Admixtures And Special Concretes

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Lecture -48

Mineral Admixtures - Calorimeter

Now, we have been talking about specific examples of mineral additives. We have looked at the general principles of pozzolanicity, how do we find reactivity in mineral additives and then what are specific properties of fly ash, slag, silica fume, metakaolin, limestone, calcined clay combination and then finally some agro ashes. Now even apart from these there are several examples of other mineral additives that you may actually find in literature. As I said very often we look for solutions that are either global and could be applicable everywhere or local which have relevance to particular geographic locations depending upon the availability of these materials. So you all should remember one basic tenet sustainability can only be achieved by producing local. You cannot really go for solutions that are from far off if you really want to achieve something sustainable.

So local implies sustainable. So that is where the choice of mineral additives will depend on what is available locally and how best you can get it to perform and that is what we are looking at when we deal with mineral additives.

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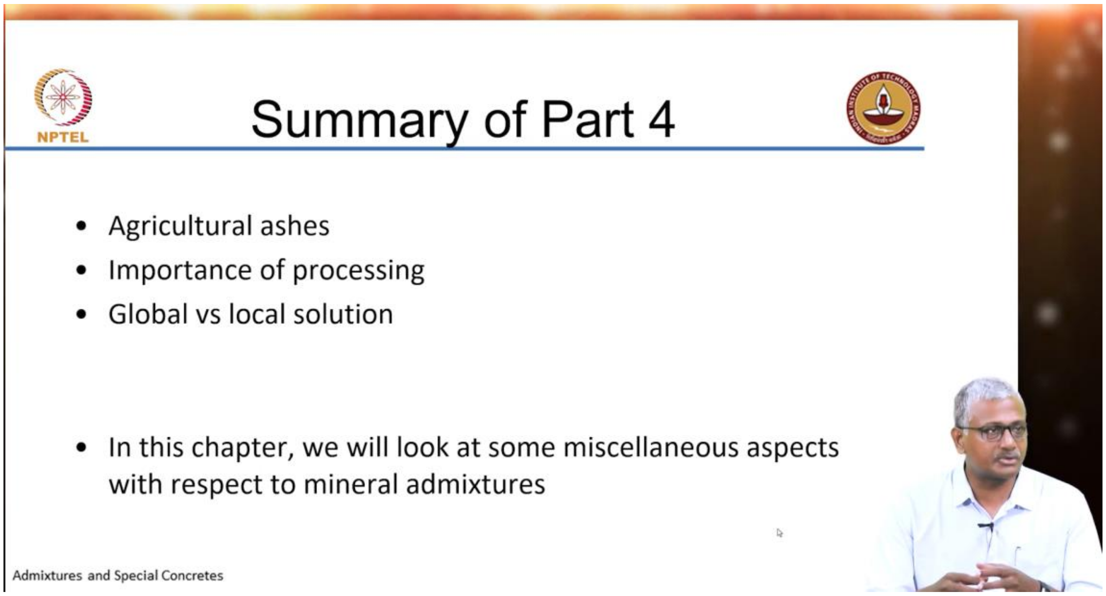

Summary of Part 4

- Agricultural ashes
- Importance of processing
- Global vs local solution

- In this chapter, we will look at some miscellaneous aspects with respect to mineral admixtures

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Now in this segment, we will talk primarily about miscellaneous aspects with respect to mineral admixtures. Apart from reactivity which we have already discussed in the first chapter, let us talk a little bit about other things what it does to the microstructure, what kind of effects does temperature have on the pozzolanicity and so on.

Just some random examples I wanted to give you just to show you that when you use mineral additives in concrete as a replacement of cement you need to also look at other aspects to really work out your strategy for optimal design of mixes or optimal selection of mixes.

