

Advanced Concrete Technology
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Lecture - 06
Cement Chemistry – Part 1

So far, we have looked at different aspects of cement production. The kind of reactions that happen in cement kiln to form the different types of cementing compounds, how these compounds are present in different polymorphic state sometimes which leads to very interesting characteristics from them. What phases in these compounds actually end up determining the reactivity and so on and so forth?

We also looked at some classification of typical cements from the context of different standards. We saw how cements were classified into different types based on their purpose, sometimes, for example for rapid hardening of a sulphate resistance and you saw that primarily these standards were based on very similar guidelines that were followed across different countries. Again, just to reemphasize most of the world people either use the ASTM standards or the EN standards.

It seems like more countries in the world are shifting even from the ASTM to EN and a lot more EN based classifications will be dominating the cement standards in future. As far as the Indian standards are concerned. India is also a participant in the ISO, International Standards Organization, and the number of Indian standards are going to be now aligned now with the ISO standards as a result of which we will also probably start adopting many of the EN specifications.

Now we will now take a look at what these individual phases of cement do when they come into contact with water. Cement chemistry essentially defines a lot about the performance of the cement in the long term and much of what you learn in cement chemistry you will see that it is linked intricately to the performance of concrete whether it be hardened characteristics, fresh properties, durability, dimensional stability and so on and so forth.

So, needless to say this is possibly the most important chapter in this course. There are several research papers, textbooks which delve a lot deeper into this subject. It is also useful to get perspective from different resources because cement chemistry is been something that is been experimented upon for a long, long time now.

And much of the knowledge that has been developed in this subject sometimes can be quite controversial in terms of not many people agreeing on the same aspect and so on. Because of that it is better to get this insight from a set of different text books and journal papers to get a better understanding of this subject. Nevertheless, what put together here is what is commonly available in the general realm of civil engineering without getting too deep into the material science aspects.

I have tried to treat it at a level which can be understood fairly easily by civil engineers. But that does not mean there is no chemistry, there will be lot of chemistry. There is mentions about chemistry and the impact of the conditions that lead to the formation of different types of cementitious, hydrated cementitious products. So, this chapter will focus essentially on what are these products that form out of the reaction of cement with water, how is their structure, how are they distributed within the cement paste.

Reaction of cement with water is called hydration and you also know very well that this hydration is an exothermic reaction, it releases heat and for cements that are hydrating quicker there is more heat that is getting evolved. Now there are 2 ways of looking at it. One is you can look at the rate at which heat is getting evolved and you can also look at the overall heat that is evolved in the process of cement hydration.

Now, which do you think is more important is it the rate or the total heat that is getting evolved? It is the rate of reaction, because the rate is governing the speed of the reaction. Rate of heat evolution is actually an indicator of the speed at which the cement is hydrating with water.

Second is the rate will determine the thermal gradients that get created in the concrete because of the reaction of cement with water. Thermal gradient creation is important because that leads us to understand the nature of cracks that develop in the system as a result of thermal gradients. So

what we need to do is ensure that when we are building a concrete structure thermal gradients are kept to a minimum.

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And for that we need to understand what is the rate of heat evolution of the cement and how does it control the rise in temperature of the concrete in different segments of the structure. This is especially a problem when your structural size is large or mass concreting is done. A dam is definitely the best example for mass concrete, but you can also bring something closer to what you deal with on a day to day basis; a raft for instance is mass concrete.

These days it turns out that in high rise buildings we are increasingly using shear walls and these shear walls are also massive concrete segments which can have thickness of up to 2 meters and because of the fact that they are typically made with very high cementitious contents, amount of heat generated in these shear walls can also be quite large. So, again, we are dealing with mass concrete like situations even with conventional reinforced concrete elements.

So, because of that we need to pay a lot of attention to the rate of heat evolution and of course this heat evolution will depend a lot on what is the chemical composition of the cement because we know very well that certain components of the cement are faster to react as compared to the others and interestingly it also depends on the clinker morphology. It was already mentioned earlier about the fact that depending upon the processes that take place in this cement kiln, the kind of crystal sizes that may end up coming out in the form of a clinker may be quite different for the same grade of cement even. So, even if we have 2 cements which have exactly the same composition they may still have a different heat signature if the morphology of the crystal, the size of the crystals, the shape of the crystals if that comes out differently. There is a lot that governs this rate at which heat is evolved.

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Heat evolution

Heat of hydration of pure cement compounds

Compound	HOH (J/g)
C ₃ S	502
C ₂ S	260
C ₃ A	867
C ₄ AF	419

Handwritten notes: Red arrows point from the values 502, 260, 867, and 419 to the text "C₃S + C₃'". The value 419 is circled in red.

