Advanced Concrete Technology
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Lecture - 07
Cement Chemistry – Part 2

We were talking in the last lecture about the heat evolution patterns produced by isothermal and adiabatic calorimeters and you saw primarily that each one of these calorimetry techniques had their own advantages. You can measure the heat evolution right from the time 0. It is more accurate because we are actually measuring the heat directly. In the case of adiabatic calorimetry, we are measuring the temperature and converting that to the heat. And assumptions are need not be made for isothermal calorimeter related to the heat properties of different ingredients correct.

What about the advantages of adiabatic calorimetry? We can have a very large sample size. You can actually test the exact concrete mix appear intending to use in job site so that we can actually get to know what is the potential temperature rise that we can expect in the system.

Especially in the presence of pozzolanic materials, the study of heat evolution can help us analyze the reactivity characteristics of the pozzolan quite nicely. With slag and fly ash you cause some changes to the heat pattern; primarily with fly ash the peak temperature as well as the peak heat rate are considerably reduced, when fly ash is used, especially in larger levels of replacement of cement by fly ash. The same is not true for type C fly ash where you may see some delay in achieving in the peak heat rate.

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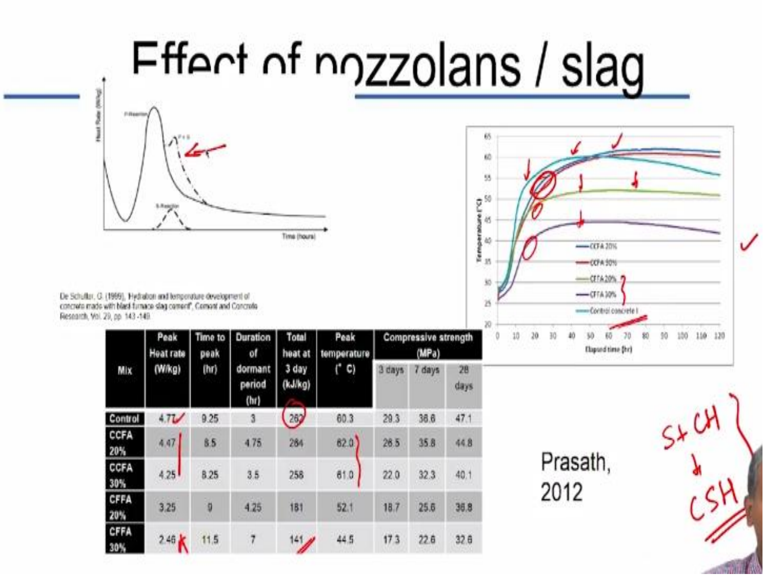

Effect of pozzolans / slag

De Schutter, G. (1999), "Hydration and temperature development of concrete made with blast furnace slag cement", Cement and Concrete Research, Vol. 29, pp. 143-149.

Mix	Peak Heat rate (W/kg)	Time to peak (hr)	Duration of dormant period (hr)	Total heat at 3 day (kJ/kg)	Peak temperature (° C)	Compressive strength (MPa)		
						3 days	7 days	28 days
Control	4.77	9.25	3	282	60.3	29.3	38.6	47.1
CCFA 20%	4.47	8.5	4.75	284	62.0	28.5	35.8	44.8
CCFA 30%	4.25	8.25	3.5	258	61.0	22.0	32.3	40.1
CFFA 20%	3.25	9	4.25	181	52.1	18.7	25.6	36.8
CFFA 30%	2.46	11.5	7	141	44.5	17.3	22.6	32.6

Prasath, 2012

But overall heat rate is not that much different as compared to the original cement. So you see here the detail for type C fly ash at 20 and 30% replacement seems to indicate that it is almost similar to cement. Now when Portland Pozzolana cement is produced what type of fly ash is used? Is it type F or type C. Now here it just depends on the availability.

If you have type C fly ash is available more than type F definitely, that might get used in the production of Portland Pozzolana cement. Now as a result of this the quality and the characteristics of the PPC that you obtain may have some variation because of the type of fly ash that you actually have.

As you saw here in the seat pattern itself when you have type F fly ash as a cement replacement you actually see a reduction in the peak heat rate whereas if you have type C fly ash there is no major change and the kind of characteristics exhibited by this concrete in terms of long term strength and durability also may be quite different when you are talking about type F versus type C. So in a cement company there obviously make do with whatever is available for the least cost.

But sometimes they also get a variety of fly ashes in different locations and based on the quantities needed they may actually need to blend some of these fly ashes together. So it is often a big challenge for cement companies to maintain the kind of chemical and physical characteristics that you need in a fly ash or in a blended cement when you have fly ashes coming from so many different places.

In fact, in certain parts of the country for example where you have thermal power plants but you do not have sources of coal like north Chennai, they import it from various regions within India or abroad like Indonasia and this coal when burnt it can give quite different characteristics with respect to the fly ash that is produced.. So reactivity, colour all these vary quite a bit depending on where you get the fly ash from. For slag it is also being reported that sometimes you may actually get an additional peak for the slag heat evolution pattern that relates to the reaction of the slag itself and that is especially seen when the slag is very reactive.

In most cases, slag reacts much slower than cement, so it may need a lot more time for the reaction to really initiate. But in some cases when the slag is reactive we may actually see this secondary peak which is associated with the slag reaction. Slag contains the same sort of oxides the cements, calcium oxide, silicon dioxide, aluminum oxide, and iron oxide. But then there are some combined phases calcium silicate, calcium magnesium silicate phases and so on which are not as reactive; that are very finely graded silica particles in slag which could be reactive and produce that high heat peak very early in the hydration stages. So this may or may not be observed when you use pozzolanic materials, but what you will observe in some cases is the presence of an additional peak which is barely discernable in this case of a heat evolution pattern comparing different types of cement blending materials.