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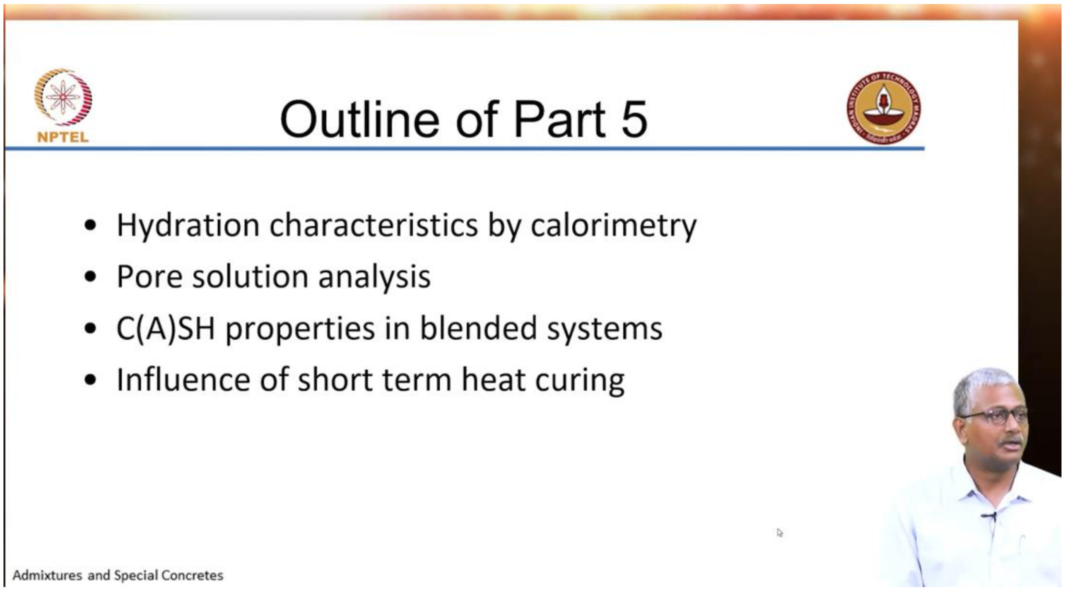

Outline of Part 5

- Hydration characteristics by calorimetry
- Pore solution analysis
- C(A)SH properties in blended systems
- Influence of short term heat curing

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So in this part we will primarily look at how the hydration characteristics are seen with respect to calorimetry. We will look at some examples of pore solution analysis when you extract pore solution from a concrete which has cement replaced with mineral additives, how does the composition of pore solution look like, the calcium silicate or calcium alumino silicate hydrate properties in blended systems and some examples of short term heat curing and what it does to the overall system.

Calorimeter:

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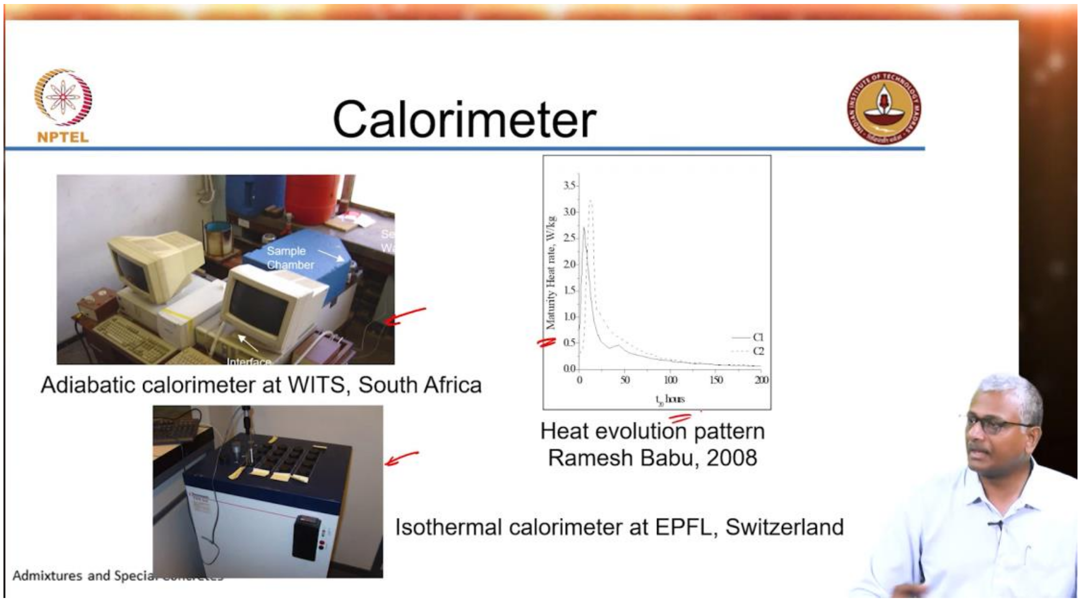

Calorimeter

Adiabatic calorimeter at WITS, South Africa

Heat evolution pattern
Ramesh Babu, 2008

Isothermal calorimeter at EPFL, Switzerland

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Now of course there are different types of calorimeters that can be used to detect the heat of hydration of cementing materials. There are examples of adiabatic calorimeters or isothermal calorimeters.

What is the difference between adiabatic and isothermal? okay. So adiabatic measures the temperature of the system whereas isothermal measures the heat output given by the system, why? What is the principle of an adiabatic system? No exchange of heat between the system and its surroundings that is adiabatic condition. What is isothermal? Constant temperature. System is maintained at constant temperature but you know that when cement hydrates its temperature is going to go up. So how do you maintain an adiabatic condition around a cement that is hydrating? Cement hydrates, temperature increases, so how do you maintain the surrounding system? Increase the surrounding temperature also at the same rate as the cement temperature or cement system temperature. So that is what is done usually you have a sample in a sample chamber instead of large tank which is filled with water and then water has a heater inside, you measure the cement concrete or cement paste temperature and heat up the water at the same rate as a cement temperature is rising. So that way there is no heat exchange between the cement paste or concrete and the surroundings.