Bogue: ½ of total heat is evolved between 1 and 3 days, about ¾ in 7 days, and 83 – 91% in 6 months

For the most part we know very well that C₃S and C₃A evolve a lot of heat upon hydration, C₃A being the highest. This is the approximate quantity in terms of joules per gram of the heat evolved. This is the total heat that is evolved and not the rate. So, obviously rate should be measured in the unit of rate which is Joules per second or watt.

Rate of heat evolution is measured in watts per gram; gram implying that it is the gram of the cement. It is needed to ensure that we are normalizing this with respect to the amount of material that we are reacting. So, this is per gram of material reacted what is the extent of heat that is getting produced. So, C₃A is highest followed by C₃S and then you have C₄AF and C₂S.

We discussed about the fact earlier that C₄AF is a material that may not end up reacting for long period of time and in fact in long term itself you may not be able to find too much of C₄AF that is actually reacted in the system. So this extent of heat that is coming from the C₄AF may not be significant enough to contribute much to the temperature rise in concrete. So primarily concrete temperature rises at least in the early ages especially when we are talking about the first day, first 3 days, first 7 days.

It is essentially being contributed by the C₃A and the C₃S. So, initial heat rise in the concrete is getting contributed by C₃S and C₃A and Bogue, who had earlier proposed the chemical composition of cement or cementitious compounds based on the oxide compositions. He had also done several investigations on the heat evolution and based on the cements tested during his time

which is probably the middle part of the 20th century the estimation was that about half of the total heat is getting evolved between 1 and 3 days, about 3/4 of the heat in 7 days and close to 90% by about 6 months. This assumes that your concrete is continuously being cured; only when curing happens you can ensure that hydration of cement continues to happen.

If you stop curing there is no water available because internal water also will start drying out, so your cement will not theoretically hydrate anymore. So, if we assume that curing or condition of hydration has been maintained throughout it is fair enough to estimate that about 90% of heat evolution will happen in 6 months. This is essentially the cement that was used in Bogue's time.

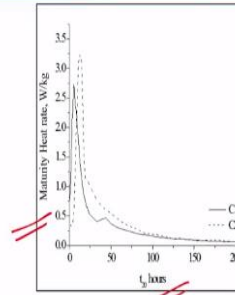
Now since then we have seen market changes in the way that cement reacts. But, that cement has to react very fast or we need very rapid rates of strength development to match the kind of timelines we have for our construction projects. Because of that, it turns out that most of our heat today, may be even about 3/4 of heat may get released as early as 3 to 7 days itself. Sometimes up to 3 days itself we may be releasing much, more than 3/4 of the heat which means there is lot more greater risk of cracks or thermal cracking happening, because of the very high rates of heat evolution in the early ages today. So, that is one thing we should always design for whenever we are looking at the construction project. Temperature rise in the concrete has to be compensated properly by a proper choice of engineering design to ensure that we do not get the thermal gradients that are very large. So how do we measure this heat? Heat is measured with the help of calorimeter and the calorimeter could be of different types.

(Refer Slide Time: 10:39)

Calorimeter



Adiabatic calorimeter at WITS, South Africa



Heat evolution pattern
Ramesh Babu, 2008

Temperature



Isothermal calorimeter at EPFL, Switzerland

Advanced Concrete Technology

Heat

Manu San

You can have an isothermal calorimeter like what is shown in the bottom left of this picture that is an isothermal calorimeter or you can work with, what is called an adiabatic calorimeter. Now, Isothermal implies you are keeping the material at the same temperature.

So, what is happening is that if you keep cement which is reacting with water at the same temperature, there is going to be heat released from the cement. So you have to remove it from the system to ensure that you have the temperature maintained. So in other words, what you are simply doing is measuring the extent of heat that is coming out directly. So, in an isothermal calorimeter you measure the heat that comes out in the system by keeping the sample at a constant temperature. Typically, constant temperature used is 20°C, in most isothermal calorimeters.

Another kind of calorimeter is adiabatic calorimeter. Adiabatic condition is that when there is no heat exchange between the material and its surroundings. In other words, we should not allow heat to flow out nor allow heat to come into the system. But as cement is hydrating the temperature of the concrete will also increase. So we need to ensure that the temperature of the surroundings also increases at the same rate so that there is no heat exchange between the surrounding and the concrete.

