

Advanced Concrete Technology
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Lecture - 39
Durability issues in concrete – Part 3

Today, we will resume our discussion on sulphate attack. In the last class, we saw how sulphates penetrate the cementitious system, interact with the hydrated cement phases and form different kinds of compounds starting from the surface to the interior.

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Does ettringite formation cause the expansion?

Let us talk a little bit about whether ettringite formation causes expansion. Of course, we know very well that ettringite has a structure which is prone to expansion primarily by imbibing the moisture and this expansion can lead to stresses in the surrounding environment that causes cracking, but what is the direct evidence and what are the conditions under which ettringite will lead to form expansion in the concrete system.

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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 from outside**
- Delayed ettringite – internally suppressed ettringite growing at later ages (DEF)
(Odler, 1997)

Now we know that the primary ettringite is an ettringite that actually forms very early in the process. So in a regular cement hydration when cement phases like the aluminates react with the sulphate that are added into the cement we form the early ettringite and this early ettringite later converts to monosulphate because there is an excess of aluminate present in the system. Now there is also an evidence of late primary ettringite forming.

And that happen in cements where more sulphate is available so that means you continue to deposit ettringite for a fairly long substantial period of time. Now this happens because of the internal sources of sulphates. External ettringite is when we have sulphates coming in from external environments due to penetration of sulphate from the outside. Apart from that we can also call delayed ettringite formation as a phenomenon which looks at the formation of internally suppressed ettringite which grows at later ages.

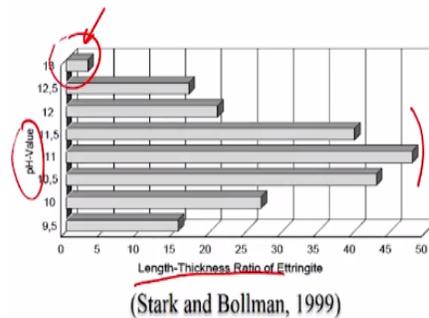
So this means that ettringite because of some reasons did not form at the early stages and some other kind of combination of factors has lead it to form in a hardened state obviously when an expansive material form inside the harden concrete that is when you have major damage because of that and that is also known as DEF or delayed ettringite formation.

That is a common terminology that is given for delayed ettringite formation. Truly speaking any sulphate attack process leads to formation of ettringite in the late harden stages. So any formation

of ettringite is secondary ettringite formation that means we are distinguishing it from the primary ettringite that forms due to a regular hydration of the cement.

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Ettringite crystal habit



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



If you look at the type of crystalline material that is formed because of production of ettringite, ettringite is known to form in the needle shape. It forms like needles, which has a long dimension and basically what happens is the length, the thickness ratio of the ettringite depends on the pH of the surrounding environment. Now it turns out that when you have very high pH levels, they are not really forming very long needles of ettringite.

We are forming shorter, stubby ettringite crystals, but somewhere in between, between 12 and 10 we are actually forming ettringite needles which have very high lens. So what would happen is that in the early stage of cement hydration you would actually form these microcrystalline ettringite where the length is actually quite small and length to diameter or rather length to thickness ratio is quite small.

But when the ettringite expands you can think about a scenario when you have an external sulphate attack and ettringite expansion where moisture has been imbibed and ettringite actually expand it may actually start exhibiting the crystal habit that is shown by a higher length. So microcrystalline ettringite at high pH levels is seen in fresh concrete, what we typically expect in early hydration.

Now according to researchers and this has been well documented that microcrystalline ettringite with water absorption capability leads to high expansions and this generally happens when the pH conditions are fairly high. So if you come to as sulphate exposures where the pH is brought down for example when you have lower pH levels in the surrounding environment, then it may turn out that the ettringite that is actually formed in the system may not be highly absorptive.

And when this ettringite does not absorb or imbibe water it does not lead to very high expansions. So ettringite formation can lead to expansion primarily only in those conditions where the external pH is also high enough. Now this explains to a large extent why we do not really see expansions happening in field based specimens. In lab specimens we see a very high level of expansion.

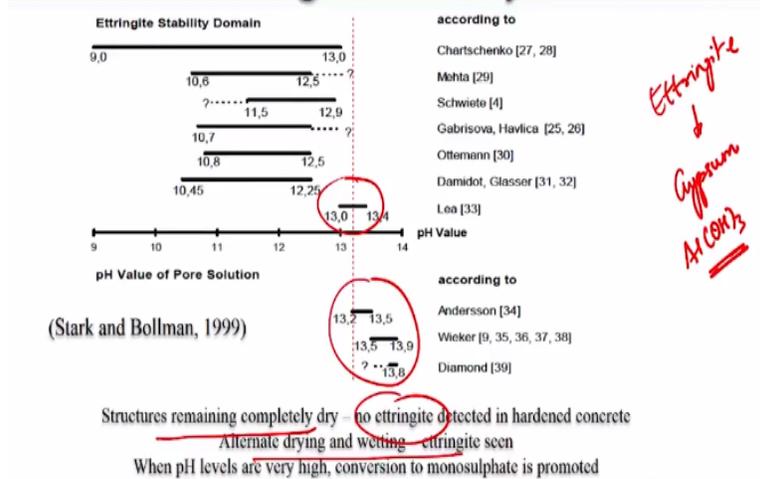
But at the same time, in the actual performance in the field which is accompanied by continuous replenishment of the attacking solution because you have the ground water which is continually recharging the attacking solution. In addition to that we also have the presence of other ionic species that may bring down the pH of the surrounding solution. Now when that happens, the ettringite that is actually forming may not end up being as reactive.

Or rather as expansive as what forms inside the system in a regular immersion condition. So what happens when you take a beaker and put a sulphate solution inside and put a concrete specimen inside? So concrete is having a very high pH 13. So what is happening when you put it inside a sulphate solution of pH 7 or 8 you will have a leaching of the line from the concrete into the outside environment and the pH of the outside solutions starts getting stabilized to a very high level.

We get to a level > 12 in some cases. So in those conditions the ettringite that is actually forming is of an expansive nature. When you have high pH in the surrounding solution ettringite is expansive and that may lead to the expansion that is typically associated with sulphate attack in the laboratory studies, but in the field we do not see the same kind of expansions.

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Ettringite stability



The stability of ettringite also is dependent on the pH levels that are existing in a particular environment. So here for example, when the pH is very high or the pH in the range of between 9 and 13 and that is generally the range of stability of our ettringite solution so again different researchers have provided various ranges of pH across which ettringite is stable. When the surrounding conditions become acidic in that environment ettringite may not be very stable.

So you have to look at the existing conditions around to check whether ettringite is going to be stable so in an acidic environment for example the ettringite may actually readily convert to gypsum, aluminum hydroxide especially if there is carbonation also happening you may actually form calcium carbonate phases along with aluminum hydroxide and gypsum. So ettringite in an acidic environment will convert to gypsum and aluminum hydroxide.