In isothermal system what is going to happen? Cement is going to hydrate and generate heat, what will you have to do to keep the system at the same temperature? Either you can cool the system or you can extract the heat from the system, you can extract the heat from the system to keep it at the same temperature. So that is what is done typically in isothermal condition, the heat generated is essentially extracted out of the system and of course, this involves some cooling of the system to ensure that at the same temperature, the power output essentially that comes out of the system is because of the heat that is generated in the system. So from both ways, you get what is known as the heat rate curve, so the heat rate is plotted against the time elapsed and that is how you generate your heat rate curves.

Calorimetry- An important tool:

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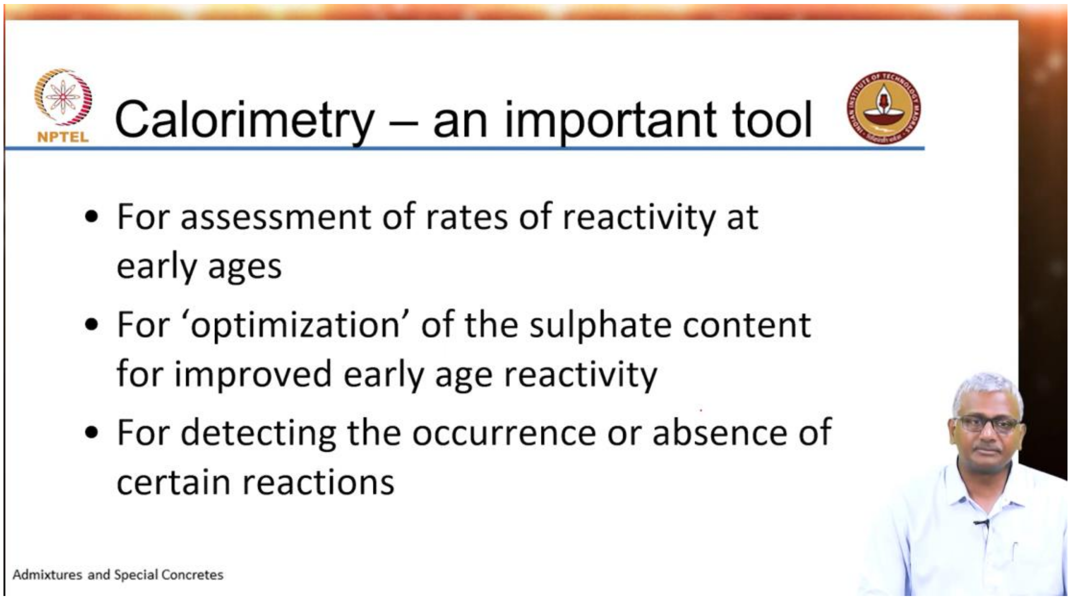

Calorimetry – an important tool

- For assessment of rates of reactivity at early ages
- For 'optimization' of the sulphate content for improved early age reactivity
- For detecting the occurrence or absence of certain reactions

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We will not go into the full assessment of calorimetry here, but calorimetry is very important tool to assess the early age reaction. It is also a very good tool for optimization of sulphate content and I will talk about this aspect in just a minute and also it can be used to detect the occurrence or absence of certain reactions and that way calorimetry has become almost a very important tool for study of any cementing material.

IIT Madras Adiabatic Calorimeter:

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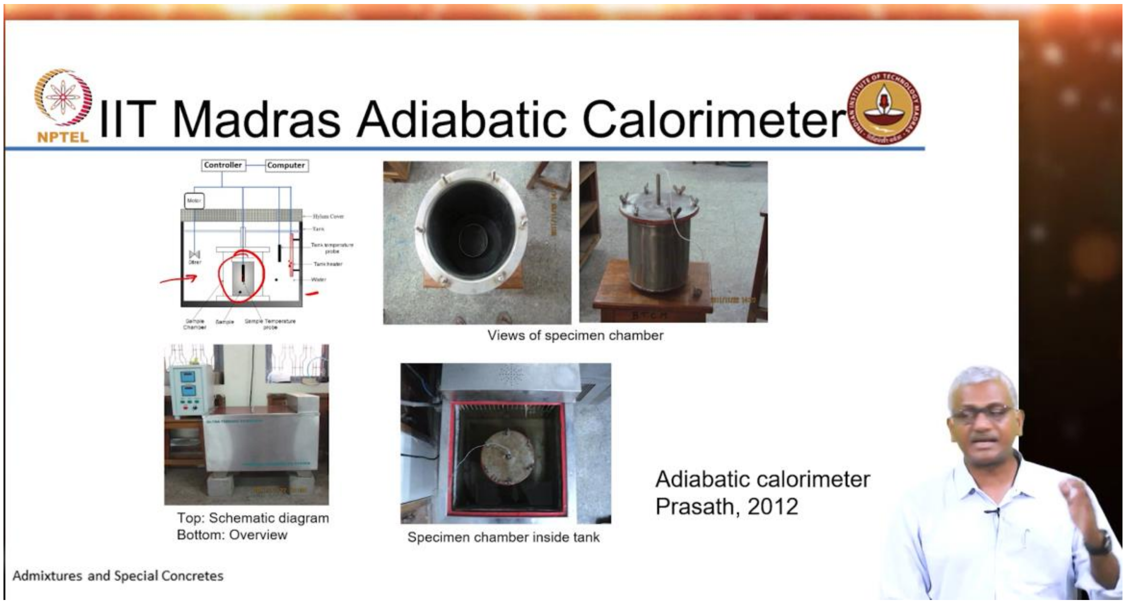

IIT Madras Adiabatic Calorimeter

Views of specimen chamber

Top: Schematic diagram
Bottom: Overview

Specimen chamber inside tank

Adiabatic calorimeter
Prasath, 2012

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So in IIT Madras, we have been using the adiabatic calorimetry tool, so here as I said you have the system, so you sample inside a chamber and this chamber itself is enclosed in a water bath, so this is a water bath and the water bath has a heater, so the temperature of the concrete is measured with the help of a temperature probe and fed into a controller which then kicks on the heater inside the system to heat the water bath at the same rate as the sample temperature. So that way there is no exchange between the sample and the surroundings and all you keep doing is measuring the increase in sample temperature.

Heat Evolution pattern:

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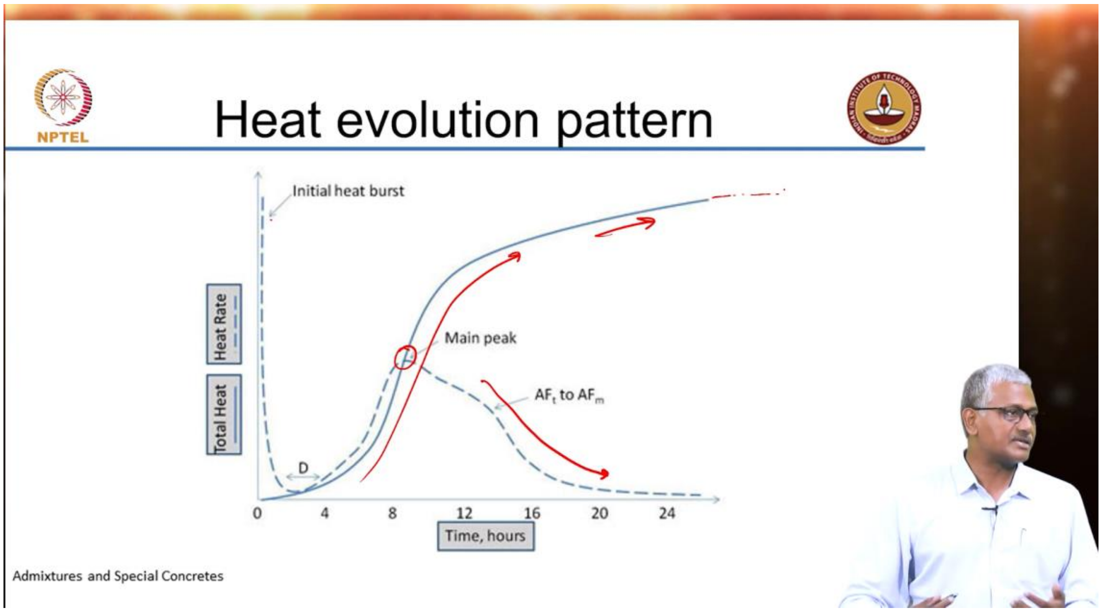

Heat evolution pattern

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And so just to remind you the heat evolution pattern of cement system looks like this, where you have the heat rate initially there is a heat burst, but then there is a dormant period and then you have the peak heat rate and then there is a slow down in your reactions. Reactions do not completely disappear, if there is curing happening reactions will continue to happen, there will be some level of heat that is continuing to get evolved, but at a much slower rate. In terms of the total heat it keeps on developing, but beyond a certain point it may start becoming close to zero change, but never zero completely, but close to zero change because the reactions will continue as long as there is water available, as long as there is space available for the hydration products to grow and so on and so forth.