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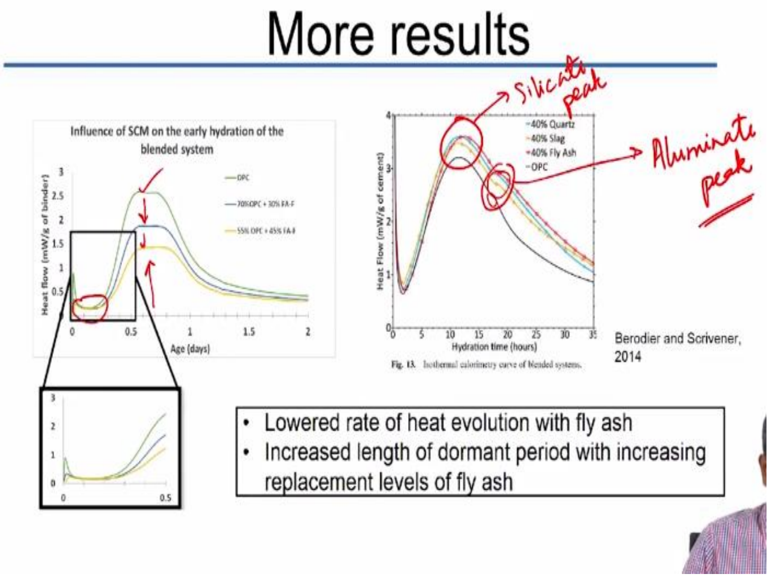

More results

Fig. 13. Isothermal calorimetry curve of blended systems.

Berodier and Scrivener, 2014

- Lowered rate of heat evolution with fly ash
- Increased length of dormant period with increasing replacement levels of fly ash

So again here you can see that the secondary peak that are seen which is barely seen as hump in the case of ordinary Portland cement which is a black line. The other curves are showing a slightly bigger peak which are indicating a replacement of cement by other blending materials like quartz, fly ash, and slag, and that is basically related to the aluminates, called the aluminate peak. So if you were to differentiate this heat evolution pattern into 2 parts you would say that this primary peak is the silicate peak and the secondary peak that appears after the silicate peak is the aluminate peak. Now I told you earlier that cement has to be proportioned carefully. You need to use the right amount of sulphate in the system. So what happens is if you have excess sulfate in the system or if you have too much sulfate in the system this aluminate peak may start occurring at a time which is even sometimes before the silicate peak. Now the silicate peak is very crucial for you to get the right level of early strength attainment. If you do not have the silicate peak you will have a problem with attaining the right levels of strength in your system.

So you need to proportion the gypsum in such a way that this aluminate peak always follows the silicate peak. Now this can become a concern only in the case of extremely reactive pozzolanic systems that have aluminates in that, for eg., clay. Calcined clay will give you a highly relative aluminate system and in that case we need to be extra careful that you have proportioned your sulfate well enough so that this aluminate peak always follows the silicate peak. So that you get a normal strength attainment because of hydration of silicates.

Now again this heat evolution pattern in the left again captures the effect of replacement by type F fly ash. So you see here that compared to OPC which is at the top, the peak heat rate has significantly reduced. The duration of the dormant period also seems to be increased, when fly ash is used as a cement replacement, which means it will take more time for the cement to actually set when you have fly ash as a cement replacement.

Showing a magnified view of the same image that was produced in the left so here you can actually see that the kick off of the hydration is happening much faster for OPC and slower when fly ash is used as a replacement for the cement.

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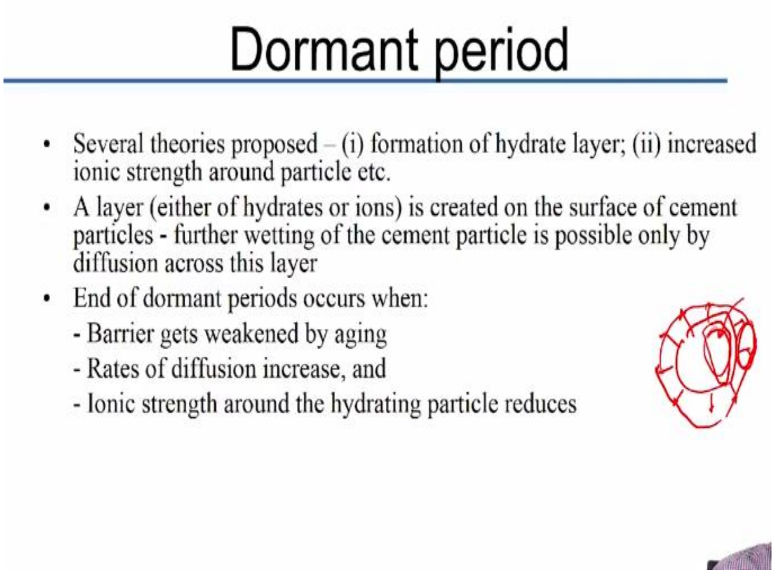

Dormant period

- Several theories proposed – (i) formation of hydrate layer; (ii) increased ionic strength around particle etc.
- A layer (either of hydrates or ions) is created on the surface of cement particles - further wetting of the cement particle is possible only by diffusion across this layer
- End of dormant periods occurs when:
  - Barrier gets weakened by aging
  - Rates of diffusion increase, and
  - Ionic strength around the hydrating particle reduces

As discussed already about why dormant period happens, apart from the theory that there is a barrier of hydration products around the cement, there can be other possible explanation also. One is increased ionic strength around the particle because you know that when the cement particle is put in water there is immediate dissolution from the surface and that increases the ionic concentration around the particle.

And because of this obviously the penetration of water to react or interact with the remaining part of unhydrated cement may get difficult, because ionic strength around will also act like a barrier. So you have to overcome this barrier to actually react with the cement that is inside. So the barrier layer is probably the theory which is most agreed upon by researches and that seems to agree well with the kind of changes that happen when we replace cementitious systems with other blending materials.

So end of the dormant period occurs when the barrier gets weakened by aging in a long period of time let us say 3 to 4 hours. You slowly have this barrier breaking because it is already a very thin membrane. The rate of diffusion of water through the barrier increases to a level that is high enough to start causing the reaction with the cement and the ionic strength around the hydrating particles is reducing because again you are starting to form the precipitates.

