Lecture 11
Calorimetry: Application of Calorimetry

(Refer Slide Time: 00:16)

Hi everyone, today we'll continue our lecture on calorimetry. So, yesterday we ended the lecture on the estimation of activation energy. So, we'll quickly go over it, so that you are clear how to calculate activation energy. First you have to understand the importance of calculating activation energy, because we know that cement hydration is influenced by temperature. And if you have a data for a particular temperature, you want to predict the hydration characteristics at different temperatures (either lower or higher temperature), then you have to use Rate Law.

You have to know the dependence of reaction rate on temperature. So that is the basis for doing this. And we all know that the reaction rate can be expressed using Arrhenius relationship, where you see 'k' is dependent on activation energy and the temperature. So it is important to calculate the activation energy. Once you know the activation energy, then you will be able to calculate the reaction rate at different temperatures.

How do you do that? So from calorimetry, we know that we will get the heat rate and the total heat. So basically the output of calorimetry would be a curve where you have the Y-axis as heat and X-axis as time. So, this is the typical curve (Refer drawing at 2:15 in slide - Figure 1) you

get from calorimetric measurement (in this case, we can say isothermal calorimetry). Now, we want to calculate activation energy, how do we do it?

Figure 1 Output curve from calorimetry measurement

So, from this curve we can calculate degree of hydration, because degree of hydration influences your heat released during the hydration. Suppose you want to calculate heat of hydration at particular age, so you know the time, you know the corresponding heat. Suppose H(t), and if you know the ultimate heat or total heat (H_u) from the reaction you can calculate $\alpha(t)$. So, it is your degree of hydration.

So that information now you have at each time step, because you have this continuous measurement, you know the heat at particular time and you can calculate degree of hydration. Only thing you have to know is, calculate the total heat available for reaction. Now, if you know the composition of your cement, that is, if you know how much C_3S, C_2S, C_3A, C_4AF you have, you can calculate the total heat, because you know how much heat will be released if pure phase is completely reacted, and so based on that, you can calculate the total heat.

Suppose we do not have any information on cement composition, then an approximate way would be just to extend this curve that we have (Figure 1), so that we know the ultimate heat, but that could be approximate. So it is obvious that we are seeing this typical S curve.

If you plot α versus time (t), we'll also get a similar curve because we are deriving this curve from heat curve. Now we want to know, which form this curve can take, so we from equation (4), we know that

$$\alpha(t_e) = \alpha_u . \exp\left(-\left[\frac{\tau}{t_e}\right]^{\beta}\right)$$

Where you have τ as a hydration time parameter, and β is hydration shape parameter, that defines this curve.

And it is obvious to see if $t \to \infty$, then $\frac{1}{\infty} = 0$, then $e^0 = 1$, hence we attain $\alpha = \alpha_u$

If cement hydration is complete, that means degree of hydration will be equal to ultimate degree of hydration. So this is the typical curve. So basically what you have to do, you have to know the hydration time parameter, τ and β. That you can get by fitting your curve.

So you have this, $\alpha(t_e)$ curve, now you have to get these parameters from it because you have this data, α and t, now you have to fit it so that you get this τ and β.

(Refer Slide Time: 05:49)

We saw how to calculate activation energy. Quickly let's go over it again. So we saw that, the rate dependence. We can write the Arrhenius relationship in this form $\left(k_1 = A. \exp \frac{-E_a}{R.T_1} \right)$, that is the reaction rate (k_1) at temperature T_1. Similarly you can write it at different temperature $\left(k_2 = A. \exp \frac{-E_a}{R.T_2} \right)$. Now from this, we can get this relationship (Equation (8) in slide), by manipulating these two equations and here we can write it as

$$-\frac{E_a}{R} = \frac{\ln \frac{\tau_1}{\tau_2}}{\frac{1}{T_1} - \frac{1}{T_2}}$$

τ is hydration time parameter. So, τ we have to get from your curve. So, that is the importance, all you have to do is get this τ. So you have data for, at different temperatures, to get different τ

values. Eventually when you manipulate these two equations, $\left(k_1 = A.\exp\frac{-E_a}{R.T_1}\right)$ and $\left(k_2 = A.\exp\frac{-E_a}{R.T_2}\right)$, you will get similar relationship, but it in the following form:

$$-\frac{E_a}{R} = \frac{\ln\frac{k_1}{k_2}}{\frac{1}{T_1} - \frac{1}{T_2}}$$

Now we are saying the ratio of the reaction rate is equivalent to ratio of hydration time parameters. That is the key. So, by calculating this τ for each temperature you can calculate the activation energy. Once you know the activation energy, then it is easy to calculate the reaction rate. Now, you know the dependence of rate on the temperature.

