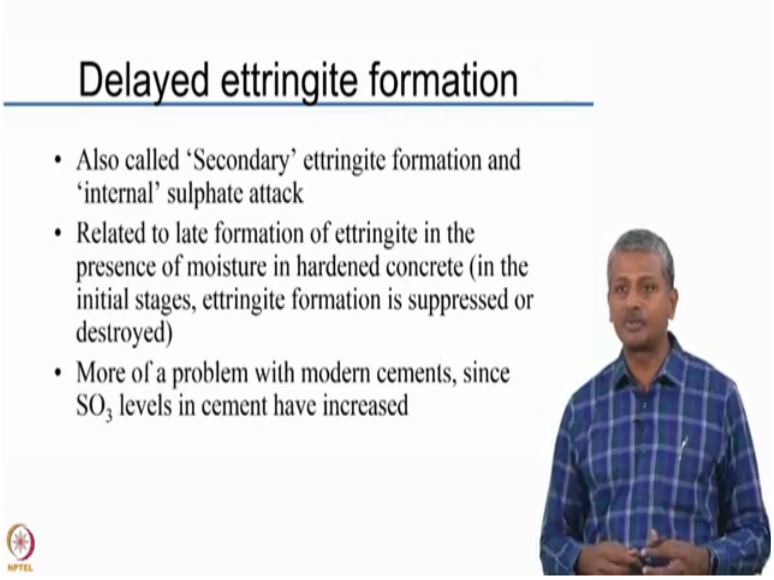

Delayed ettringite formation

- Also called 'Secondary' ettringite formation and 'internal' sulphate attack
- Related to late formation of ettringite in the presence of moisture in hardened concrete (in the initial stages, ettringite formation is suppressed or destroyed)
- More of a problem with modern cements, since SO_3 levels in cement have increased

Now moving on from an external to an internal source or sulphates let us look a related ettringite formation this is also called secondary ettringite formation or internal sulphate attack. In normal processes we want to ettringite to form in the early stages of hydration, but some conditions may lead to a change in the early hydration situation and you may not form ettringite early enough and these ettringites slowly forms in the later ages. So ettringite formation can be subtest or destroyed in certain cases, again and modern cements there is a lot of sulphate available so this can become a real problem.

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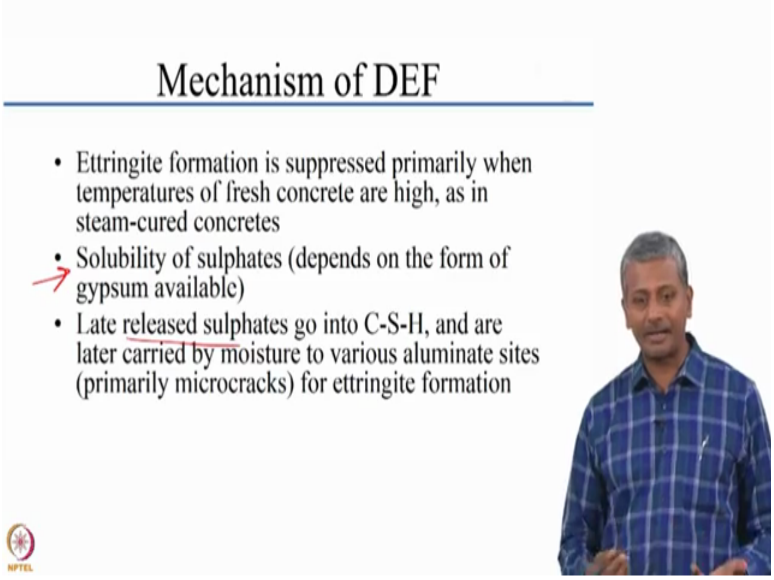

Mechanism of DEF

- Ettringite formation is suppressed primarily when temperatures of fresh concrete are high, as in steam-cured concretes
- Solubility of sulphates (depends on the form of gypsum available)
- Late released sulphates go into C-S-H, and are later carried by moisture to various aluminate sites (primarily microcracks) for ettringite formation

So in what conditions is ettringite formation not happen? This ettringite does not form in its normal way when you are raising the initial temperature of the concrete. For example when you are doing steam curing or when you have mass concrete where the interior temperature of the concrete can reach to very high levels, the ettringite formation in the interior environment may not happen in the normal way because of which this ettringite will tend to appear at a later age because sulphates are still there, aluminates are still there they can recrystallize and form ettringite and that ettringite formation will happen in a harden concrete structure.