For example, if you have calcium ions coming out from the particle you may start precipitating calcium hydroxide. That means the ionic strength will reduce, you will start forming more solid precipitates as a result of this it is easier entry of water towards the location of the unhydrated cement. So this seems to indicate a specific mechanism of interaction of the cement with water.

So if you have a cement particle, the first stage of interaction relates to the dissolution of cement particles or ions from the cement particles outwards. There is some dissolution outwards, but then I said later you have water diffusing through this initial hydrate layer that is forming on the surface. Water actually then diffuses inside and then interacts with the particle in its given location and you can quite easily distinguish that the CSH that forms outside the cement grain that is called outer CSH and the CSH that actually forms inside the cement grain that is called inner CSH and that is exactly because in the nature of the hydration process for a start hydration happens because of dissolution and then later it happens because of inward diffusion of water and subsequent hydration in situ. So we will talk about that once again when we get to the structure of the CSH.

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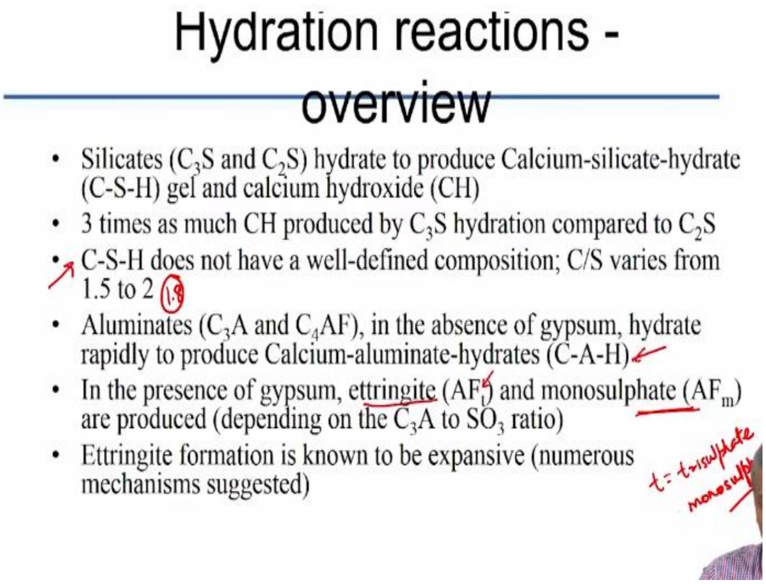

Hydration reactions - overview

- Silicates (C_3S and C_2S) hydrate to produce Calcium-silicate-hydrate (C-S-H) gel and calcium hydroxide (CH)
- 3 times as much CH produced by C_3S hydration compared to C_2S
- C-S-H does not have a well-defined composition; C/S varies from 1.5 to 2 1.8
- Aluminates (C_3A and C_4AF), in the absence of gypsum, hydrate rapidly to produce Calcium-aluminate-hydrates (C-A-H)
- In the presence of gypsum, ettringite (AF_t) and monosulphate (AF_m) are produced (depending on the C_3A to SO_3 ratio)
- Ettringite formation is known to be expansive (numerous mechanisms suggested)

t = trisulphate
monosulph

So let us now look at what are the reactions that take place in the system. We know that silicates, that is C_3S and C_2S will react directly with water to produce CSH calcium-silicate-hydrate. You know very well that CSH is the primary binding component of cement paste and it also produces calcium hydroxide. Now I will show you the stoichiometry of this reaction later; for an easy purpose we can actually have a nicely balanced reaction, but that is not the exact reaction.

Nevertheless, you will see that from that reaction 3 times as much calcium hydroxide is formed by C_3S hydration as compared to C_2S hydration. In a normal Portland cement you know that there is lot more C_3S than C_2S. So you can expect that substantially large amounts of calcium hydroxide will also form upon hydration after C_3S reacts with water.

CSH is given such a name, representing C for calcium oxide, S for silicon dioxide, H is H2O or water of hydration. So CSH, calcium silicate hydrate is just a common terminology given to this gel like substance that is actually forming. Now gel does not mean it is a colloid.. It is a solid, but it resembles a colloidal appearance because of high surface area which it is called a gel. Then we say CSH because we have no exact identification of the exact amount of C, exact amount of S, and exact amount of H in the structural CSH. So that is why we call it loosely as CSH.

But in general the calcium to silica ratio in CSH varies between 1.5 and 2 more typically it is around 1.8. Gypsum has to be present otherwise aluminates can rapidly react to form calcium aluminate hydrate. We do not have the situation in normal cement because we do have gypsum because of which the reaction actually leads to the formation of a compound called ettringite which is also written as AFt, where A aluminate and F is ferrite or Fe2O3 and t is basically the trisulphate phase. That means there are 3 sulphates in the ettringite. And this ettringite can convert later to what is called monosulphate where AF is the same aluminoferrite and M is monosulphate. Occurrence of this depends a lot on the amount of aluminate and sulphate that is actually available in your system. And the ettringite that forms from the reaction of C_3A with gypsum is known to be expansive. There are numerous mechanisms of expansion.

But in early hydration we are not worried about any expansion because the cement is still plastic and moldable. So any expansion that happens in the system is not really going to cause damage in the concrete only when this expansion happens when the concrete is hardened in that case we will get damage in the concrete. In the fresh state, the paste is able to take up these expansive stresses. So you do not really have a problem with the expansion of ettringite.