Effect of w/c:

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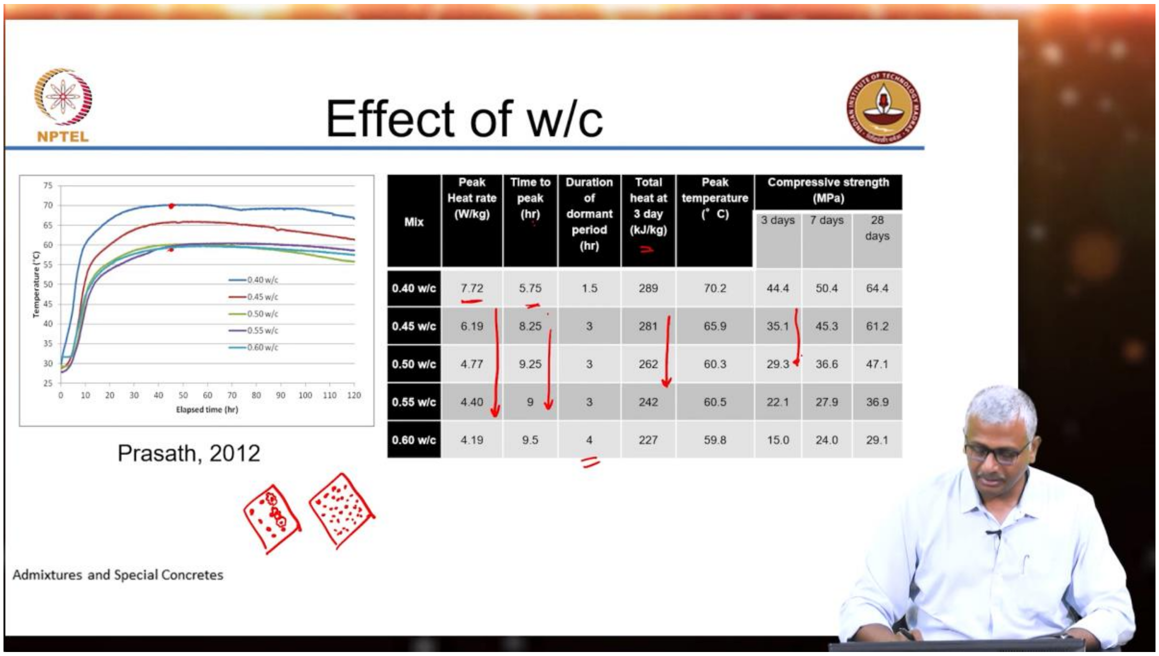

Effect of w/c

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
0.40 w/c	7.72	5.75	1.5	289	70.2	44.4	50.4	64.4
0.45 w/c	6.19	8.25	3	281	65.9	35.1	45.3	61.2
0.50 w/c	4.77	9.25	3	262	60.3	29.3	36.6	47.1
0.55 w/c	4.40	9	3	242	60.5	22.1	27.9	36.9
0.60 w/c	4.19	9.5	4	227	59.8	15.0	24.0	29.1

Prasath, 2012

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So, to look at calorimetry done with the adiabatic calorimeter, here is the result produced by one of our master students with respect to effective water-to-cement ratio. Now if you have more water in the system, the temperature of the system will not go as high as when you have less water in the system, why is that? These are concretes produced with different water-cement ratios 0.4 to 0.6. So you can see clearly the system with 0.4 water cement ratio seems to reach the highest temperature whereas the 0.6 water-cement ratio is 0.55, 0.6 these are very low temperatures, why? When there is less water-cement ratio is the reaction accelerated or slowed down? It is not that difficult to imagine, let us say this is your concrete, these are your cement particles or cement paste and these are cement particles present in the system. At high water-cement ratio you have less number of cement particles present, so if the hydration has to happen and close up the gaps, it will take quite a bit of time.

In the other case when you have a low water-cement ratio you have more cement particles present, so for hydration to form bridges between these particles will be much faster as compared to when you have high water-cement ratio. So you do not have to have too much hydration for the entire system to start getting rigid, so rate of reaction is much faster, there is more cement surface available for every gram of water that is available. Secondly, which phase water or cement has a higher specific heat capacity? What is specific heat capacity? The amount of heat required to raise temperature of a material by 1 degree Celsius, so does water have a higher capacity or cement has a higher capacity? If you have to produce hotter concrete, would you heat the cement in aggregate or would you heat the water? If you want to produce concrete to be placed at low temperatures you will cool the water, that is the most efficient way because water has the highest specific heat capacity of all the ingredients of your concrete. So, when you have a higher water-cement ratio there is more water available, so raising the temperature of the system requires much more heat to be given. So, generally when you lower the water-cement ratio, the temperature of the system goes higher than with higher water-cement ratio.