So temperature of the concrete is increasing and you maintain the surrounding temperature at the same level to ensure that there is no heat exchange. So what are you measuring here is temperature. Now, to convert temperature to heat you need to have some idea about the specific heat capacity of the materials and based on that you can actually convert the rate of temperature rise to the rate of heat evolution. Results of the calorimeter are typically plotted in terms of the heat rate on the Y axis versus the time on the X axis. The curve shown in the above slide is only a representative curve developed based on the results of the adiabatic calorimetry. A much more well accepted curve that you see in most textbooks will be shown later. So, calorimetry is definitely a very important tool- not just for determining the exact amount of heat evolution but also for looking at the assessment of rate of reactivity at early ages.

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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

It gives you a good comparison between different sorts of cementitious systems without really getting into a comprehensive study of the concrete mix design and understanding the strength development by doing tests after 28 days and so on. You can actually get a quick estimate of the system very early through the measurement of calorimetric heat evolution.

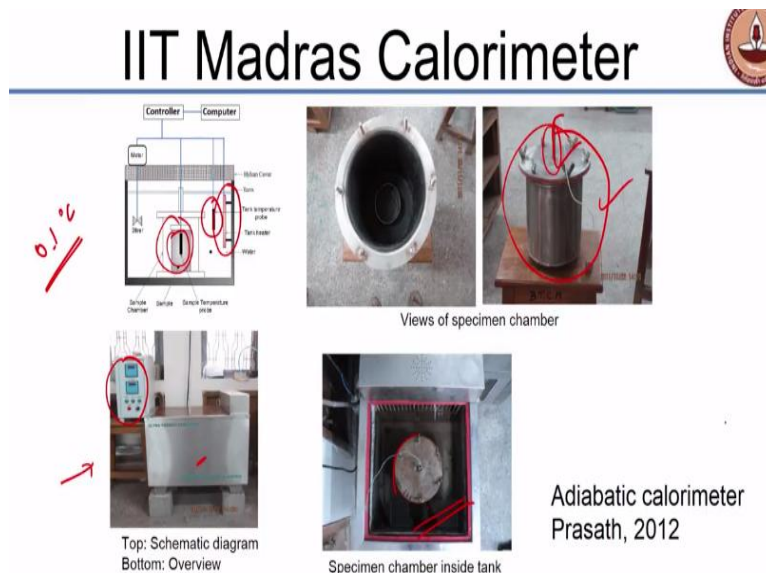
We know that gypsum is added during final stage of the cement manufacture to act as the set regulator. It ensures that you have a controlled setting of your cement. If you add too much gypsum, it may increase setting time too much. If you add too little gypsum you may not be able to sufficiently react the C_3A well enough. So, you want to have just the optimum amount of

gypsum. And this becomes even more critical when we replace cement with other binding materials like fly ash or slag. In those cases, the reactivity can get affected if you do not have the right amount of sulphate in the system, because of that a very quick way to estimate the extent of sulphate that you actually want in the system for getting the desired reactivity

The amount of sulphate that is required can be determined directly by calorimetry rather than going for casting cubes in determining the strength and so on, which is a lot more involved and cumbersome. So calorimetry can be a very useful tool there and calorimetry can also help you detect whether certain reactions are happening or not because their signatures can be directly picked out from the calorimetry pattern to see whether the reactions are happening or they are getting overcome by some other conditions that are being created because of some choice of temperature as well as the choice of composition. It will be discussed in more detail about how calorimetric measurements are done and then we will look at some patterns of calorimetry to try and understand what these patterns actually mean in terms of heat evolution.

The IIT Madras calorimeter what we have developed in our lab, is shown below, based on the systems that was developed first at University of Witwatersrand.

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So, here the bottom left shows you the overall system. This has a large water tank and a controller, shown in the left. What we need to ensure here is that while we are measuring the

concrete temperature, the water tank surrounding the concrete also has to start getting heated up at the same temperature. So, there is sensing of the temperature in the concrete, there should be sensing of temperature in the water tank.

And there should be some circuit to start the heating of the water tank every time there is a difference in the temperature of the concrete in the water tank. So that is what is essentially being done in the system. So, here you have the top view of the water tank which is shown and the specimen chamber or the sample chamber that is sitting inside, completely immersed inside the water tank.

What is the difference between a sample and a specimen? Specimen is something which has definite dimensions. For example you have a cube or a cylinder it is a specimen.

But if we have a concrete, fresh concrete and you take a scoop of it, it is a sample. When you take cement for your analysis it is a sample of cement, not a specimen of cement. But when you prepare a small cube of cement mortar it is a specimen. So here we have a plastic cylindrical box which has a lid. All you do is as soon as you mix your concrete you put it inside the cylindrical container, you close the lid, the lid has a hole on top through which you can actually insert a thermocouple or a temperature probe. In this case we used a RTD temperature probe which was inserted directly into the concrete and the temperature probe within the concrete sample chamber comes out of this top opening which is provided with the lid of the sample chamber.