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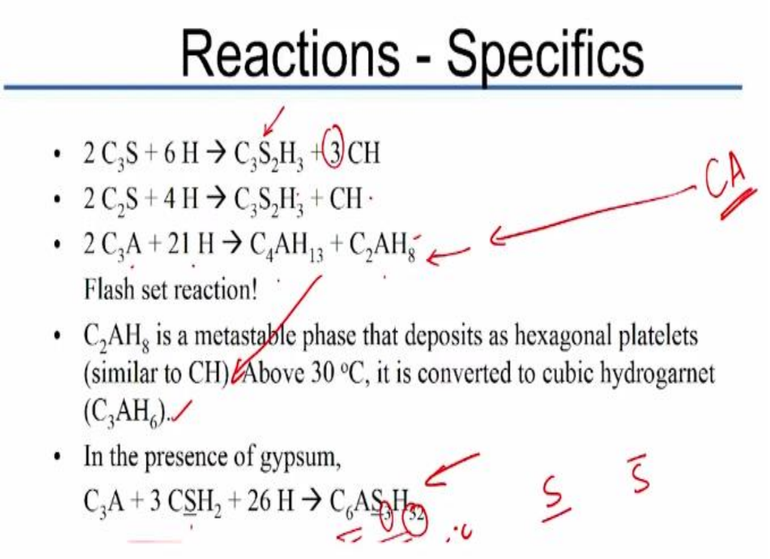

Reactions - Specifics

- $2\,C_3S + 6\,H \rightarrow C_3S_2H_3 + 3\,CH$
- $2\,C_2S + 4\,H \rightarrow C_3S_2H_3 + CH$
- $2\,C_3A + 21\,H \rightarrow C_4AH_{13} + C_2AH_8$
  Flash set reaction!
- C_2AH_8 is a metastable phase that deposits as hexagonal platelets (similar to CH). Above 30 °C, it is converted to cubic hydrogarnet (C_3AH_6).
- In the presence of gypsum,
  $C_3A + 3\,C\underline{S}H_2 + 26\,H \rightarrow C_6A\underline{S}_3H_{32}$

So specifics of the reaction shown above; these are only approximate reactions. They are not the exact reactions they are written from the purpose of solving stoichiometric linear equations that is all. So you have 2 C_3S + 6 H → $C_3S_2H_3$ + 3CH. So here it seems to indicate that calcium to silica ratio is 1.5 which may or may not be the case. This is just written in a way that they can have a nicely balanced reaction.

So sometimes people use x and y for the C and S instead of 3 and 2. So this is not an exact reaction, but it is written because it can nicely be balanced. Similarly, with C_2S when it reacts with water you form CSH once again and calcium hydroxide and based on this reaction you can see that you form 3 times as much calcium hydroxide with C_3S as you do with C_2S. So there is lot more calcium hydroxide generation with C_3S.

The aluminate reaction is called a flash set reaction because the cement sets rapidly with a very high evolution of heat in the absence of gypsum and so you have aluminate plus water giving you 2 different forms of calcium aluminate hydrate. Now these phases that form because of aluminate hydration are metastable phases that means they won't remain in that same structure for a long time.

So there is a reorganization that actually happens and then these systems get converted to C_3AH_6 especially when the temperature is high like over 25°C. That is good enough to actually start causing a change in the structure of the cements to a slightly different crystal structure. It is an interesting phenomenon with the aluminate phases because with the change in the crystal structure there is also a major change in the kind of hydration products that form; in the kind of structure of the hydration products that actually forms.

There are special classes of cements which we call as high aluminate cements orhigh alumina cement. It is also called a calcium aluminate cement because in that case the primary compound that is present in the high alumina cement is calcium aluminate ‘CA’ and like cement is produced from a mixture of lime stone and clay the high alumina cement or calcium aluminate cement is produced from the mixture of lime stone and alumina from bauxite. So limestone and bauxite are the ingredients for the formation of calcium aluminate cement.

With calcium aluminate cement you will get these metastable phases when the calcium aluminate cement reacts with water and these metastable phases later convert to more stable hydrate phases. Interestingly what happens when this conversion occurs is that the porosity of the system increases several orders of magnitude, several times. If you have certain porosity with the metastable phases, that porosity undergoes a major increase when it changes to the other forms of hydrate.

What do you think will happen to the system now? The strength will decline. Now calcium aluminate cements came into prominence especially after the Second World War in Germany when they were trying to reconstruct the cities they wanted to use concrete that could be put into service very early because of that they started using calcium aluminate cements for the concrete construction and the strengths attained initially were excellent.

But after about 15 to 20 years of service many of these building started collapsing because the concrete strengths had really drastically reduced. You can have a reduction in strength from all the way up at about 80 MPa down to less than 20 MPa. You can have such drastic reduction in strength because of the change in the hydrated product structure of the cement. So most of these building started collapsing and because of that calcium aluminate cement started going out of favour with in the construction industry. Now calcium aluminate cements are only used for very specific applications because they are very good at extremely high temperature like about 1000°C for example, for doing the lining of the cement kiln because at that temperature the phases that are formed are excellent with respect to their heat resistance properties.

So for general purpose construction, it is not a good idea to use calcium aluminate cement primarily because it leads to a reduction in performance or strength and durability reduction with the passage of time especially at moderate to elevated temperature, about 25°C to 30°C. If your temperature is always very low ; less than 15°C mostly these cements won't undergo this kind of a change.

But if your temperatures reached normal working temperatures of 20°C, 25°C or 30°C you can see this change in the hydrated structure happening which leads to an overall reduction of the quality of the cement. But we do not have to worry about this in conventional cements because we know that in conventional cements the aluminate will first react with gypsum and not with water. So aluminate with gypsum leads to the formation of this compound called ettringite.

There are 3 sulphates in the ettringite. Important thing to understand there are 32 molecules of water bound in the structure of the ettringite. So when you produce ettringite and you heat it up to a certain temperature of about 90°C to 105°C, the loss of that bound water will lead to a very large change in mass. Now in any way this trisulphate phase is what appears first. This ettringite forms first because of the reaction of C_3A and Gypsum. Now how much C_3A do we have in our system typically? about 8% on the average about 7 to 8% in Indian cements; if you go abroad to the US or Europe your cements will have close to 10, 11% C_3A.