It is important because, lot of times you do measurement at one particular temperature, and now you have to predict the behaviour at different temperature. How do you do it? That's the thing. **(Refer Slide Time: 08:36)**
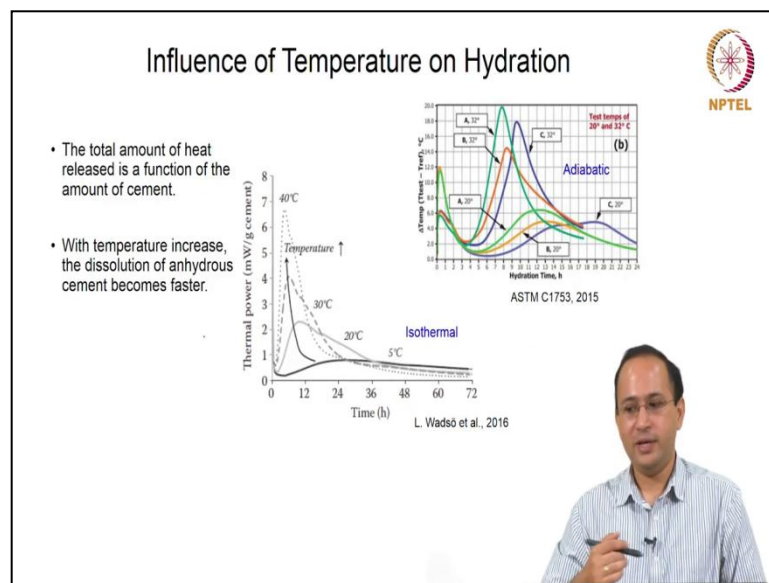
So, we are looking at various applications of calorimetry. So far what have we seen? We can determine heat of hydration, estimate activation energy. In continuation, we can also determine the influence of temperature. We can see how temperature influences your reaction rate. (Refer to Isothermal figure in slide (L. Wadsö et al. 2016))

So, I am showing isothermal and adiabatic. Let us focus on isothermal. So these are the measurements obtained from isothermal calorimetry. So you see that we are plotting Thermal power – that's the output from the calorimeter, versus time. And you see the influence of

temperature. 5 °C, 20 °C, 30 °C, 40 °C, clearly you see the influence of temperature. As the temperature increases, your reaction rate also increases.

So this simple tool can give you insight on how temperature can influence your hydration. And the difference is obvious, if you further increase, it might even increase more. So, it's important to know how much influence of temperature is there on your reaction rate. So, this is the data from isothermal calorimeter. Now similar trend we can also see from adiabatic calorimeter (Refer to Figure on the right in slide – Adiabatic (ASTM C1753, 2015). In adiabatic calorimeter as you know, we calculate or we measure temperature.

So you see on the y-axis we have temperature. Basically it's the temperature difference between test and reference, temperature measurement is there. But the point is, you can see similar trend. So, here we are comparing 20 °C versus 32 °C. So you see shift in this (towards left) direction. So basically both techniques can be used to understand the influence of temperature on the hydration. That's the idea here. And we can say now that with the temperature increase, the dissolution of anhydrous cement also become faster that is what leads to this increase in the reaction rate.

To find more detail about this you can refer to this ASTM C1753 on the adiabatic measurement.