So again if you look at the evidence from the field the structures that remain completely dry there is absolutely no ettringite detected in hardened concrete. So if you are not having any moisture you are not really seeing the formation of ettringite at the later stages and when you have alternate drying and wetting there is some ettringite that is seen, but because of the drying you will probably not have a condition where the ettringite formation causes expansion.

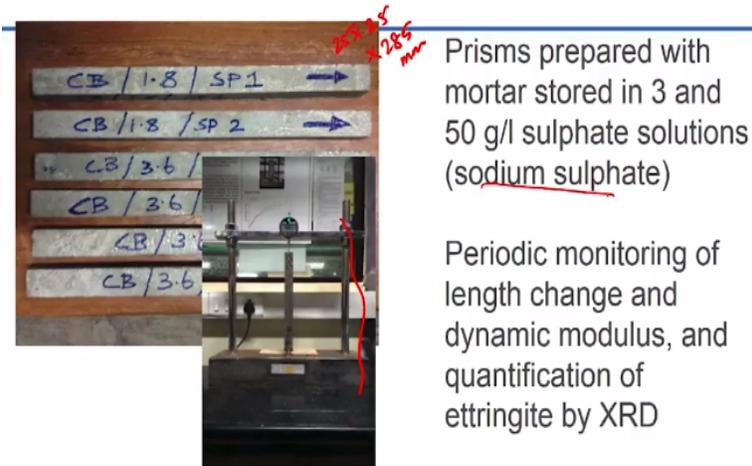
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Some examples from recent lab studies

Now I will just show you some recent lab studies which will show you the recent lab studies which will show you the relationship between ettringite formation and expansion.

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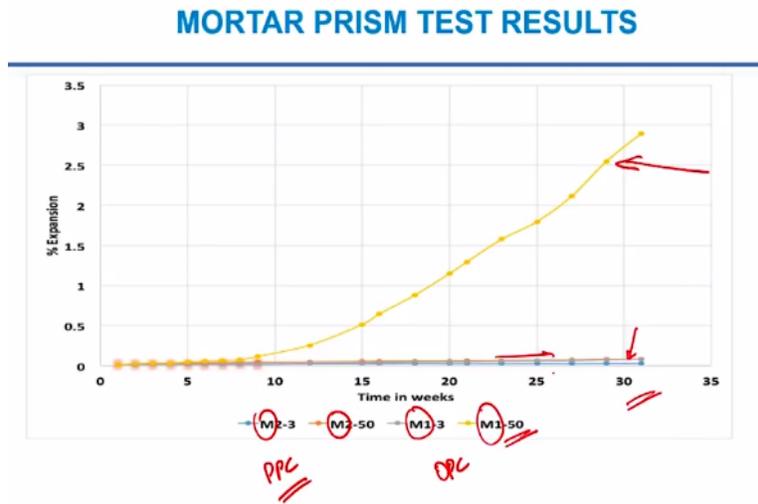
MORTAR PRISM TEST



So in lab studies typically we study using Mortar prismatic specimens which are typically 25 x 25 x 285 mm and these are stored inside the sulphate solutions completely immersed inside the sulphate solutions and periodically the specimens are removed from the solution and the length is measured using a length comparative which is shown here. So this is prisms prepared with mortar stored in 3 gram and 50 gram per liter sulphate solutions.

In this case it was sodium sulphate, so you do not expect any secondary mechanisms arising out of the cation effect like we discussed earlier with magnesium you have the effect of the cation also that is quite serious to be considered. So what we did in this project was we are periodically monitoring the length change and also we were doing quantification of the ettringite by x-ray diffraction analysis.

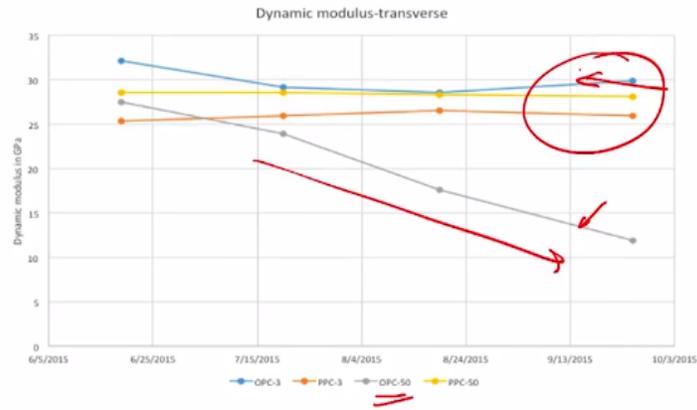
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So here this is showing you the extent of expansion that is happening with different mortar specimens over 32 weeks of exposure and these are 2 mixes, 1 was with ordinary Portland cement and M2 is with Portland pozzolana cement that means cement which has 30% fly ash in it. So you can see that after 32 weeks the only specimens that show substantial expansion where the OPC concrete or OPC Mortar specimens which were stored in the high concentration sulphate solution. In 3 grams per liter solution, you did not really have too much of an expansion although there was some increasing trend that was seen towards the later part of the storage.

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MORTAR PRISM TEST RESULTS



When you look at the change in dynamic models, dynamic models here was measured actually by ascertaining the resonant frequency of the material. So we took the prismatic specimens and looked at the resonant frequency. So what happens in concrete is as the deterioration of concrete happens. The resonant frequency also will reduce. So this is dynamic model is indirectly measured using a nondestructive test.

So here you can see for the Mortar specimen that was stored in the high concentration sulphate solution, ordinary Portland cement based Mortar, you can see that the dynamic modulus reduced significantly in the 32 weeks of exposure while all the other specimen seems to have a fairly consistent dynamic modulus without any decrease.

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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 | 0.0818 | 2.8993 |

% Expansions

ASTM
 C1012
 >0.1%

So let us look at the quantification now this is again the percentage expansion presented as a table rather than as a figure. Now if you can see the OPC 50 gram per liter the expansion was almost as high as 3%. That is a very high level of expansion. When you do this ASTM test, this is as per ASTM C1012. When you do this test method for typical Mortars, if your expansion crosses 0.1% within a period of 6 months of exposure you turn that mortar.

Or that particular combination of binder in Mortar as not being resistant to sulphate solutions. That is only an arbitrary sort of an approach. It does not really bring out the true behavior that you can expect from concrete and sulphate rich environment, but in this continuous immersion test if your specimen ends up having an expansion of more than 0.1% within 6 months then it is supposed to be a cement nonresistant to sulphate attack.

However in this case, expansions as high as 3% were recorded in just 32 weeks of exposure so that is about 8 months, 7 to 8 months of exposure you add 3%. If you look at 3 gram per liter OPC it is still not reach that point 1% mark whereas when you have 50 gram per liter of solution and PPC based Mortar it is still < 0.1%. The expansion is still < 0.1%. PPC in 3 grams per liter the expansion is barely anything I mean it is almost hardly noticeable. You can see this hardly any change from the time of immersion to the last measurement that was done.