The ordinary Portland cements will have very high C_3A levels. So we have around 8% C_3A and about 3 to 4%. So there is always an excess of aluminate present. So this reaction will not be the end product of the reaction of aluminate and sulphate. You may have a further reaction that actually takes place because the sulphates have already been consumed and there is still aluminate that wants to react because of that this phase will then get transformed

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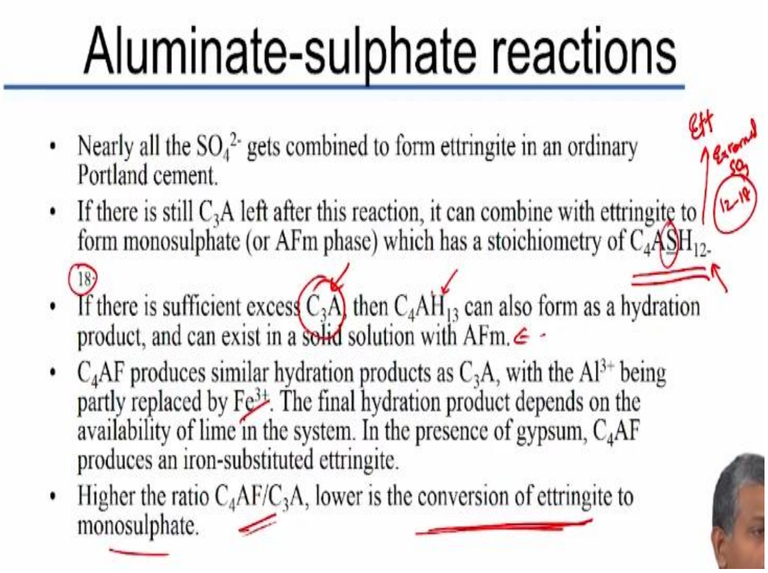

Aluminate-sulphate reactions

- Nearly all the SO_4^{2-} gets combined to form ettringite in an ordinary Portland cement.
- If there is still C_3A left after this reaction, it can combine with ettringite to form monosulphate (or AFm phase) which has a stoichiometry of $C_4A\underline{S}H_{12-18}$.
- If there is sufficient excess C_3A, then C_4AH_{13} can also form as a hydration product, and can exist in a solid solution with AFm.
- C_4AF produces similar hydration products as C_3A, with the Al^{3+} being partly replaced by Fe^{3+}. The final hydration product depends on the availability of lime in the system. In the presence of gypsum, C_4AF produces an iron-substituted ettringite.
- Higher the ratio C_4AF/C_3A, lower is the conversion of ettringite to monosulphate.

Ett

External SO_3

12-18

into something called monosulphate. So, all sulphate gets combined to form ettringite in an ordinary Portland cement, so there is excess aluminate which is still left in the system. It reacts with this ettringite to form monosulphate and which has a stoichiometry of 1 sulphate. In ettringite there were 3 sulphates, in monosulphate there is 1 sulphate and there is lesser water of hydration 12 to 18.

It is 12 to 18 molecules of water of hydration in the case of monosulphate. Now interestingly, this change also changes the structure of the crystalline products that are actually forms. Ettringite typically appears as needles and then it changes to platelets of monosulphates. So there is a change from ettringite to monosulphate in the crystal structure also.

Now if there is sufficient excess aluminate still left even after formation of monosulfate then it reacts with water and starts forming calcium aluminate hydrates. Mostly what happens is you do not form very large crystals of these aluminate hydrates because already your C_3A crystals are extremely fine in size because of which you will find that had a very micro-molecular scale; you will find these aluminate is mixed with the AFm phases.

So the aluminoferrite hydrates that actually forms with water will be found to be intermixed with the AFm phases within the structure of hydrated cement paste. When you have ferrite or calcium aluminoferrite the reaction is quite similar to what you have with C_3A except that part of the alumina is replaced by iron. In the structure of ettringite or monosulphate part of the alumina is replaced by iron and you form iron substituted ettringite or iron substituted monosulphate. We discussed earlier that for different types of cement, you need to maintain a balance between the C_3A and C_4AF contents. When C_3A is low automatically C_4AF will be high. And C_4AF; by and large it is a nonreactive phase, because iron bringing it to solution takes an inordinately long time.

So you cannot really get good reactions with the C_4AF anyway. So higher the ratio of C_4AF to C_3A, lower is the conversion of ettringite to monosulphate. Now I presented some facts here I said ettringite formation is known to be expansive. In fresh cement paste that expansion does not cause any problem because fresh cement paste is still plastic and moldable. It can take care of that expansion. In fresh cement paste this ettringite is not a stable phase, it converts to monosulphate.

In ordinary Portland cement, monosulphate is a stable phase. Now what happens when the cement gets hardened and then is exposed to an external sulphate solution? You already have monosulphate as a stable phase and you may still have some unreacted C_3A also left in the system not all of it will react all the time. But you may have either C_3A or mostly monosulphate + C4AH13 or other calcium aluminate hydrate products. So when you expose these to external sulphates, again ettringite will form. So this monosulphate will reconvert to ettringite in external sulphate attack.

So that will be accompanied by volume changes that will cause cracking in the system. So volume changes cannot be accommodated by hardened concrete because of which it will start cracking. So this reconversion happens from monosulphate to ettringite in the case of an external sulphate attack.

For sulphate resistance cements we keep the C_3A content very low 0 to 4%. If you remember the standards C_3A content of sulphate resistant cement is 0 to 4%. So in that case there will be probably very little monosulphate. It is possible that your ettringite may be a stable phase at the end of the hydration itself and you will not have excess monosulphate available that can further react with sulphate from external sources to reform ettringite in a hardened cement paste.

So in a sulphate resistant cement you have very little conversion of ettringite to monosulphate. So in other words ettringite is a stable phase that forms in sulphate resistant cement. So the premise of making cement sulphate resistant is primarily to prevent the reformation of the ettringite in the hardened status, but that is only solving part of the problem. There is also another problem that sulphate attack which we will discuss later in more detail when we talk about the durability.