So using this adiabatic calorimetry, we are getting okay, we can convert this temperature time graph to a heat rate graph also, there is a lot of mathematics that is involved there, it is not too difficult if you understand the heat flow equation. Then based on that you can actually get the peak heat rate and the time at which this peak heat occurs. You can imagine that when you increase the water-to-cement ratio the peak heat rate will reduce because the reactivity or the speed of reaction also reduces. The time to peak also increases, you achieve that peak at a later period. Your dormant period also is increasing as you increase the total water available in the system.

Now your total heat at 3 days is the amount of heat that is accumulated by the system up to 3 days of hydration. Again, you can clearly see this is going down as you increase the water-to-cement ratio and you can readily imagine the strength also will go down as I increase the water-cement ratio. Typically, you can relate the strength very nicely with the total heat that is generated by the system, which is why calorimetry can be a very good tool during mix design also. Not just to assess the rate of reactivity, not just to assess the amount of temperature rise that can happen in your system, but to also correlate with strength. So many projects even use the study of temperature of concrete as a predictor of the strength that has been obtained.

Anyway, that is the subject of a different course or a different discussion.

Effect of pozzolans/ slag:

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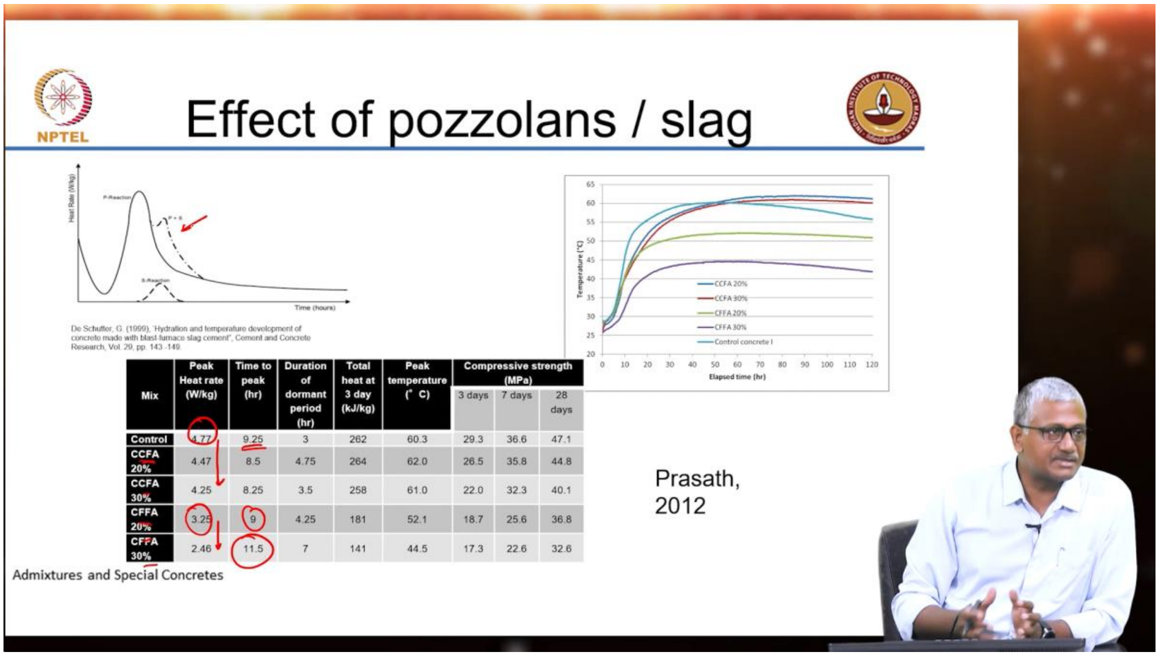

Effect of pozzolans / slag

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	262	60.3	29.3	36.6	47.1
CCFA 20%	4.47	8.5	4.75	264	62.0	26.5	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

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But the primary idea was to see what happens when you use pozzolanic materials or slag as a replacement of cement. You can imagine when type C fly ash or type F fly ash is being used your peak heat rate as compared to Portland cement is coming down. The time to heat rate, time to the peak is also changing, but not significantly. Why do you think time to peak does not change significantly even though the peak heat rate comes down with fly ash? If you remember, we discussed the fact that the presence of these silica particles and other finer particles of the mineral additive allow space for CSH nucleation and growth that will lead to some acceleration. But at the same time, the fact that the pozzolanic material is reacting very slowly will lead to some retardation.