And it is connected to the circuit which is measuring the different temperatures. So, we have a temperature measurement inside the water bath also, and temperature probe inside the sample chamber and both these are actually measured.

There is a controller which is then telling the heater which is present inside the tank, at what rate should the heater get kicked or start heating up so that the temperature differences are maintained within 0.1 degree Celsius. So, we don't want at any time the concrete temperature to be more than 0.1 degree Celsius of the water temperature. So, every time there is a difference of 0.1 degree, the relay tells the circuit that I need to start the heater.

So, the problem here is that most heaters take time to start and because of that you need to have a good system built in to ensure that the heater can have a very rather rapid temperature rise time, to ensure that it is matching or mimicking the concrete sample that is sitting inside the container.

In the isothermal calorimeter where we are testing the heat that is getting released from the system, the samples are typically cement powder which are stored in very small vials which will be very few grams of cement. To start the reaction is you drop the water into the vial. That means, you can start capturing the heat right from the moment that water comes into contact with the cement and that can be a substantial amount of heat that gets released there.

So, in an isothermal calorimeter you have very small sample of cement, very few grams in a vial and you put some drops of water to get the reaction started and you can start measuring the heat right from that point. The problem with adiabatic system is you need to mix your concrete outside and then put it inside the sample chamber and then assemble the entire outer assembly of the sample chamber, immerse it into the water tank and then start your measurements.

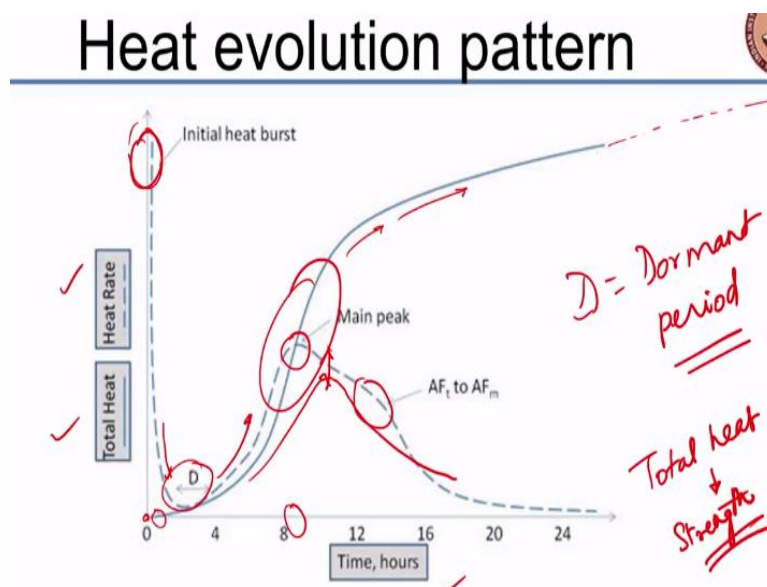
So you may lose the initial 20 to 30 minutes of data. So, the initial heat burst cannot be captured by the adiabatic calorimeter. I will show you that later when I show you the actual heat evolution pattern, but of course what you can get is the main heat release peak that happens because of the main hydration reactions of the cement. Another advantage of the adiabatic calorimeter is that you can actually alter the concrete mixture to the exact one that you are using for a particular project.

For example, if you are building a mass concrete structure and you have some concerns about the extent of heat that may be evolved or extent of temperature rise that may be there in the system you can actually test that very system in this adiabatic calorimeter set up directly whereas in the case of an isothermal calorimeter you are only testing the cement or the binder if it is mixed with fly ash or slag or any supplementary cementitious material.

Here you are actually able to test the exact concrete mixture that you are using for the project. So there are pros and cons for both approaches. Isothermal calorimeter you have very small samples. You are only testing the cement or the binder. You are not reflecting how it is actually going to perform in the presence of the aggregate that you are using for the concrete, how the actual mixtures and the concrete may affect the heat release and so on and so forth.

But accuracy is much better because you are capturing the heat very early. Secondly, you will be measuring the heat directly. So there are no assumptions. In the case of adiabatic calorimeter, you will need to assume the specific heat capacities of the different ingredients of concrete which may start differing every time we change the aggregate for instance and converting the temperature to heat rise or rate of heat evolution may be a tricky task.

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So this is what actually comes out of a typical isothermal calorimeter. You have the heat rate plotted on the Y axis versus the time on the x axis. Also plotted in the same curve are the total heat versus the time. Total heat is nothing, but the integration of the heat rate time curve. So let us look at first the heat rate curve, because that is going to be the more important part of the heat evolution pattern.