So this was discovered primarily by accident by some researchers in UK where they saw that lot of railway sleepers precast railway sleepers which were made out of precast concrete had cracked and they were trying to understand what is causing this problem because they did not have an alkali reactive aggregate in that concrete, they use normal aggregate, but then they found that it was happening because lot of ettringite seems to have formed at the system and they then related this to the fact that when you do early age curing at high temperatures or steam curing you suppress the formation of ettringite and this ettringite can form later on when there is sufficient moisture available from the external environment, please remember again you will need moisture for reformation of ettringite to happen in the system, okay.

So it can also happen when your system has very low soluble sulphates, okay. The form of gypsum either anhydride or natural anhydride or gypsum or any hydrate the type of gypsum that you have in your system can lead to a slow release of the sulphates in the system very slow release that can form ettringite at very late ages, okay. These late release sulphates go into the C-S-H and if there is sufficient water available they carried to locations of aluminate where ettringite can actually happen.

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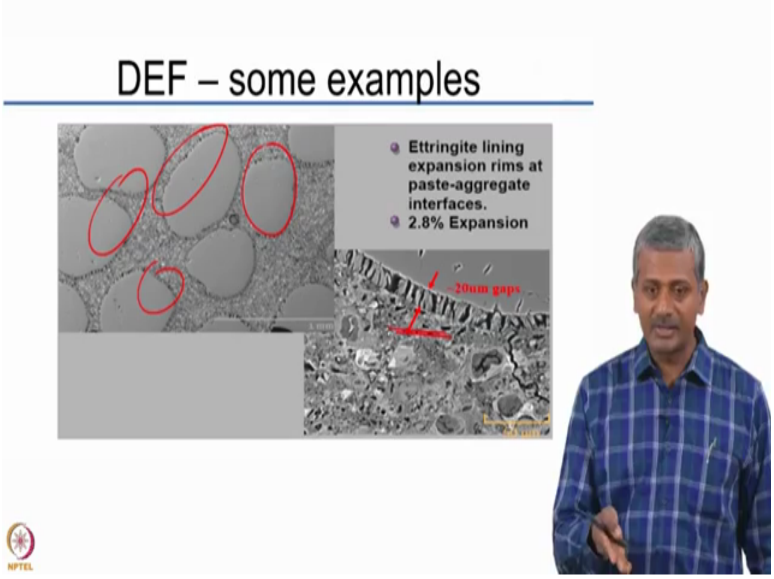
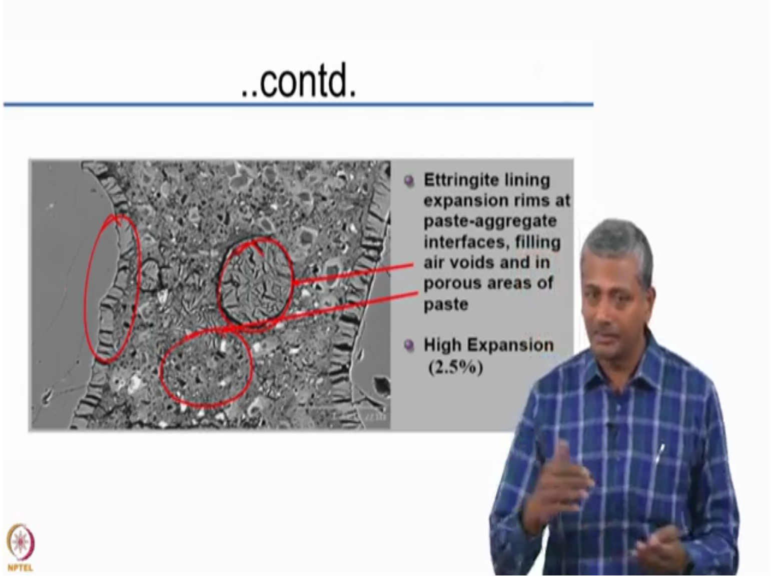