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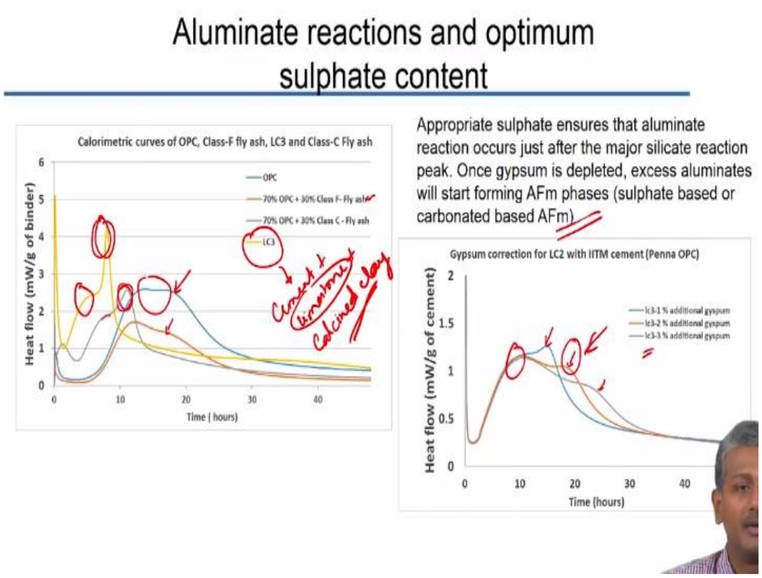

Aluminate reactions and optimum sulphate content

Appropriate sulphate ensures that aluminate reaction occurs just after the major silicate reaction peak. Once gypsum is depleted, excess aluminates will start forming AFm phases (sulphate based or carbonated based AFm)

With respect to heat evolution patterns you can again study these aluminate reactions. So appropriate sulphate content I told you that you need to optimize sulphate in your system so that this aluminate reaction occurs just after your silicate reaction and happens early enough to produce a good early strength. So you want to optimize this cements to get the right early strengths.

But at the same time you want to have it in such a way that the silicate reactions happen first followed by the aluminate reactions. So here we have different systems on the left side of slide. In OPC, you can see that there is a very broad peak here. It is possible that some of the aluminate reactions are getting overlapped in the silica reactions itself. When you start replacing OPC with components that may have reactive aluminates you may start picking up this distinct reaction peak.

You have 3 different systems; 1 is with type F fly ash which is not really producing an aluminate peak which can be very clearly noticed. With type C fly ash after the silicate peak you are able to see some aluminate peak also. And with the LC3 system which is basically a mixture of cement + lime stone + calcined clay, because of the highly reactive alumina contributed by the calcined clay these aluminate reactions can have a substantially high rate of reactivity.

Because of which you see the aluminate peak is much higher in terms of the actual rate of heat evolution even compared to the silicate peak that is happening because of a clinker reaction. So you need to choose your amount of substitution of clinker and the reactivity of the substitute material in a careful manner so that the silicate reactions from the clinker happen first followed by the aluminate reactions that can be contributed by the pozzolanic material.

Now what we found was interestingly with some of the LC3 cements when you are raising the initial temperature of hydration what ended up happening was the aluminate reaction was accelerated so much that it happened even before the silicate reaction and as a result of that we did not get a proper strength development in those mixes. So you need to have a good control by optimizing a sulphate in such a way that this aluminate reaction takes place after the silicates have really started. So the idea is you want to push this aluminate peak slightly away from the silicate peak to ensure that you get proper strength development and this is done through optimizing gypsum amount. So you optimize it towards this 2% gypsum rather than 1% because there you have really too close to the silicate peak. So appropriate sulphate ensures that aluminate reaction occurs just after the major silicate reaction peak and once gypsum is depleted your excess aluminate will start forming AFm just like we talked in the last slide.

When we talk about LC3 specifically that since lime stone is also contributing carbonate this AFm phases need not be only restricted to monosulphate. You can also get a phase called monocarbide with the LC3 system. So that is an additional hydration product that you actually form with the LC3 system.

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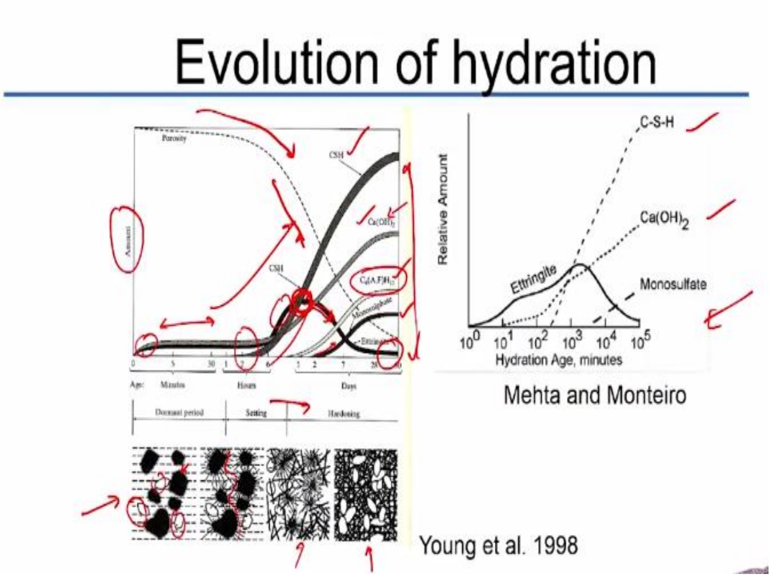


Evolution of hydration

Mehta and Monteiro

Young et al. 1998

So to put all this in perceptive let us look at how the cement paste actually evolves. So I would like you to pay attention first with bottom left again which shows your picture of cement particles in water. So you have these cement particles in water and you also see some well formed crystals very early within the dormant period. So this is actually the picture taken during the dormant period. What is happening in this dormant period?

You have the barrier layer of hydrates present on the cement particles which you can see with the needle like substances in the cement particles. You also have some well defined crystalline materials that are formed away from the cement particles that is because calcium that is coming out is able to form calcium hydroxide. So you have formed these hexagonal crystals of calcium hydroxide may be slightly away from the cement particles.

So that is your dormant period where your reaction is proceeding at a very slow rate. Towards setting you start forming sufficient hydrate that you have a network of hydrated products throughout your system. You do not have too much free water available in the system. So this network of hydrates is enabling the setting of your cement to take place.