In the beginning, that means as soon as cement comes into contact with water, there is an initial heat burst. A small amount of heat is released very quickly which causes the heat rate to be very

large. This is happening within a few instance and because of that the rate of heat evolution is high and it may or may not be captured, depending upon how good your calorimeter is.

In any case most isothermal calorimeter will be able to capture this initial heat evolution also. Now we will look at the reasons why this happens in just a minute. This is followed by a decline in the rate of heat evolution and there is a period which is marked as D. Please pay attention to the dotted line or dash line which represents the heat rate not the solid line which is actually representing the total heat.

So if you look at the dash line there is a period where the rate of heat evolution is very less and marked as D which is basically the dormant period. Does that mean that my reaction is stopping entirely? No! because the rate of heat evolution is still positive which means my cement is still hydrating, but it is probably doing so at a rate which is too low to release any substantial amount of heat.

So that is called the dormant period and that is very critical from our concreting applications point of view because we want some time to be able to work with the concrete in order to place it, compact it, finish it and so on. All that is taken care of by this dormant period and essentially this is happening because you have picked the right quantity of the ingredients, you have picked the right amount of gypsum in your system to ensure that the reactions do not get started within the dormant period. So the dormant period indicates the time that is available with you to use the concrete on site. So in other words it is going to have a direct reflection on the initial setting time.

Beyond this dormant period, you see a rapid rise in the rate of heat evolution until you reach what is called the main peak and then you may or may not have secondary peaks that come right after the main peak I will describe these in just a minute. That is the heat rate pattern. So you start with the very high heat rate you come to a dormant period then you go up to the main heat peak and then you start slowing down the rate of heat evolution and you may see a secondary peak depending on the extent of the aluminates that represent your system.

Focusing on the time taken, main peak is approximately being reached between 8 and 10 hours which is shown for plain Portland cement. When you substitute cement with fly ash the main peak you may get delayed because fly ash reacts much slower than cement and also your peak heat rate also may get reduced because you have lesser amount of clinker now. So you can now look at reactivities of different systems by simply a comparison of the peak heat rates at the time that the peak heat rates is actually take to appear.

Now if you integrate this curve you get the total heat curve which has to obviously start at 0. This is because there is no reaction there and it does not develop much total heat even though your initial heat burst leads to a rapid rate of heat evolution, that is because it is happening over a very short instant. So the overall heat generated in that system is very small in that point of time. The real rate of heat development is the point which corresponds to the appearance of the main peak. That is where the slope of the total heat curve starts increasing tremendously and then after reaching a certain value it starts slowing down. The total heat evolution starts slowing down, which does not mean that in 24 hours it is going to stop completely. The heat in the system will continue to accumulate even beyond that and interestingly if you do proper experimental design, what you will end up seeing is that the total amount of heat evolved is a fair indicator of the strength attainment of the system; how much strength the system actually attains. So, total heat can be a good indicator of the strength attainment of the system. Hence calorimetry can also help you assess the rate of strength development of cementitious systems because you can actually study that from the total heat evolved. **(Refer Slide Time: 27:46)**

Heat peaks



- Peak I: 'Heat of wetting' + some early C-S-H formation *ettringite*
- Dormant period: Very slow rate of heat evolution
- Peak II: Main peak; associated with the rapid dissolution of C_3S to form CSH and CH, and formation of ettringite (AF_1) from C_3A
- A slowdown of the hydration process beyond the main peak leads to lower rates of heat evolution. A broader peak (III) is associated with the conversion of ettringite to monosulphate (AF_m)

So let us look now at the reason that these heat peaks actually come into being.

First peak or peak 1 which is the initial heat burst can be because of multiple things. One of the things is heat of wetting. The idea is that each particle of the powder is a solid and it has got some surface active atom. So when you cover this particle with water you form a new bond between the surface and water.

The surface atoms have a very high energy. So this new bond that is forming is taking some of that energy, and the balance energy which is going to be released as heat is called the heat of wetting. This is because the surface active atom which are forming a new bond with water are releasing the extra energy that is left as heat and this will happen with any powder whether it is reactive or not.

So this initial heat burst could be a mixture of the heat of wetting as well as some early formation of CSH that could happen if some of your particles that are extremely small; they get started with the reaction with water very early. Not just CSH, you can also have ettringite formation because of the aluminate. Aluminate and sulphate together can form ettringite. But some initial formation of CSH and ettringite can happen that leads to the initial heat burst. Then at dormant period there is very slow rate of heat evolution. This is followed by the main peak which is associated with rapid dissolution of C_3S to form CSH and formation of ettringite from C_3A . So that is the

primary peak that they concern with that dictates the rate at which your strength evolution is taking place.