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MORTAR PRISM TEST RESULTS

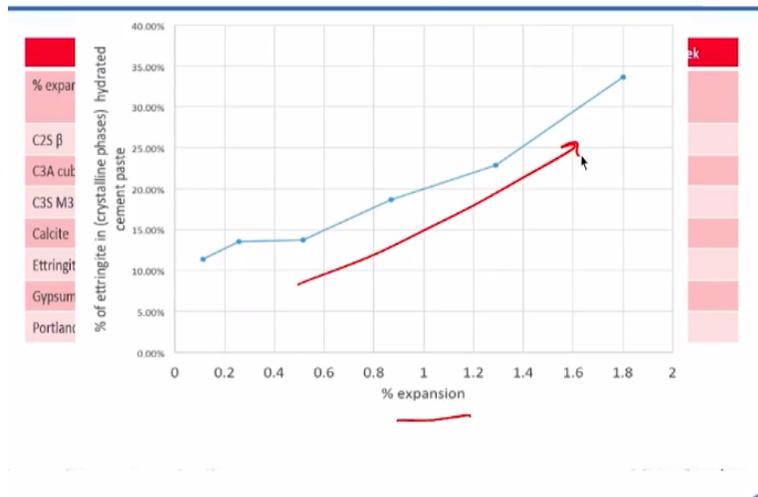
| | 9 th week | 12 th week | 15 th week | 18 th week | 21 st week | 25 th week |
|-------------|----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| % expansion | 0.114 | 0.256 | 0.514 | 0.870 | 1.290 | 1.800 |
| 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

So how does this translate into the ettringite content that is actually forming in the system? So now x-rayed refraction was done to detect the phases that were present, only the crystalline phases and between the crystalline phases the amount of ettringite was also determined. So again here the ettringite amount is given in this row here. I can see that there is a steady increase in the quantity of ettringite that is forming with increase in the time of exposure from 9 weeks to 25 weeks. So what we did was we sort of plotted.

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MORTAR PRISM TEST RESULTS



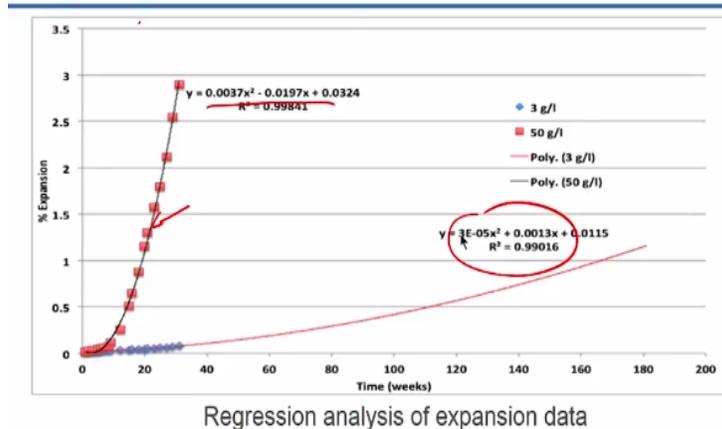
So we plotted the ettringite content determined from x-rayed refraction. This was only percentage of all the crystalline components that were actually present versus the percentage of expansion and you can see is a fairly well defined relationship. So this is a set of points that were

taken from the intermediate readings that we have taken in this process. So this clearly shows that there is some evidence that in a continuous immersion study the expansion is very much dictated by the amount of ettringite that there are actually forming in the system.

But then again whether this translates into reality or not depends on the conditions existing around the concrete structure whether we are in an environment where the pH is always high or whether we are in an environment where the pH is low where other forms of ettringite can actually happen or when ettringite can actually decompose to other products which may not be actually causing the level of expansion that we associate with that ettringite.

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MORTAR PRISM TEST RESULTS



Of course we, engineers always like to see some models see the linear or quadratic or something fitted through the data. So this is just to satisfy that requirement. So you see here with the 50 gram per liter solution the OPC Mortar is showing you a very high level of expansion and again if you fit that into a quadratic sort of a relationship you can get the constants associated with the quadratic equation.

Similarly, for the 3 gram per liter solution again the fit is quite good with a quadratic relationship, but then again what is this leading you towards? It may help you to some extent in predicting the time at which the expansion will exceed a certain critical value. Although that

critical value is stated is 0.1% in ASTM C1012, you can decide based upon the kind of conditions prevailing in your site what you want that critical expansion to be.

So based on that you can suitably modify the test and suggest a different way of interpreting the data. No in this case, there is no shrinkage happening. So in this case, shrinkage is totally avoided because your specimens are continuously inside the sulphate solution. So there is no drying and wetting in this case. So during drying and wetting the specimen stays inside the solution for a certain period of time, then you have in a drying environment and then you put it back into the system. So that may produce a net length change which would also go towards shrinkage.

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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 *SRC*
- Use of high alumina cement
- Use of supersulphated cement
- Use of pozzolanic materials and mineral admixtures
- Low w/c and good impermeability!! ← *MgSO₄ & Solubility poor*

Of course talking about various means of protecting your Mortars or concrete against sulphate attack the first and full most is the use of low C_3A cement, because again we have seen very clearly the link between expansion ettringite formation, but low C_3A cements tend to change the chemistry in such a way that the primary ettringite that forms in the early hydration process remains stable throughout.

It does not convert to other forms of sulphate like monosulphate which have the tendency of reconversion to ettringite when external sulphates come into the concrete. So low C_3A cements form the basis for sulphate resistance cement. We call it SRC or sulphate resistance cement. Now

it is also useful to have a cement that is low in C3S and that is from the point of your production of calcium hydroxide upon hydration.

You know very well that 1 mole of C3S produces 3 times as much calcium hydroxide as compared to C2S. So if you have more calcium hydroxide there is greater tendency to form gypsum because when external sulphates react with calcium hydroxide they form gypsum. So reduction in gypsum formation can also help improve the resistance of the concrete or Mortar to sulphate attack.

High alumina cement and super sulphated cements are not really utilized in the large extent today primarily because of the other problems we talked about that they have related to the stability of the hydrated phases. Now in terms of sulphate exposure both these cements perform very well because again there is no formation of late ettringite that actually happens in these systems.

Now of course we are mainly left with 2 major aspects that probably would form part of most protection mechanisms when we talk about durability related problems. One is use of pozzolanic materials and mineral admixtures. Now this can be advantageous in most cases because it brings down the extent of calcium hydroxide that is there in the system so less gypsum is forming. If there is less gypsum forming obviously.

There will be less conversion of the existing monosulphate and aluminate to ettringite because as we discussed earlier gypsum formation happens to be first step in the process. So if you are trying to restrict that step the next step will not take place automatically. So you have less gypsum that means good for sodium sulphate. Now what happens when you have less calcium hydroxide present in the system.