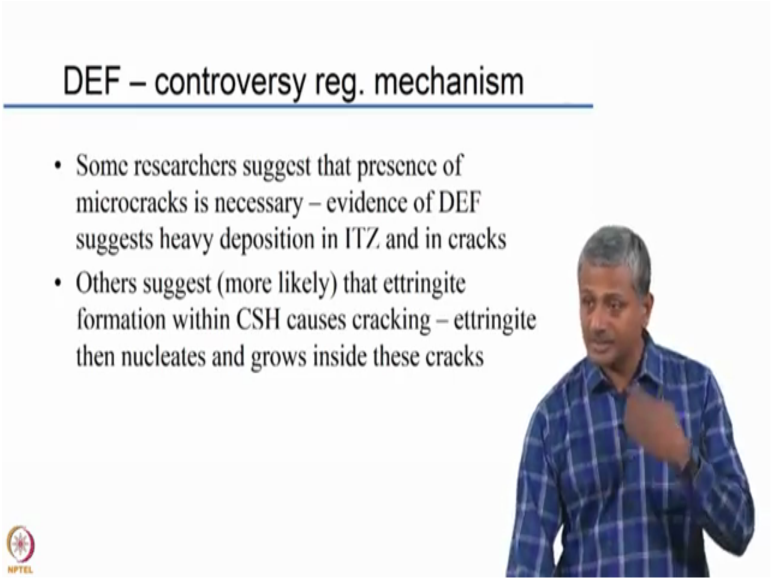
DEF – some examples

- Ettringite lining expansion rims at paste-aggregate interfaces.
- 2.8% Expansion



..contd.

- Ettringite lining expansion rims at paste-aggregate interfaces, filling air voids and in porous areas of paste
- High Expansion (2.5%)



DEF – controversy reg. mechanism

- Some researchers suggest that presence of microcracks is necessary – evidence of DEF suggests heavy deposition in ITZ and in cracks
- Others suggest (more likely) that ettringite formation within CSH causes cracking – ettringite then nucleates and grows inside these cracks

Now this is a picture from a microscopic image taken from a mortar subjective to delayed ettringite formation, you can see all around the aggregate you have major deposition of the ettringite and you can see very clearly the close up of the ITZ showing lot of ettringite that is actually forming there. Now interestingly this is a stage which is already too late ettringite formation has already happened lead to massive cracking and interestingly all these cracks are now being deposited with ettringite, but the formation of ettringite around this dream is not the reason for the cracking.

The reason for the cracking is the formation of the ettringite inside your C-S-H just like what we discussed earlier for ettringite to be expansive it has to imbibe water by forming in the microcrystalline size scale within your C-S-H and that is basically imbibing moisture and increasing in size leading to cracking and once that cracking happens there is sufficient space now for the ettringite to grow and recrystallize, you have now sufficient space for that to happen.

So this formation of ettringite in ITZ is not the feature of the initial part of DEF. Now interestingly because of this happening lot of researchers tended to believe that ettringite formation had to happen in cracks to lead to DEF related problems, but later people understood that essentially it is because the ettringite formation within the small C-S-H pores of C-S-H that leads to expansions and further cracking.

So there was controversy now people are fairly clear that microcrystalline ettringite is what can lead to expansive characteristics in the concrete, whether it is internal sulphate attack or external sulphate attack.

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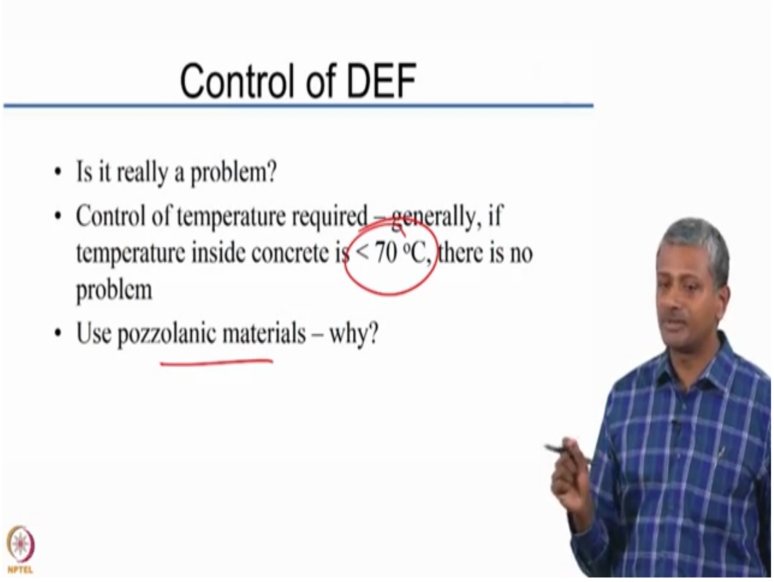

Control of DEF

- Is it really a problem?
- Control of temperature required – generally, if temperature inside concrete is < 70 ºC, there is no problem
- Use pozzolanic materials – why?