When we go from setting to hardening what it means is most of the free water that is present in a system is starting to get consumed to form the hydrated cement phases and you form a more densely packed structure. At about 1 day you have lot of open porosity by 7 days and 28 days most of the porosity have started getting closed and your hydrated structures properly developed in your system.

This representation is quite nice because it also helps us understand the effect of the water to cement ratio. So just like we discussed earlier when you have lesser water cement ratio, in the same volume you have more cement particles because of which filling up the gaps between these particles becomes easier. In other words, you will start attaining your strength and durability much faster.

"What about the extent of hydration? Will it be greater at low water cement ratio or lower? It is quite obvious looking at this diagram when you lower the water cement ratio the degree of hydration also should be lowered. But we all know that when you low the water cement ratio the strength is increased. So is hydration not necessary for strength? Strength means extent of solid material that is present in your system that means the reduction in porosity of the system.

We need to have sufficient hydration to ensure that the porosity gets sealed properly, but we do not want all of our cement particles to react because it is first of all physically not possible secondly these particles even if they do not react still function as fillers. They are still blocking the empty spaces in the concrete because of which at low water cement ratio you are automatically getting a higher strength even though your degree of hydration may be much lower.

So there is more water available there will be more hydration, but low water cement ratio you do not get as much hydration at the same time you get higher strength development because you are blocking all the pores effectively. The unreacted particles do not affect durability because they are unreacted. They are sitting there the system blocking the pores reducing the interconnectivity of the pores and they are not participating directly in any reactions that happen later. The amount of work it would take for any water or aggressive chemicals to get to the unreacted particles may be substantial.

Because it has to make its way through a densely populated barrier of hydrated cement products. So the presence of these unhydrated particles is not going to affect durability. So the durability is primarily a function of the interconnectivity of the porosity that is there in the system. So the higher the water the more interconnected the pores, lower the water, the lesser interconnected the pores that is why we get better durability at lower water to cement ratios.

W know that your initial hydration which happens within a few minutes' will may be form some calcium hydroxide because of the quick dissolution from the surface of the cement particles and may be some early CSH; it may also form some ettringite.

The black line in slide which goes up and comes down is ettringite. So this initial aluminate reaction and initial silicate reaction that may lead to the formation of calcium hydroxide and ettringite. In the dormant period you do not really have anything else that is forming, in substantial quantities anyway. Now at the end of the dormant period you have the primary heat peak that is appearing that is because of the reaction of the silicates and that silicate reaction leads to a rapid rise in the CSH formation in the system. There is also a corresponding rise in the ettringite formation because the aluminates are also reacting at the same time. Your silicates and aluminates from the clinker are reacting to produce CSH and calcium hydroxide; as well as ettringite from the aluminate is getting produced. Now beyond about 1 to 2 days what is happening to the ettringite?

It starts getting converted to monosulphate. So the amount of ettringite starts coming down beyond 1 or 2 days and may end up close to 0 at higher hydration ages or sometimes we may still find ettringite remaining in the system, because reaction is not just subject to the availability of the reactants. The several other conditions that need to be satisfied for reactions to get completed.

So this ettringite monosulphate conversion need not be complete. Some ettringite may still remain in the system. We will see later that especially when you do heat curing there are all kinds of changes that you end up doing to the system, but we will talk about that once we get that. So once ettringite starts getting depleted, the monosulphate starts increasing. The other black line here is the monosulphate.

So the decrease ettringite is compensated by the increase in monosulphate phase and of course with the appearance of the monosulphate you also start the appearance of the calcium aluminate hydrate phases because there is always excess alumina available that will lead to the formation of aluminate hydrates. So if you look at long term, the products that are present in your cement paste are calcium silicate hydrate, calcium hydroxide, calcium aluminoferrite hydrates and monosulphate.

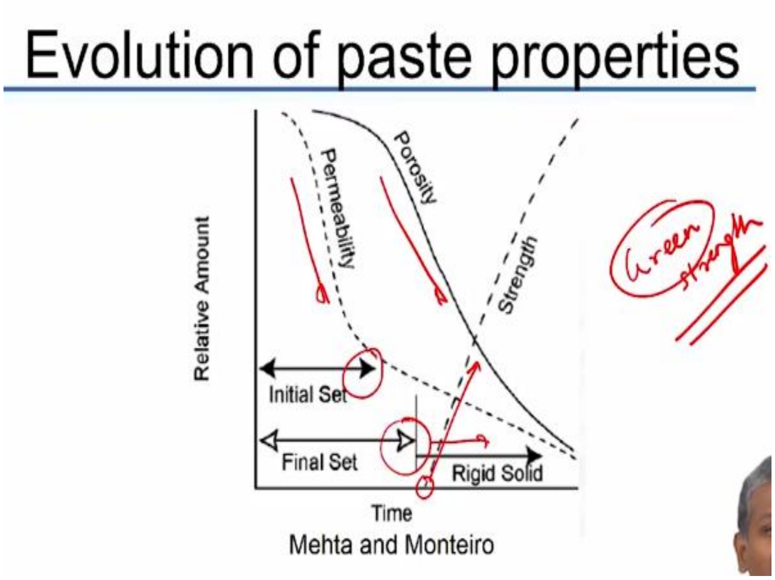
So these are the 4 primary phases that you will form at long term. Now of course this is not showing you the amount exactly to the right scale most of your cement will be calcium silicate hydrate. Most of the cement paste will be calcium silicate hydrate. It forms nearly 50, 60, sometimes 65% of volume of calcium silicate hydrate in the system and you form nearly about 15% of so of calcium hydroxide the remainder is your aluminate and monosulphate phases.

As the reactions are happening to produce more and more hydration products your porosity is obviously going down. Your porosity in the system gradually declines in the beginning and then rapidly declines during this period of quick hydration and then again the rate of decrease in porosity slows down as your hydration proceeds beyond 7 days. In modern cements beyond 7 days we do not get substantial increases.