And then later you may see a peak which relates to a conversion of your ettringite or rich sulphate phase to monosulphate or low sulphate phase. So this is basically the description of what you are actually observing in the rate of heat evolution pattern. But we need to understand one thing that unless you are perfectly insulating your system you will not be able to get a clear relationship between the heat evolution and temperature. So if you are measuring your temperature or doing adiabatic calorimetry studies, then you need to ensure that your system is properly insulated. Then the other aspect is your heat pattern may also depend on the amount of water that you have in a system. So if you are measuring your heat signature for a particular binder or cement you need to be careful about stating what is the water cement ratio used to do the measurement. Because the more water you have; water has a very high specific heat capacity as supposed to solids; increase in temperature of water takes most of that heat generated because of hydration of the cement. If I have excess water available lot of the heat will be spent in raising the temperature of the water. So because of that more water cement ratio systems may end up generating more heat as suppose to higher water cement ratio systems.

This from the point of view of measurement of the heat, but in terms of real performance of concretes that is a very strong thing that you need to observe that when you have low water cement ratio systems there is greater heat potential as suppose to higher water cement ratio systems. When you are moving from low strength concrete to high strength concrete you are automatically going to cause an increase in the rate of heat evolution.

So this is one of the factors contributing to it that you do not have excess water available that would take up that heat to raise the temperature of the water itself. In the other aspect that you need to look at is that as soon as cement comes in contact with water there are alkali sulphates that are present on the clinker particles and these alkali sulphates dissolve rapidly into the water releasing the alkali ions because of which my pH of the water that is surrounding the cement rapidly rises to very high basic values 12 to 13.

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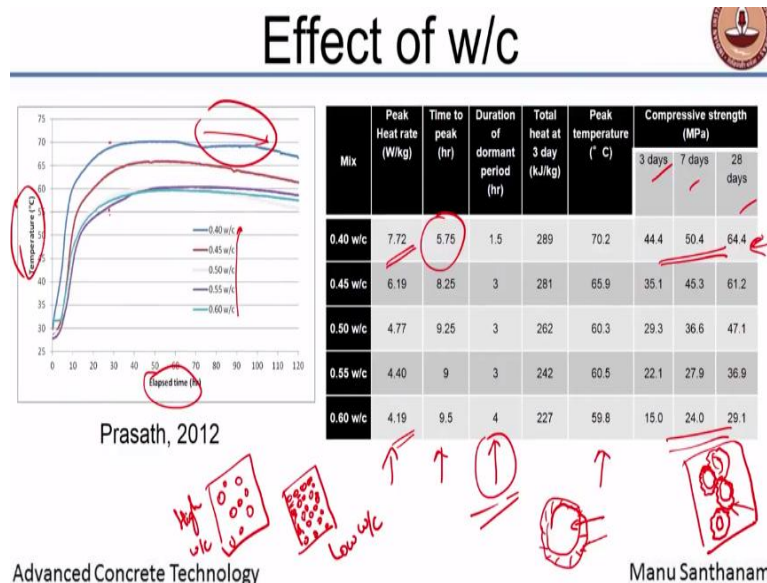
Points to ponder..

- Difficult to obtain the correct relationship between heat evolution and temperature unless the system is perfectly insulated
- Dependence on the water to cement ratio: Water has a much higher specific heat than cement, thus when more water is present, a higher degree of heat will be required to increase the temperature of the system.
- Cement contains highly soluble alkali oxides (Na_2O and K_2O). The dissolution of these compounds is responsible for the high alkalinity (pH 12 – 13) of the pore solution. Thus, the hydration of cement actually takes place in the pore solution, and not in water.

So my hydration of cement is not taking place in water, but in an alkaline pore solution. So you have to keep this in mind while understanding what reactions takes place in the system and how the heat liberated can be measured and related to the individual reactivity of the compounds.

So let us look at some effects whether we can actually capture them with the help of calorimetry or not. What is shown below are some results of adiabatic calorimetry.

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So the temperature of the concrete inside the sample chamber is plotted against the elapsed time and what you see here is as you have a lowering of the water cement ratio from 0.6 to 0.4. You are changing the total temperature that is inside the system or the peak temperature that is inside

the system. So top is 0.4 water cement ratio, the bottom is 0.55 and 0.6; not too much difference between 0.55 and 0.6.