When you have an acidic sort of a mechanism which is brought out let us say the magnesium sulphate. What will happen in that case? So concretes with mineral admixtures which have lower Portland contents; how will they face magnesium sulphate solutions? Will they be good or bad as compared to OPC? They will be worse. As far as magnesium sulphate is concerned any attack, any sulphate based attack which produces acidic conditions in the system.

So SCM will be poor in terms of the resistance. Now of course we are only addressing here the chemical mechanism. We are not truly addressing the physical mechanism of sulphate penetration which is dictated by the permeability of the system. Now when we use SCMs real concrete specimens in the field which are exposed to sulphate solutions will tend to resist to a large extent the penetration of the sulphate solution inside.

Now chemically the absence of calcium hydroxide in mineral admixture based concretes may be negative aspect as far as magnesium sulphate attack is concerned, but as far as physical penetration of the attack solution is concerned that is going to be limited to a large extent because of the lower permeability in the system, but then if you look at chemicals studies which are done as far as sulphate attack is concerned with magnesium sulphate.

Most often you will find that the performance of concrete with mineral additives is not very good and that is something we will see later in acid attack studies also, but of course the most important characteristic that we still need to worry about is maintaining a low water cement ratio in the concrete and making concrete impermeable that is probably the first line of defense that you can give against penetration of sulphate solutions.

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Influence of C_3A

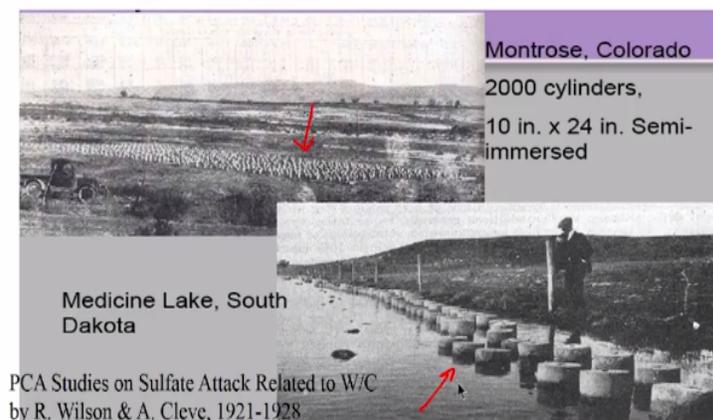


Now this is some laboratory evidence about the influence of C3A in sulphate attack and this is from Canada. So here you can see very clearly that if you have a very high percentage C3A in your cement 12.3% C3A you cannot even make out what type of specimens these were. These specimens were completely immersed in sulphate solutions and here you have 3.5% C3A.

The cylindrical specimens are actually intact after exposure to the high concentration sulphate solutions. So C3A directly because of the kind of studies that we do in laboratory based on immersion you can clearly see the performance of concrete with less C3A to be much superior as compared to the performance of concrete with higher C3A.

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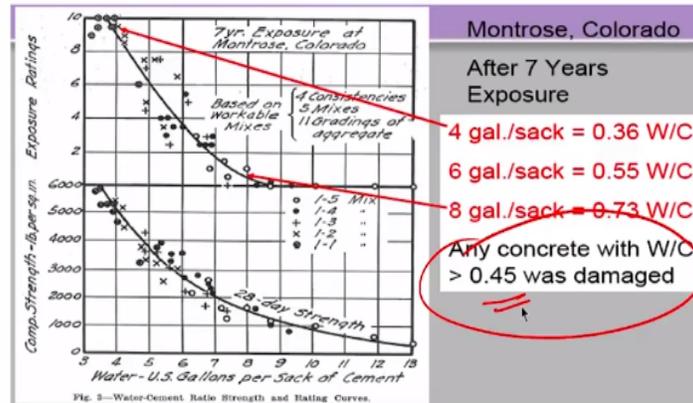
Influence of w/c – PCA study



Now when you go to real site based studies the best example of this kind of a study is what was carried out by the Portland cement association, PCA in the US they had a study which lasted for several decades nearly 30 to 40 years of data they collected on these concrete specimens that we actually immersed in Colorado inside sulphated soils as well as these specimens that were immersed inside Medicine Lake in South Dakota which are a high sulphate content. So these were partially immersed to bring out the realistic effects what could happen in the concrete when they are in a sulphate rich soil.

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PCA study (contd.)



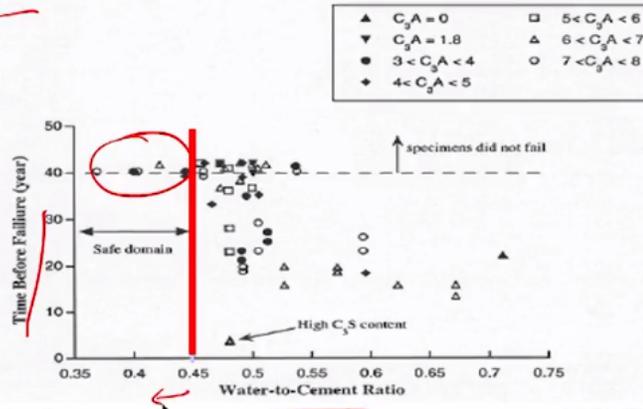
Interestingly what their study showed very clearly was that any concrete with water cement ratio of more than 0.45 was damaged in this exposure. So this was realistic exposure. The sulphate solution was not highly concentrated. It was actually what was found in reality. The concrete specimens are not extremely small. They were fairly large cylinders and after 7 years of exposure they came up with this conclusion that any concrete with more than 0.45 water cement ratio was damaged.

That is quite interesting to show that 0.45 is the limiting water cement ratio as far as sulphate rich environments are concerned and this 0.45 reflects in most of the coral specifications also in terms of protection of concrete against sulphate, the first and foremost thing that is prescribed in specification is reduction of water cement ratio to < 0.45 .

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USBR 40 year data

Monteiro, K.E. Kurtz / Cement and Concrete Research 33 (2003) 987-993



And again this same data was actually analyzed later by researchers at University of California Berkeley, who presented this data in a different approach later. So the time before failure was plotted against water to cement ratio and what they were able to show is the concretes that were safe even after 40 years, the concrete that still remains safe irrespective of the C3A content of the cement.

All these concretes had water cement ratio is of < 0.45 . So even if there was a high C3A cement available in the system if the water cement ratio is kept below 0.45 the performance was still very good. So all concrete is survived beyond 40 years where the ones which had water cement ratio < 0.45 .

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ASTM – Cement limits

| Type | I | II | III | V |
|---|-----|-----|-----|------|
| SO ₃ (C ₃ A ≤ 8)* | 3.0 | 3.0 | 3.5 | 2.3 |
| SO ₃ (C ₃ A > 8)* | 3.5 | N/A | 4.5 | N/A |
| C ₃ A | --- | 8 | 15 | 5** |
| C ₄ AF+2(C ₃ A) | --- | --- | --- | 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?