Now control of DEF of course we have to understand whether it is really a problem depending upon the situation it can be a problem, if you have very high temperatures during precasting so generally because of that most concrete it says the specification for concrete construction typically put a limit on the maximum temperature permissible inside the concrete.

Now in case of mass concreting this can be a very realistic temperature, it can easily be obtained. So because of that you need to ensure that you are reducing your overall temperature of the concrete at the time of placement so that the iteration does not produce a large temperature rise. Pozzolanic materials can be beneficial in DEF, why? Again because control of permeability is paramount with pozzolanic materials you control the permeability, you do not allow moisture you get in easily and again coming back to the original system ettringite formation in a pozzolanic system may not be as expansive as it is in a cementitious system because of the pH differences in the system.

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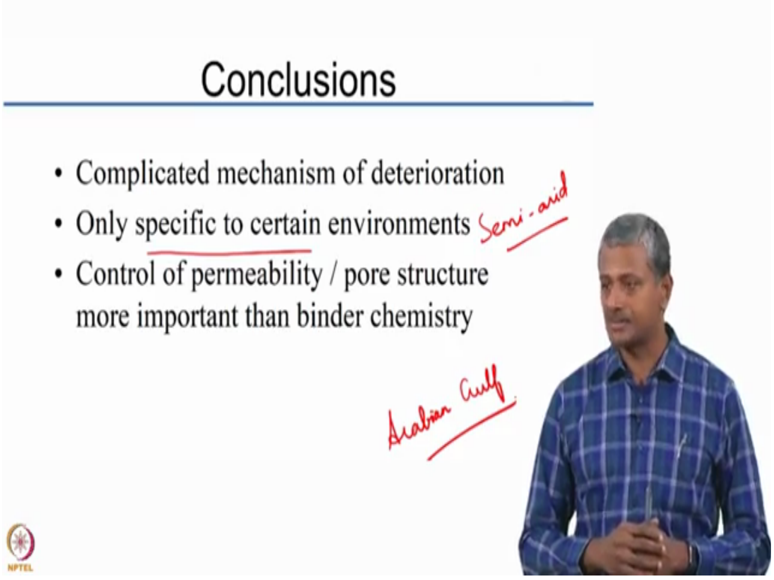

Conclusions

- Complicated mechanism of deterioration
- Only specific to certain environments Semi-arid
- Control of permeability / pore structure more important than binder chemistry

Arabian Gulf

So just to conclude sulphate attack is accompanied by a complicated mechanism of deterioration. In many cases you can control sulphate attack in a large way by a control of permeability of pore structure more importantly than controlling your binder type and water to cement ratio but in any case in most circumstances you will have a very good performance when you replace cement with mineral additives like fly ash or slag, you generally have much better control on the permeability and as a result you reduce the level of sulphate deterioration that happens to the concrete.

Again this is specific to certain environments, it is not something that you see white spreads all across the world there are very specific environments. For example the semi-arid regions can be places where you can see a lot more attack because of sulphate because of the combined mechanisms of penetration as well as you have drying and wetting that happen in these kind of environments.

If you have completely dry, completely wet you do not always see that unless of course your marine conditions sometimes have very high amount of sulphates. If you look at the Arabian gulf region the Arabian gulf region is probably subjected to one of the most adverse environments ever because you have very high chlorides, the Arabian gulf water have very high sulphate and added to you have high temperatures.

So your concrete is really having to service itself or rather having to perform in a very difficult environment where control of chloride, sulphate and the high temperatures in that prevailing at that regions. So designing concrete for such tricky conditions can be quite a challenge, but anyway the idea was to give you a glimpse of what sulphate attack can do in concrete and what are the different ways in which this can be studied in the lab and how we need to understand the limitations or what we can assist in the lab and apply it carefully to the field. Okay, so again control of permeability, pore structure is way more important than control of cement chemistry as far as sulphate attack resistance is concerned, thank you all.