But in 0.4 water cement ratio, you are causing your heat to be significantly larger as supposed to the higher water cement ratios. So you are getting almost up to about 70°C. Now you may notice that there is a small decline in the temperature; that was because of an improper design of a calorimeter in the beginning. I showed you earlier the picture of the calorimeter. You see that there is a lid on the top in the previous slide on calorimetry.

After you put the sample chamber in the water bath you need to cover the entire thing with the lid so that the water baths do not start losing temperature to the surrounding environment. But what happened is that, with excess heat the kind of cover material that we have chosen started warping and because of that the heat started coming out of the system because of which you are observing that there is a small decrease in the temperature after the peak temperature has been reached.

So the peak temperature and the time to attain the peak temperature has been listed in this table in the slide and the peak temperatures are also converted to the heat rate in watts per kilogram of the binder that is available in the system or watts per kilogram of the cement. You can clearly see now that when you have a very low water cement ratio you are generating very large amount of heat at very early stages.

At high water cement ratio rate of heat evolution is substantially lower and you start attaining this high rate of heat evolution also significantly early when you are reducing the water cement ratio. So, needless to say, when you are working with high strength concretes you need to pay particular attention to the choice of your concreting process to ensure that you are keeping in mind that your temperature rise can be significant in these systems and you need to control the rate of temperature rise if it is critical in your concrete.

For example, if you are designing very thin concrete structures it is not a major issue, but if I design mass concrete where temperature differentials can be significant this heat rise can create

lot of problems. Another thing which we were able to pick out although not very accurately was the duration of the dormant period. You can see you have low water cement ratio in the system the duration of the dormant period is lower.

When you have more water the duration of dormant period is higher. That seems to tell us something. Why is this dormant period actually coming into place first of all? Why is this dormant period there? What is creating this dormant period? It is not gypsum because it is entering into reaction, but we are saying that the reaction rate has reduced considerably leading us to a time where the rate of heat evolution is low enough or hydration is low enough for us to be able to work with the concrete. So something is causing this dormant period to happen.

So let us consider a cement paste system which are cement particles in water. So let me say those circles drawn in the bottom of the slide are cement particles and the white space surrounding the cement particles is water. This is high water cement ratio system. Now I have another view of a system that is a low water cement ratio system, drawn right next to the earlier picture. So I have more cement particles in the low water cement ratio system obviously because my water is low so overall volume of the cement will be higher.

So what is happening in the system that leads to initial set to take place? What is the initial set? That means I am not able to move my concrete anymore. It is starting to assume some sort of a stiffened form, or it loses its plasticity, loses its ability to work or ability to get molded. So when do you think that will happen in the system looking at these 2 images? For example, look at the low water cement ratio image. Essentially the water between the cement particles starts getting consumed to a level that is enough to produce sufficient amount of hydrate around the cement particles and these hydrate particles which are around the cement particles start getting connected. That is when we are getting setting. So these hydrates that are around the cement particles need to start getting connected and form a network and that is basically a setting. I still have water in the system, but I do not have a continuous network of water available. Until I have a continuous network of water available my cement will not set. Water is available to freely move around, but here my hydrates have created a condition which is basically merging with the surroundings of neighbouring cement particle and so on. So that basically is the attainment of setting.

Coming backwards here into the dormant period, dormant period is a stage where setting has not happened. When water is added to cement particles, it is starting to react. So it creates some sort of a hydrated layer on the surface. So what is being created on the surface here a layer of hydrate has been created because of which it can reduce the penetration of water. The water has to actually now get through this barrier to react with the cement. So that barrier of cement that forms initially on the cement particle now is preventing the water from reacting with the rest of it; that is the reason for the dormant period.