And again if you look at most specifications the cement limits basically talk more about the extent of C₃A present in the system where type II cement are typically the moderate sulphate resistance cement. So they have about 8% C₃A, type III generally will have high C₃A content because we need the rapid hardening characteristics from these cement, but type V cements, which are sulphate resistance cement.

I am talking about ASTM specifications here, type 5 is sulphate resistance cement and there the C₃A content should be controlled < 5%, but problem is most type 5 cements are never tested for sulphate resistance assuming that you are always having C₃A < 5%. People assume that when you use the sulphate resistance cement you automatically get protected from sulphate attack. Now why is this a problem?

Why should we still conduct tests for sulphate resistance even if we sulphate resistance cement? Because we are not really establishing the mixtures clearly if you do not choose the water cement ratio that is one thing. Second is we know that there are other forms of damage also happening in this system related to physical salt attack and related to gypsum formation and the other aspect that ettringite may not be the dominant mechanism of failure in actual concrete specimens.

In a laboratory study where we do continuous immersion, the formation of ettringite we can clearly show is directly linked to the expansion, but in a realistic condition ettringite may not be

stable first of all. It may convert to other forms of sulphate and it may not really be the dominant mechanism of damaged your structure so even when you use type 5 cements we should expose it to sulphate related tests and ascertain whether we are actually getting the performance that we desire which is why the testing standard for sulphates.

That is ASTM C1012 which is based on a continuous immersion that is question by many researchers it is not really bringing out truly speaking the actual resistance to sulphate attack for the concrete, because you are not truly incorporating the effects of the permeability of the system. Anyway that is beyond the discussion.

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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.

That we would like to have here just wanted to recapitulate the different testing methods that I prescribed in the ASTM standards. What is most often used is ASTM C1012 where you have Mortar bars which are exposed to 5% sodium sulfate or 5% magnesium sulphate or they even say you can also use a mixture of sodium and magnesium sulfate. Now the kind of mechanisms or kind of the reactions that you get from these would be quite different.

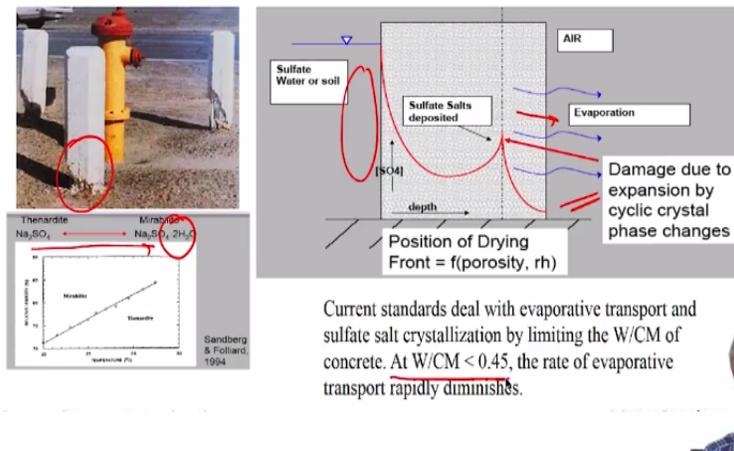
So you have to be very careful about how you are actually going about doing the test, selection of the right sulphate solution is very important and expansion is measured typically for 6 or 12 months after the concrete or the Mortar actually attains 20 megapascals only it is exposed to the

sulphate solution. That is to ensure that there is some minimum level of strength that has been developed already in the system.

So again the test solution is 50 gram per liter, sodium sulphate solution and again this 20 megapascals allows the supplementary cementing materials also to react. So that means we are not saying that we only cure for 7 days. In 7 days OPC may react to a different degree as compared to fly ash. So what we say is until all the specimens attain the same level of strength only after that we expose them to the sulphate solution.

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Salt crystallization – physical attack?



Now the other kind of sulphate related mechanisms that you may see on the field also include what is called salt crystallization. We talked already about the fact that columns embedded in sulphate with soils will actually have more damage at the soil air interface rather than in the part of the column that is actually completely submerged inside the soil and that is essentially because of this additional effect of salt crystallization.

And salt crystallization basically relates to the deposition of the salts inside the pores, evaporation of the water and subsequent crystallization of the salt and you can see that when you change between different forms of the sulphate that leads to a change in the expansion or change in the levels of the crystallization levels because you are incorporating waters of hydration, the

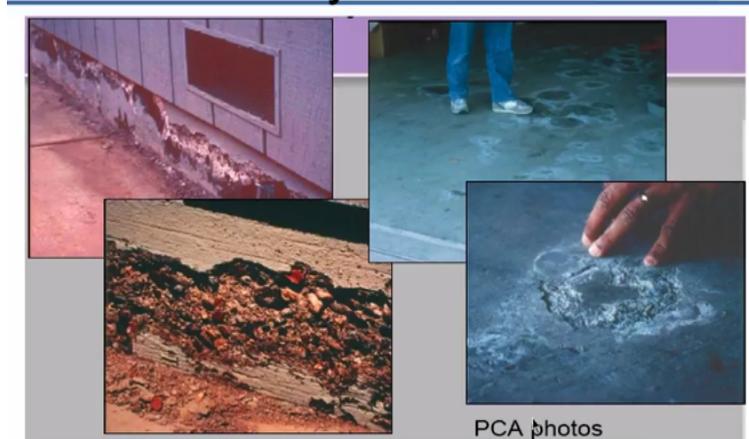
size of the crystal also changes because of which you generate crystallization pressure in the system.

And added to this you have the other aspects of we talked about the evaporative transport that is wick action that is quite dominant in cases such as this when you have wetting on 1 side and completely dry environment on the other side. Interestingly it is again shown by research that if you water cement ratio < 0.45 in your system the rate of evaporative transport that means the rate at which the suction will happen diminishes significantly.

So this 0.45 seems to make sense not just from a chemical point of view but also from a physical attack point of view.

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Salt crystallization



Again these are evidences of salt crystallization from Portland cement association.

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Role of w/c



And this is actually a long term study done by PCA for concretes which had type V cement that means both were made with sulphate resistance cement. One had a very high water cement ratio of 0.65, the other had 0.39 and you can see very clearly the performance. After 12 years, the visual rating of concrete was 5 that means they are deteriorated to the maximum level.

Here after 16 years the concrete was still having a rating of 2 that means it had long way to go before it got completely deteriorated. So again what has been shown in most sulphate related research studies is that the role of water cement ratio is critically important not just the C3A level, but water cement ratio is the primary factor that determines sulphate resistance.

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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 different types of sulphate attack is delayed ettringite formation. So how this is discovered or investigated in concrete for the first time. It happened when some railway sleepers in the UK started showing some cracks. now railway sleepers are produced in a precast yard typically these are prestressed, precast railway sleepers and they are subjected typically the heat curing to increase the rate of strength development and these sleepers started showing kind of map cracking or random cracking after about 15 to 20 years of service.