(Refer Slide Time: 11:15)
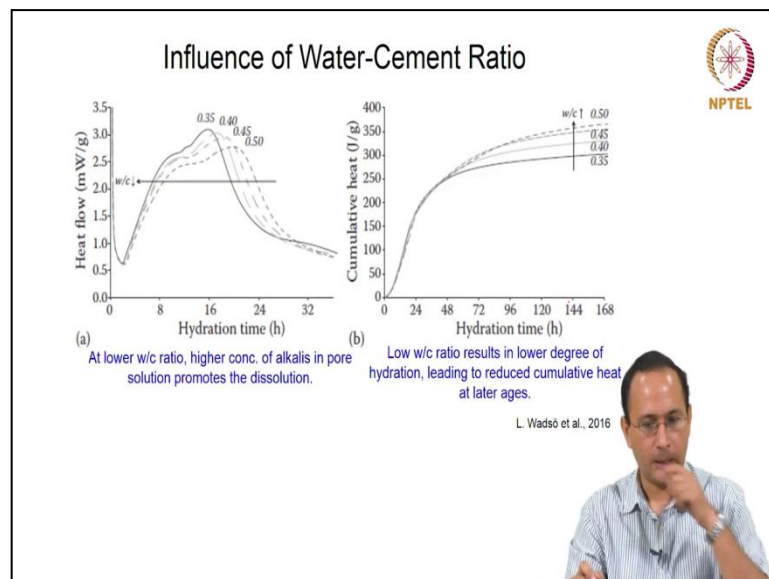
Now we can also understand the influence of water-cement ratio. We all know that depending on the condition we choose different water-cement ratios. So, how does that influence your heat

flow, for an example, like cement hydration? So, let us look at the left plot (Figure in slide on the left), what we see here, we are plotting heat flow, the power basically versus time at different water-cement ratio, 0.35, 0.4, 0.45, 0.5.

See the difference? The curves are not same. They've shifted towards right, as you are increasing water-cement ratio. What does that tell you? So basically, what happens, at lower water-cement ratio, you have a higher concentration of alkalis in pore solution, and so that promotes the dissolution of cement. That could be the reason. And now if you plot the cumulative heat, basically what you have to do is you have to integrate this curve, and you will get the total heat.

And you see that low water-cement ratio results in lower heat of hydration, leading to reduced cumulative heat at later ages, because we don't have enough water also. Simply you don't have enough water. So even if you look at the total heat, it's lower for low water-cement ratio.

(Refer Slide Time: 13:07)
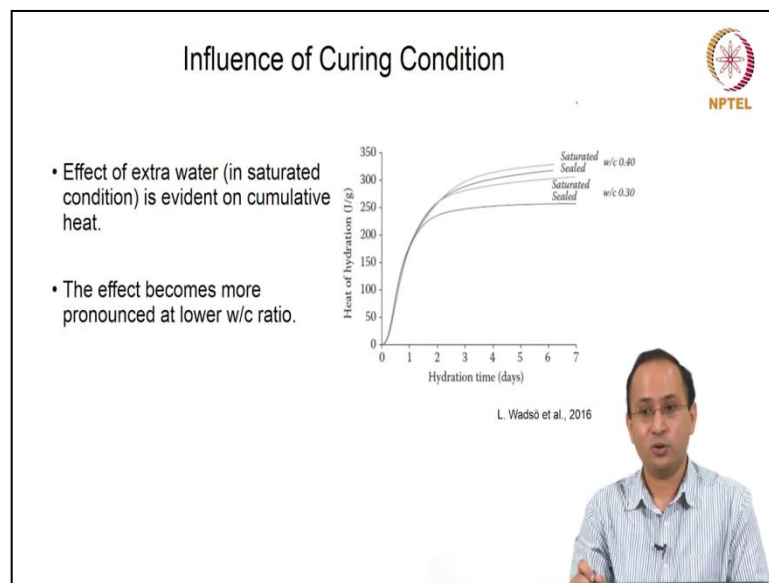
Another thing we can also understand is the influence of curing condition. Lot of times, we cure concrete sometimes in saturated conditions, sometimes in sealed conditions. So it is important to understand its influence on the hydration. So, here what we see, basically 2 different water-cement ratios are considered and for each water-cement ratio you can see the effect of saturated curing. Basically it is the effect of extra water you have. When you have a saturated condition, you have extra water that promotes hydration. So leads to higher cumulative heat. So you see this trend, compared to sealed condition you have a higher heat of hydration for the saturated condition. And we can see that, the difference becomes more pronounced at lower water-

cement ratio. See the difference between sealed and saturated conditions, at low water-cement ratio, the difference becomes more pronounced.