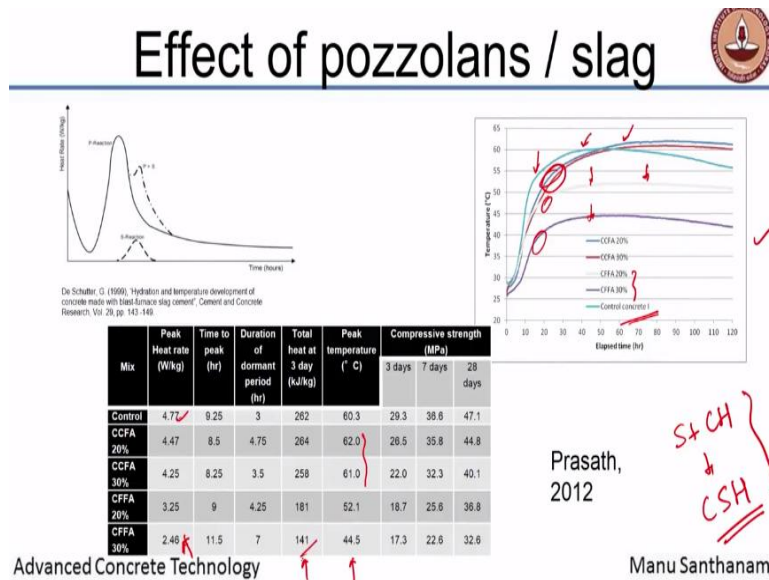
You are forming a hydrate barrier on the cement particles. So water is still freely available to provide you workability but since this barrier is only very thin, it gets weakened with time and because it gets weakened it breaks. When it breaks there will be further entry of water inside. Secondly there will be diffusion of water through the barrier layer. Slowly but surely this water will diffuse and react with the rest of the cement particle also. So that means you have to break that barrier to initiate the process of further hydration and that basically relates to the length of the dormant period. So now you can see the reason why when we have lower water cement ratio, the length of the dormant period is smaller because now, I do not have that much water present in my system. I have more cement particle present. Attaining that rapid reactivity can be much faster in that case. The other aspect that contributes to the fact to that is since you are releasing more heat there is greater temperature rise in the system more temperature implies greater rates of diffusion of water. So you will have a much faster end to the dormant period.

To talk about whether gypsum has a role in that diffusion; No, gypsum does not have a role in diffusion. Gypsum has a role in the rate at which this initial hydrate layer will form and gypsum has definitely a major role in the main heat peak that is attained as well as any subsequent reactions that take place with the aluminates.

In the table shown in slide, you can see the data for compressive strength development time also you have strength at 3 days, 7 days, and 28 days. And as you can rightly estimate that when you have a higher water cement ratio obviously your strength of the concrete will be lower and that is exactly what you are seeing here. The rate at which the strength is attained also is significantly different for the low water cement ratio concrete and the high water cement ratio concrete.

In the case of a low water cement ratio concrete you are obtaining a large fraction of your strength at 3 days itself whereas in the high water cement ratio concrete your strength attainment at 3 days is about half of your overall strength. So there is a difference when we choose cements of or concretes of different water cement ratio.

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What happens when I change my cementitious binder and substitute cement with the pozzolanic material or slag? What I will end up doing is altering the chemistry of the system; first of all I am reducing the amount of the readily hydratable clinker phases like C_3S and C_3A and I am putting in some reactive silica in the system. The issue the reactor silica is it needs to wait for lime to be available from the cement. So cement hydration will produce lime or calcium hydroxide. The reactive silica wants that calcium hydroxide to produce CSH. That is the pozzolanic reaction, but it is not going to happen at a very early age because you do not have enough lime available in the system

So mostly what pozzolans will end up doing, for example, if you consider this heat evolution pattern provided on the slide you will see that as you are substituting control concrete, which is plain ordinary Portland cement which is here with fly ashes, the rate at which you obtain the peak temperature is lowered substantially for concretes which have cement replaced by fly ash and the total heat or the peak temperature in this case is lowered significantly when your cement replaced by type F fly ash that is low calcium fly ash. There are two types family of fly ashes,

one is the high calcium fly ash and others are low calcium fly ash. High calcium implies that there is lot more calcium oxide in that system as supposed to a low calcium fly ash. In a high calcium fly ash, the calcium oxide content also will speed up the extent of reaction that happens. So because of that in a high calcium fly ash the peak temperature that is reached in the system is nearly the same as the control concrete. The time at which the peak is attained is a little bit longer in the case of the high calcium fly ash. For the low calcium fly ash you are attaining much lower peak temperature in the system.

So that automatically gives you information that substitution of cement with type F fly ash is a great choice for a concrete which has to liberate less amount of heat. Converting the temperature and the heat rate you can clearly see here that the peak heat rate is nearly half even when I substitute 30% of the cement with fly ash. Here 4.77 watts per kilogram is the peak heat rate with control concrete. When I replaced 30% of the cement with type F fly ash I am reducing the peak heat rate to 2.46. That is a substantial reduction in my peak heat rate. Also we can clearly see from this picture itself that the temperature also is reduced significantly. So again your peak temperature from 60°C has come down about 44°C. You see that the peak temperature with the type C fly ash is very much nearly the same as the ordinary Portland cement concrete.

But with type F fly ash major reductions in temperature are possible. Again an indication of the slower rate of strength development is directly there from your heat that is totally evolved at 3 days in terms of joules per kilogram or kilojoules per kilogram. You can see that the heat that is totally released with type F fly ash at 30% is just a little bit greater than the half of the control concrete. So the advantages of using 20 to 30% replacement of cement by fly ash can be directly seen by this adiabatic calorimetry result.