So the people who investigated thought that this was because of alkaline silica reactivity. But then they later saw that the reactive aggregate was not really there in the system and these cracks had to be associated with something else. When they started doing microstructural analyses they found that these concretes were actually showing the formation of lot of ettringite in the system and lot of these ettringite are actually started occupying the sites of the cracks and the voids.

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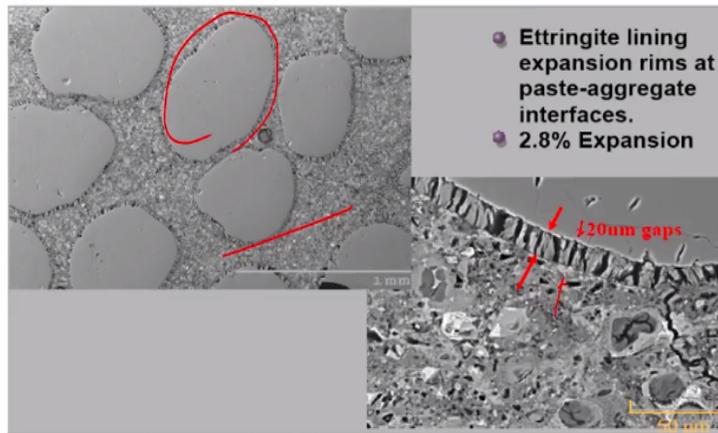
Mechanism of DEF

- 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

I will show you some pictures a little bit later.

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DEF – some examples



This is the interface between cement paste and aggregate you can see and lot of ettringite that is deposited in this interface and also you can see ettringite all across the interface in several of these around several of these aggregates are actually see the formation of ettringite. So this was detected in the microstrucral study and then they came to a conclusion that this ettringite was something that had reformed in the system after the concrete was hardened.

Because it could not form in the initial stages and this initial stage suppression of ettringite formation happens primarily because of the heat curing of the system. If you are providing a very high level of heat to the system, we are generally talking about temperatures more than 70 to 75 degree Celsius at that stage the formation of ettringite get suppressed. Or if you have sulphates which are probably not of a type that are easily soluble.

If the sulphates are not easily soluble in the beginning, then you would probably do not have the formation of ettringite in the early stages as you have in normal concrete. So ettringite formation is suppressed primarily when you have high temperature as in steam cured concretes. If you have very low solubility of sulphates in the system, then again ettringite formation could be suppressed.

So what happens to these sulphates which are not released early enough is that they go into the CSH. The sulphates are getting absorbed by the CSH indeed if you take heat cured cements or

heat cured concretes you will see very clearly when you do an analysis of the CSH that it contains a lot of sulphur in it and this sulphate would have otherwise gone into reaction products like ettringite or monosulphate.

So these sulphates that go into CSH later recombine with the aluminates whenever moisture is available to form ettringite in a hardened concrete and that leads to expansive pressures that causes cracking of your concrete. So again this is some evidence of concrete which was heat cured showing ettringite formation in the interfacial transition zone. Now interestingly a lot of the research that showed microsectional evidence showed that ettringite was actually forming in the ITZ and also in cracks and inside large voids.

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..contd.



So this voids are entirely filled with ettringite. So this lead many researches to believe that the mechanism of formation of ettringite required that apart from the late release of sulphates the other condition that had to be satisfied was the presence of microcracks and voids in the system that is what researchers tended to believe earlier, but later upon subsequent understanding of this phenomenon people have come to an agreement that it is not that the ettringite that forms in the pores and voids that leads to expansion.

It is the ettringite that forms within the CSH that causes expansion. So this CSH here which has very little space for the ettringite to form and expand that is where the ettringite forms. it creates

an expansion and after expansion happens and the cracks occur the ettringite from here starts going to zones where it can nucleate and grow and forms much larger deposits for example into the voids and into the interfacial transition zone where there is more porosity available in the system.

So the formation of ettringite and pores, voids, and cracks of the manifestation of the later part of your delayed ettringite formation where the ettringite recrystallizes into these pores and voids. So the primary ettringite because of DEF still forms within the CSH and then you get expansive pressures and then finally ettringite moves to the zones where it can nucleate and grow in a very large extent.

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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



So again this was a topic of debate among researchers earlier, but later it was clearly showed that ettringite formation within CSH causes cracking and then ettringite re deposits in the cracks leading people to believe that actually it formed there in the first place.

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Control of DEF

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

So DEF; is it really a problem? It is not as long as you control the temperature to < 70 degrees in your concrete. Now we often know that the temperature of steam curing you can definitely control by reducing the temperature steam to < 70 , but the issue is because of cement contents being very high in the concrete during the early stages of hydration when you add heat curing to it the internal temperatures may actually rise to much more than 70.

So we have to be extremely careful when we are doing heat curing of concrete especially high performance concrete which have much higher cement contents and lower water to cement ratios. But when we are dealing with high performance concretes you also have to look at the other aspect. The fact that there is very little porosity in the system would not permit much more moisture to enter this type of concrete.

If there is no moisture available ettringite expansion will not really happen in the system. So automatically if you choose a concrete with low water cement ratio it will be resistant to DEF irrespective of the early stage processes that you adapt in the system. Using pozzolanic materials also helps. Why is that? Again we bring down the porosity and permeability of the system and then we are again creating conditions of pH which are slightly lower as compared to what we have in plain Portland cement.

So ettringite formation and pozzolanic concretes may not lead to as much expansion as it leads in regular cementitious concretes. So there are beneficial effects of adding pozzolanic materials. First of all, you reduce the amount of aluminate available which can form ettringite that is the direct effect also when you have pozzolanic material you reduce your mode of eliminate that can form ettringite. So automatically ettringite formation is reduced when you have pozzolanic materials inside the system.

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Chloride attack

- Solutions bearing chloride ions can also react with cementitious compounds, although the products that form as a result do not cause any expansions
- Consumption of cementitious phases could lead to increase in porosity, reduction of pH, etc.
- C₃A can bind Cl⁻ ions; thus, high C₃A cements are good against chloride attack
- Some figures of MgCl₂ attack are presented..

*C₃A + SO₄
C₃A + Cl⁻
C₃A + Cl⁻ + H₂O
Friedel's salt*

Moving on to other forms of chemical attack so we talked extensively about sulphate, if we look at chloride attack, we are not really bothered too much about how concrete gets deteriorated by chloride, but we are more worried about how this chloride can actually penetrate into the concrete and reach the level of reinforcing steel where it causes corrosion of the steel. So products of chloride attack or chloride reaction with cementitious hydration products does not lead to expansion in the system.

The kind of products that form actually do not cause expansion although the kind of reaction is quite similar. Please remember the sulphate reaction you had C₃A + sulphate. Here you have C₃A + chloride that lead to the formation of chloroaluminate. C₃A + sulphate led to the formation of calcium sulphoaluminate. C₃A + chloride will form calcium chloroaluminate. So one of the common forms of that is friedels salt calcium chloroaluminate.