So, if you have high contents of type F fly ash you are getting a very delayed reactivity, but when you have around 20 percent it is not really changing much as compared to your control system. So the overall heat rate is coming down significantly from 4.7 to 3.2. So what I was trying to say is with calorimetry you can then establish the rate of reactivity of your concretes with mineral additives and there have been some suggestions that when slag is used you can also get an additional peak in the heat rate curve which could be attributed to the reaction of the slag.

Now this is not something that is consistent with much of the literature that is there, but nevertheless, this has been reported that for slags you may see an additional peak that comes up.

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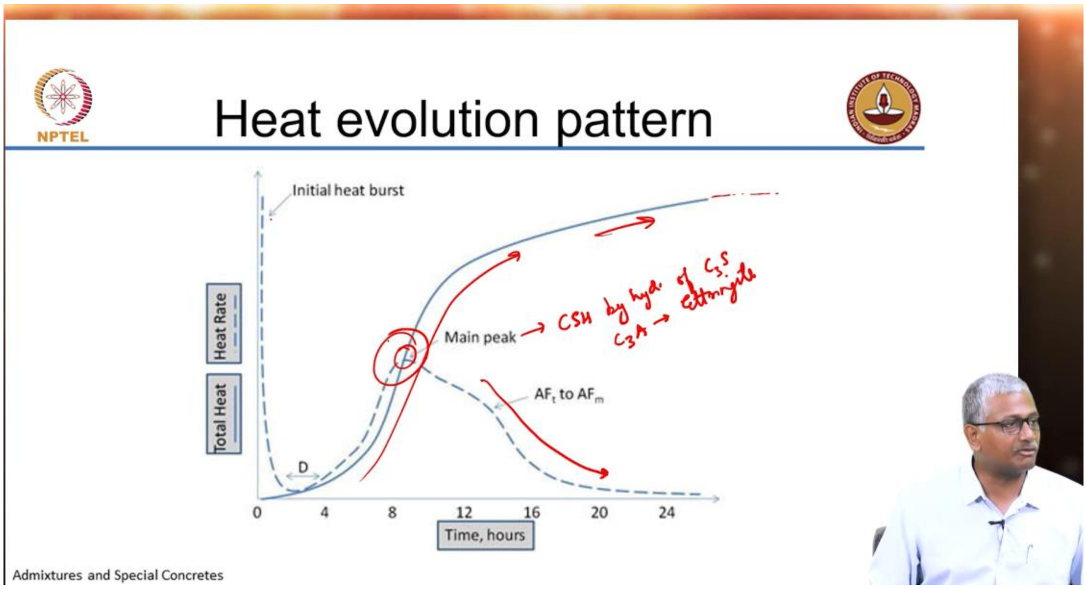

Heat evolution pattern

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Now very often we have to go back to the original heat curve to really understand what these peaks are coming from. If you look at the mean peak it is from the production of CSH by hydration of C_3S. At the same time you also have C3A producing ettringite. Now in a system that contributes a lot of alumina, a lot of reactive alumina, what will happen? The alumina reaction which leads to the production of ettringite will start dominating and you may actually start seeing that this peak is getting clouded by too much alumina in the system.

So the alumina reaction starts dominating and prevents the silicate reaction from completely happening if you have too much of reactive alumina. That is where you need to start worrying about sulphate optimization.

More results:

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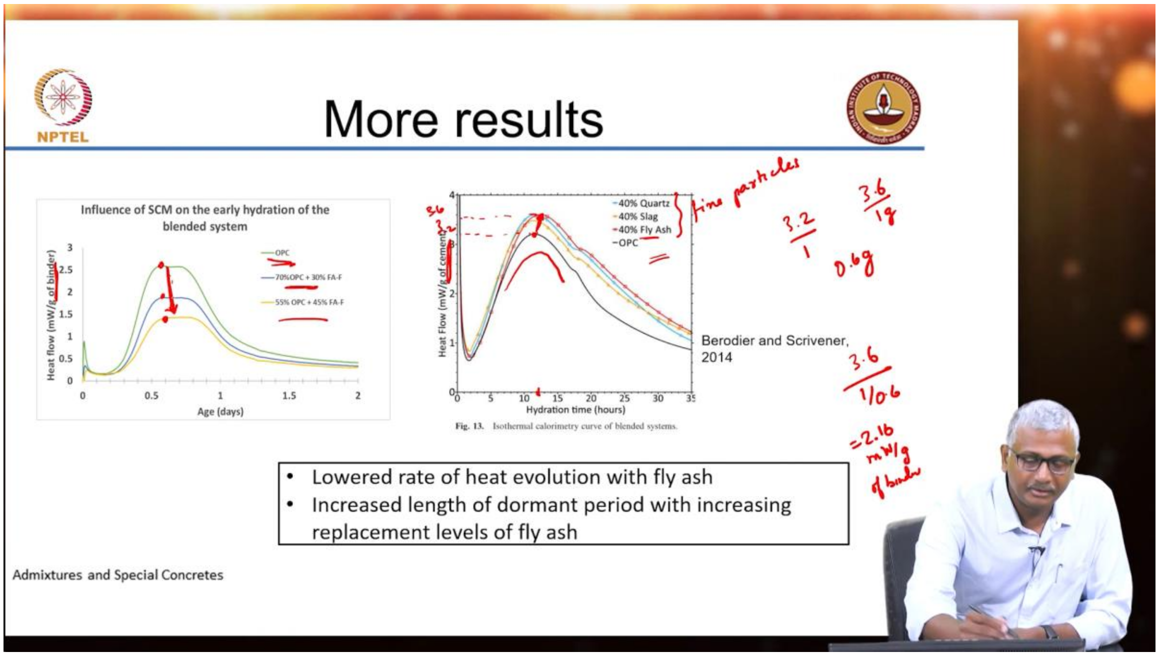