Most of our cements produce nearly close to 90% of the 28 days’ strength at 7 days itself. In fact, today, when you have to do a mix design for an M30 concrete you will design it in such a way that you get 30 megapascals at 7 days that is the kind of approach you would have because you will see that between 7 and 28 days there is hardly 5 to 6 megapascals increase. So when you do the design the 7-day strength is approximately equal to the characteristic strength.

That is a good guideline to use with the modern cements because we have a very rapidly reacting cements today. The figure shown on right side of slide is from a different text book, you see the same sort of a chart being shown, the reduction in ettringite and subsequent increase in monosulphate phase your stable calcium silicate hydrate and calcium hydroxide phases at the end of the hydration period.

(Refer Slide Time: 42:33)



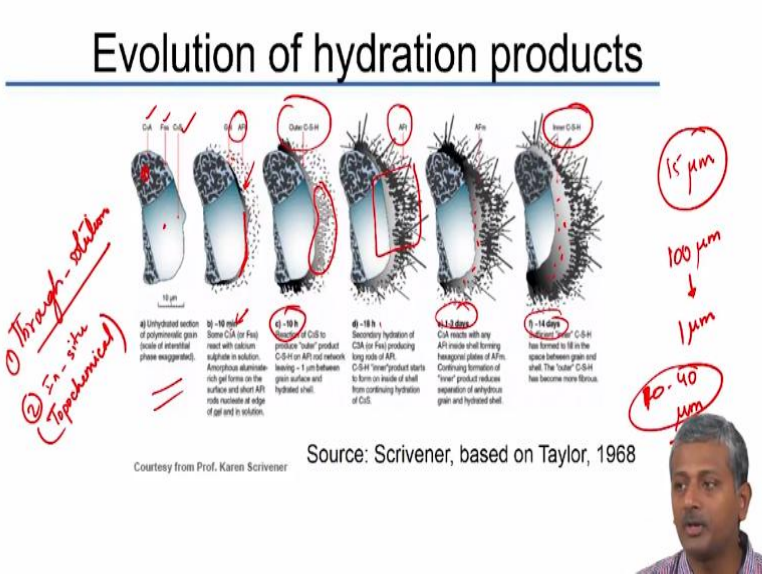
Evolution of paste properties

Mehta and Monteiro

We know very well that the initial set happens at the end of the dormant period and by the time of the initial set there is sufficient hydrated layers or hydrated structure formed which reduces the permeability drastically because porosity is also reduced significantly by that time, but what happens beyond the final set is that you get the transformation of a viscoelastic material into a rigid solid..

So cement paste turns from a viscoelastic nature to a rigid solid; mostly a brittle solid. Of course you may argue that even hardened cement paste or hardened concrete has sufficiently high viscoelasticity; which we will discuss about later, but for the most part from the point of view of understanding the behaviour of this compound in the fresh state when final set occurs that is when it changes to a rigid solid. That is why we say that beyond final set you cannot change the dimensions of the object anymore.

So at that point of time is when your strength starts increasing in the system. So in other words until the final set occurs your cement paste still has what is called green strength that means it is not strong, but it is stiff. Beyond setting it is stiff, it is not strong. So only after final set you really have the start of the gain and strength so which is why when you go abroad sometimes they say the concrete looks green. That it does not mean that the colour of the concrete is green that means it is not fully set yet. **(Refer Slide Time: 44:46)**



Evolution of hydration products

Courtesy from Prof. Karen Scrivener

Source: Scrivener, based on Taylor, 1968

I will again reemphasize that reactions with the cement particles can happen in several different stages. As I said first and foremost you have the initial dissolution from the simple particles. Now you know very well that cement particles are present in various size ranges. 15 microns is the average particle size of cement particles. But you know very well that not all particles of your cement clinker will be of the same size. Some particles may be as much as 100 microns; some may come all the way down to about 1 micron. **"Professor - student conversation ends"** There will be very few particles which are sub 1 micron. Now what will happen is because of the size of these particles the tendency to dissolve obviously will depend on the size of the particles.

The finer particle the quicker will be the dissolution. So as soon as cement comes in contact with water the finest particles will start forming this outer hydrated structure which is why you have this calcium hydroxide formation and so on. But when you look at the unhydrated larger or moderately large cement particles, about 20 to 40 micron or may be even 10 to 40 micron in size the reaction will proceed in 2 stages.

One is obviously the dissolution. As soon as cement comes in contact with water, within the first 10 minutes there is some dissolution from the particle surface. Now what is important for you to understand is a cement clinker particle need not be just 1 phase. It need not be just C_3A, it need not be just C_3S as so on. So here you see that this is actually a mixture the cement particle or a mixture of a C_3S phase and the down mass the C_3A + ferrite solid solution.

So it is marked as C_3A and FSS that means ferrite solid solution, not exactly marked as C_4AF. The other phase is C_3S. So as soon as the cement particles of size 10 to 40 microns come in contact with water there is initial dissolution which is leading the formation of ettringite in the just outside the particle and may also have this barrier of hydrates forming just around the C_3S.

And that is because of CSH and calcium hydroxide. After about 10 hours a sufficient amount of hydrate is actually formed and that is because the particle is still dissolving outwards and forming the CSH which is called outer CSH. It is also forming a substantial amount of ettringite and monosulphate phases in the outer CSH.

And because of this it is starting to create more and more dense hydrates around the cement particle. So beyond this the outward dissolution may be restricted to a large extent and because of that water will have to diffuse through this hydrate layer to the inside of the cement particle and start hydrating the particle from inside and that is when you are start forming inner CSH. So looking at the time scales, your initial dissolution and appearance of ettringite is as early as 10 minutes and around 10 hours there is outer CSH formation and at around 18 hours ettringite needles will be formed and as well as conversion to monosulphate at 1 to 3 days. By about 14 days there is a large quantity of inner CSH that has started forming. So there are 2 mechanisms which are happening with respect to hydration; one is a through solution reaction the other is called in situ reaction.

Through solution reaction produces outer CSH and the in-situ reaction produces inner CSH. The in-situ reactions are also called topochemical reaction that means on the surface of the product itself not away from it. On the surface of the reacted itself you are undergoing some changes informing CSH.