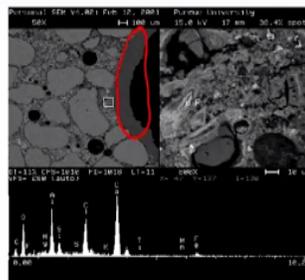
Basically is a formation similar to ettringite formation except that in sulphate you have chloride in the system and this is actually a beneficial reaction because not only you are forming a non-expansive product you are also trapping some of the chloride that got into your concrete. Chloride that gets into the concrete needs to be in the free condition to go and attack the steel surface.

If the chlorides are getting bound by the cement that means you are reducing the amount of chlorides that can cause corrosion. So binding the chloride by C3A is a primary mechanism of protection against attack by chloride solutions and this binding mechanism can actually get improved if you are substituting cement with mineral additives that have aluminates in them. For example, clay, you have slag these are contributing lot of aluminate into the system.

These aluminates can end up binding the chloride ions into a non-expansive product. In conclusion when you have cements that are rich in C3A you can actually have a good performance in chloride attack. In sulphate attack we talked about low C3A. In chloride attack it is the opposite we need cements which have a high C3A because that is what will lead to improvement against resistance to corrosion. So, improvement in terms of resistance to corrosion not against resistance. So I am just showing you some pictures from magnesium chloride attack.

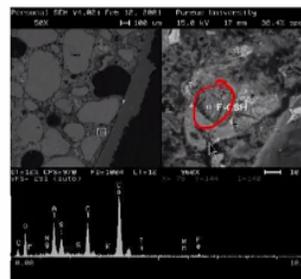
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Chloride attack – SEM observations



Porous appearance of surface zones

Thick brucite layer on the surface; evidence of chloroaluminate formation

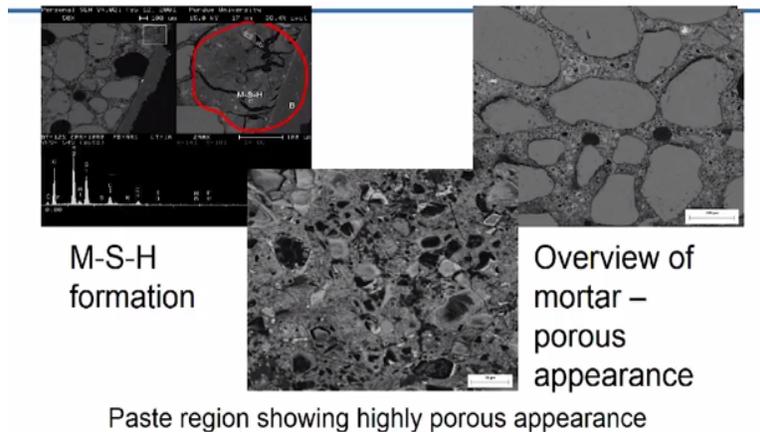


So again magnesium ion is also involved in this case so you will actually lead to the formation of this layer on the surface called brucite or magnesium hydroxide and there is also evidence of friedel salt formation which is marked by F here which is calcium chloroaluminate. Sometimes it forms in a condition that is mixed up with the CSH. So you do not often find chloroaluminate directly as a single deposit.

Sometimes it is mixed up with the CSH. Interestingly what chloride or chloride attack can do is increase of porosity of your surface zones because you are again leaching out your calcium hydroxide so you are removing of solid product and creating a porosity inside. So, because the extent of deposition of your other products is not as much.

Most of your products are soluble for example if your calcium hydroxide reacts with the chloride what it will form? Calcium chloride, which is highly soluble and gets removed from the system. In the other case sulphate attack calcium hydroxide is reacting with the sulphate to form gypsum and gypsum was not easily soluble. It was remaining in the system and showing up as deposits.

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So here you are causing an increase in the porosity that could be one of the negative effects of chloride attack, but if you have magnesium chloride attacking apart from the increase in porosity you also have the alteration of the surface and conversion of CSH into magnesium silicate

hydrate that can still happen in the system. Please remember it can happen in any system where you are removing calcium from the CSH.

Here the magnesium will remove calcium from the CSH. If you have an acid let us say if you have hydrochloric acid, the acidic conditions will remove calcium from the CSH. Even in that case will form silica hydrate. It will not form any metal base silicate hydrate. Here since magnesium is present you will form magnesium silicate hydrate.

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Acid attack

- Primarily a problem in sewer pipes
- Typically related to H_2SO_4 ✓
- Gypsum formation, and an associated softening and strength loss of the structure observed
- Loss of cementitious nature due to deterioration of CSH because of low pH

So let us quickly talk about acid attack then we will close for today. So acid attack is primarily a problem in pipes carrying sewage. Concrete pipes that carry sewage are subjected to acid attack. Even in some industrial effluents you can actually sometimes get acid formation. I will show you some examples of where acids can be found and when you talk about sewer pipes the typical problem is related to the formation of sulphuric acid.

And again sulphuric acid you have sulphate, you have acidic conditions so you are essentially lead to gypsum formation would ettringite form? Not in the zones of which are close to surface. Wherever there is acid present there will be ettringite formation. So because of ettringite not being stable at a low pH you will not see any evidence of ettringite in the surface zones. If you go interior in the specimen where some sulphate may have actually penetrated, you may still see some ettringite formation.

So gypsum formation is a common phenomenon in sulphuric acid attack and what you do get from that is strength loss because of gypsum formation and most importantly you get loss of cementitious nature because your pH is lower that causes your CSH to become unstable. Now sulphuric acid is just 1 type of acid that may damage concrete.

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Sources of acids



There are several other instances which can actually happen. Industrial manufacturing often uses sulphuric acid, nitric acid, hydrochloric acid, so all these can form, all these can damage the concrete structures that are used in these sorts of structures. Concrete sewer of course is an environment where sulphuric acid attack actually happens and that is microbially generated because of the action of bacteria.

We will talk about that in just a minute. Industrial effluents can often carry acidic strains with them which can lead to damage to concrete linings for instance. Interestingly, there is a lot of acids that are also generated from organic sources so silage production in cattle farms. You can have cattle farms where lot of organic acids can be generated like lactic acid, oxalic acid and soon and sewage treatment plants and other locations where acid generation can actually happen in the system.

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What is acid attack ?