More results

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

Berodier and Scrivener, 2014

Fig. 13. Isothermal calorimetry curve of blended systems.

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I will talk about that in just one minute. So again just to give you more examples of heat flow curves from isothermal calorimetry, here you see OPC curve with 70% OPC and 30% type F fly ash and 55% OPC and 45% type F fly ash. Again you can see that the heat flow although the peak is achieved almost at the same time, but the total heat rate is actually coming down significantly.

Now in another study, quartz, slag and fly ash were used as cement replacement and when the result is plotted in terms of heat flow per gram of cement, what you actually see is that the peak heat rate for all of the three systems where cement has been replaced up to 40% by these materials, the peak heat rate is gone up. What does this indicate? This indicates some acceleration is happening of the hydration and this acceleration was achieved when all of these were in the fine state. When you take processed replacement materials like quartz, slag or fly ash which are finer than cement, then this acceleration is clearly noticed at an early age. You can actually see that the C_3S hydration may get accelerated leading to a shift in the peak heat rate, but this is also attributable to the fact that the result is presented in terms of gram of cement per gram of cement. So here let us say this number is how much 3.2, whereas this number for the red curve with fly ash is about 3.6. Now in the first mix, there was 1 gram of cement present, so it is 3.2 by 1 heat rate per gram of cement.

In second case, 3.6 is there, but that is calculated based on 0.6 grams of cement because 0.4 gram is fly ash. There is only 0.6 gram of cement present there. OKay. So you are representing the rate in terms of either gram of cement or gram of binder, your result can look quite different. If you present in terms of gram of binder, it also includes a fly ash in your system, that is why your peak heat rate is lower. And when you are presenting it in terms of gram of cement, your peak heat rate appears higher. In reality, if you present this in terms of gram of binder, what will you observe? If you present this result in terms of per gram of binder, you will probably see the peak somewhere here. So, you should also look at how the result is represented, but this also signifies that every cement grain that is present or every C_3S that is present, the hydration of that phase has been accelerated.

So you are getting from the available cement a slightly greater amount of heat because fly ash at that early age is not going to contribute any reactivity. So, we are talking only about 12 hours here, 12 to 13 hours. In this time period fly ash is not contributing any reactivity, only the cement is contributing reactivity. Earlier 1 gram of cement was able to give us only 3.2, but now 1 gram is giving us 3.6 in the presence of these pozzolanic materials. Did you get this concept right? So, when you replace cement by pozzolanic materials which are fine, the cement hydration itself gets accelerated. So, you produce more heat rate for each gram of cement. So, 0.6 gram of cement that means how much of binder are we considering? One gram of binder we are considering.

So if it is per 1 gram of cement that means how many grams of binder are we considering? We only have 0.6 grams of cement, but we are plotting this curve in terms of 1 gram of cement. So 1 gram of cement is how many grams of binder? Cement is 60% of the binder. So 1 by 0.6 will be the number of grams of binder available.

So, actual heat rate will be 3.6 divided by 1 by 0.6 that is how much? Only 2.16 milliwatts per gram of binder. That is why the actual heat curve will actually come down when you plot it in terms of milliwatts per gram of binder. Here you have plotted in terms of milliwatts per gram of cement.

When you do heat studies with calorimetry, you need to pay attention to the fact that the result is presented either in terms of gram of cement or gram of binder. It should not look as if your entire system is becoming stronger or more reactive when you are replacing cement by 40% of fly ash. It is not imaginable because you clearly see that when you add fly ash to 45%, your overall heat flow is actually reducing. You expect that. And when you present the same in terms of gram of cement, you are clearly going to see the effect of the presentation in the form of cement hydration getting accelerated.