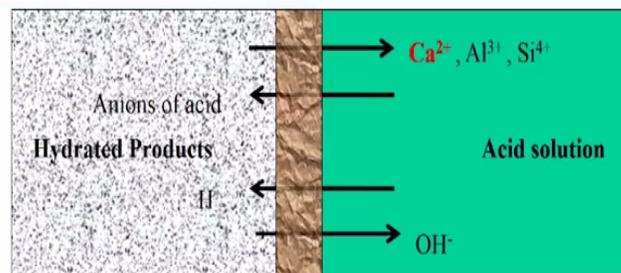
- The attack is a classic acid (HA) – base (BOH) type of reaction to form a salt (BA) and water
- The process of degradation includes ion addition and exchange reactions, leading to **breakdown of the cement matrix microstructure** and weakening of the material
- $HA_{(aq)} + BOH_{(aq)} \rightarrow B^+_{(aq)} + A^-_{(aq)} + H_2O_{(aq)}$
- Eg: $Ca(OH)_2 + 2 HCl \rightarrow CaCl_2 + 2 H_2O$
- The aggressiveness of an acid mainly depends on the solubility of salt (depends on the type of acid) and the concentration of acid

Now what is acid attack? Your primary reaction is simply a classic acid base reaction because you have acid from the external environment and your calcium hydroxide another basic substances that are found inside the cement hydration productions. So essentially you are leading to a breakdown of the cement matrix microstructure by the formation of the salts. Some salts are soluble, some are insoluble.

So when you have soluble salts you have increase in porosity. When you have insoluble salts you have deposition and possibly expansion because of the deposition in these salts in the system.

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What happens in acid attack ?



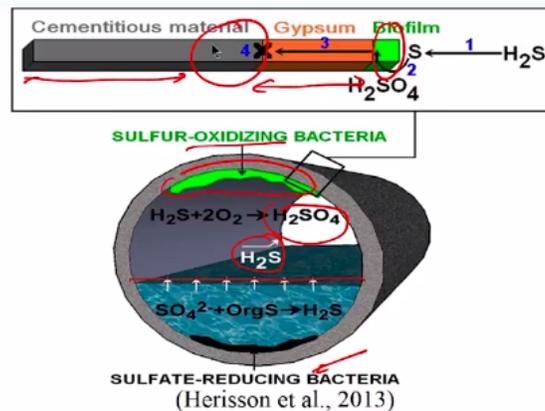
- ✗ Loss of mass
- ✗ Loss of integrity
- ✗ Loss of alkalinity
- ✗ Loss of strength/elastic modulus
- ✗ Increase in porosity
- ✗ Corrosion of reinforcement

So what happens in an acid attack? So these are hydration products and you have the acid solution in the outside. So you have anions of the acid as well as the proton H^+ which are penetrating the concrete whereas you have the outward movement of the calcium bearing species silicon and aluminum as well as your hydroxyl ions and you have a zone that forms in between because of the interaction between the outward species and the inward moving species.

And this zone basically is characterized by the type of material or type of acid that is attacking the system. So what happens to your hydrated products you end up with losing mass, you lose your integrity of the specimen, you lose the alkalinity, and as a result there is a reduction in the strength and elastic modulus, there is an increase in porosity and finally because the pH reduction can reach the level of the reinforcing steel your acid attack will generally give rise to corrosion of reinforcement.

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Acid attack in concrete sewers



Now more specifically if you look at acid attack in concrete sewers it is a very interesting problem because you have sewage which is typically carried in the lower half of your sewage pipe and inside this sewage there is anaerobic bacteria or sulphate reducing bacteria that lead to the generation of hydration sulphate gas. This gas rises up to the top condenses on the top level of the pipe where it is acted upon by a sulphur oxidizing bacteria or aerobic bacteria and these aerobic bacteria leads to the generation of sulphuric acid on the outside.

So you have acid conditions created on the crown of your pipes whereas the submerged portion of the pipe may actually be still free from damage. So you have essentially if you look at the cementitious material that is attacked by your biologically induced sulphuric acid attack what you will have in the surface is a small biofilm that is formed because of the bacterial action and then you have to large extent formation of gypsum across the certain depth of your specimen.

The gypsum formation is because of sulphuric acid attack and then you have the undamaged cementitious material that is sitting inside. With time of course what will happen is your entire cementitious nature will be lost because of the higher acidic concentration and lowering of the pH and then ultimately you will have a decomposition of your cementitious phases.

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Figure A.4.2.1 Disintegration by chemical attack from muriatic acid

Photos courtesy Prof. P. Paramasivam



Figure A.4.2.2 Disintegration of sewer pipe by chemical attack due to H₂S.

So this is again a picture from a sewer pipe from the right here you can see almost all the paste or almost all the concrete around the reinforcement is getting removed you can barely see the reinforcement as ribs there and all the concrete has got completely removed. Here again a picture from attack by muriatic acid which is basically dilute hydrochloric acid from an industry and you can clearly see the evidence of acid attack here because all the aggregates are left behind.

These are siliceous aggregate. They are left behind, whereas the past has been completely dissolved away by the acid. The aggregate being siliceous not directly attacked by the acid. So now can you tell me a mechanism of protection against acid attack if we substitute this siliceous

aggregate by a carbonate aggregate what will happen? Aggregates will also get damaged by the acid, but that is a good thing because now you have aggregate and paste that are uniformly getting damaged.

So there will be a uniform loss of cross section of your concrete whereas we use siliceous aggregates the paste gets completely dissolved away and the aggregates get loose so there is no binding present in the system. So often times what people uses lime stone aggregates instead of siliceous aggregates because then the lime stone also slowly degrades in the acid solution. So using limestone aggregate is a very good way of mitigating the sulphuric acid exposure or any acid exposure.

Alternatively, you can also use special cements like calcium aluminate cement which has very high resistance to acid attack.

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Stages of sulphuric acid attack

| pH Range | Effect |
|-------------|--|
| 12.5 – 12 | <ul style="list-style-type: none">● Calcium hydroxide and calcium aluminate hydrate dissolve and ettringite is formed● CSH phase is subjected to cycles of dissolution and re-precipitation |
| 11.6 – 10.6 | <ul style="list-style-type: none">● Gypsum is formed |
| < 10.6 | <ul style="list-style-type: none">● Ettringite is no longer stable and decomposes into aluminum hydroxide and gypsum |
| < 8.8 | <ul style="list-style-type: none">● CSH becomes unstable |

Again this is just giving you the description of different stages we do not have to look at this in more detail.

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Acid attack in sewers – microbial origins

Organic acids

- Produced by group of fungi called Fusarium
- Wide range of acids such as acetic, oxalic acid etc which will initially react with the concrete cover
- Decalcification of the cement hydration products
- Final product is a layer of silica gel

Sulphuric acid

- Produced either by oxidation or by aerobic thiobacillus bacteria
- Decalcification of the hydration products
- Final products are gypsum and ettringite
- Gypsum may allow further colonisation of bacteria

Sewage networks represent a very aggressive environment for cementitious materials

Now there are distinctions between chemical sulphuric acid attack and organically generated sulphuric acid attack. So again the kind of products that you may form in the system and the kind of alteration of your microstructure may end up being quite different. So I am just giving you this for your information not really for more discussion in this case. So sewage networks actually give you a very aggressive environment for cementitious material.