(Refer Slide Time: 14:32)
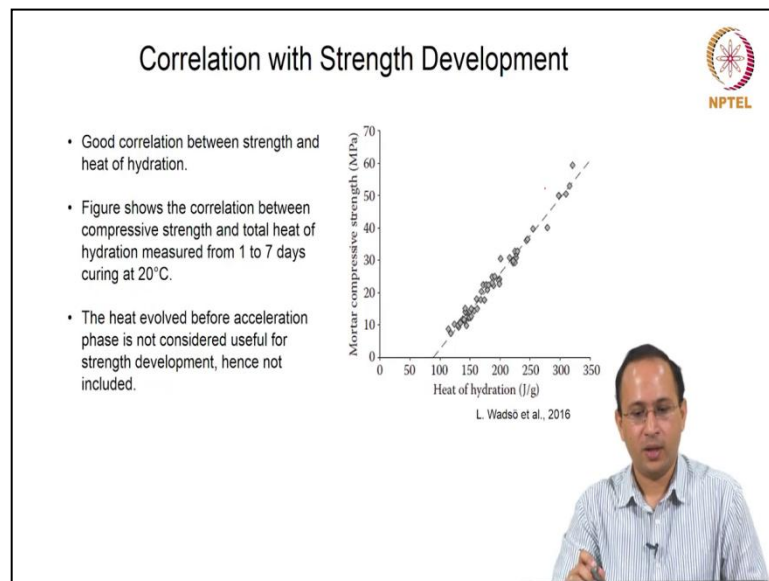
So, also this technique can be used to predict the strength development, see that is one of the most powerful uses of this. So on the Y-axis, you have the strength data and X-axis is heat of hydration at that particular age. And we see a very good direct correlation between this. So basically, what it tells you, if you know the heat of hydration, different ages, you can predict the strength.

And if you think about it, makes sense, because your strength is only because of the hydration. Cement is hydrating, and you're forming hydration products that are filling up the pores, reducing your porosity, increasing your strength. But this is a non-destructive way of measuring strengths. So there is a good correlation between strength and heat of hydration. There's a direct correlation. You can see the increase in strength.

Now the question is can we apply it to concrete? Yes, you can apply, but obviously there will be some differences. Obviously the concrete strength is also because of the hydration of cement. So, it can be translated to concrete also, but the nature of plot may change, may not be exactly like this.
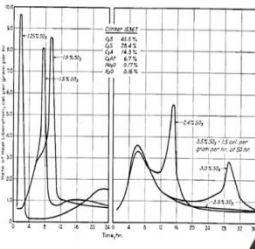
Okay, one thing is here, the heat evolved before acceleration phase is not considered. Initially you have some heat release, and in this case, the heat evolved before acceleration phase is not considered useful for strength development, and hence not included. So, once you have setting, at about 3-4 hours, the heat release beyond that has been taken into account, because before that, your cement paste or mortar may not have given strength. It's in plastic state.

Okay, another powerful use of isothermal calorimetry is for sulphate optimization. We have gypsum in our cement, i.e., we grind clinker with gypsum for optimising the strength. But for that most of the time, what you do is you change the percentage of gypsum, make cubes, test those cubes, determine the strength, get the plot, and see where you are getting the maximum strength.

But another way, you can just use this technique as a non-destructive technique, to determine the optimal sulphate. Those who are really interested can refer to this paper by Lerch, 1946. It is a pioneer work done by Lerch, exhaustive study. He analysed a lot of cements. He looked into different sulphate percentage. Here is a clinker and he increased the percentage of sulphates.

At that time, he used the conduction calorimetry for these measurements. Let us look at 1.5%, so you have this peak at around 8 hours. At 1.9% you have peak just shifted towards right. But if you look at this plot (Figure on the right, in slide), it will be clearer. So, 2.4% you see appearance of this peak. As you're increasing it to 3%, that peak is getting delayed.

And as you are increasing to 3.5%, the peak completely disappears. So, basically, this peak is because of the depletion of sulphates. Obviously when you have little bit more sulphate, there is a delay in onset of this peak. But if you have 3.5%, you don't even see that peak. That tells you 3.5% amount is good enough, if you want to optimise with respect to sulphates. That's the same number we get when we do strength test, as I will come back to it in the next slide.

So, in calorimetry, you can see that. So, the particular reaction, you can get some insight from the calorimetric data.

(Refer Slide Time: 19:43)
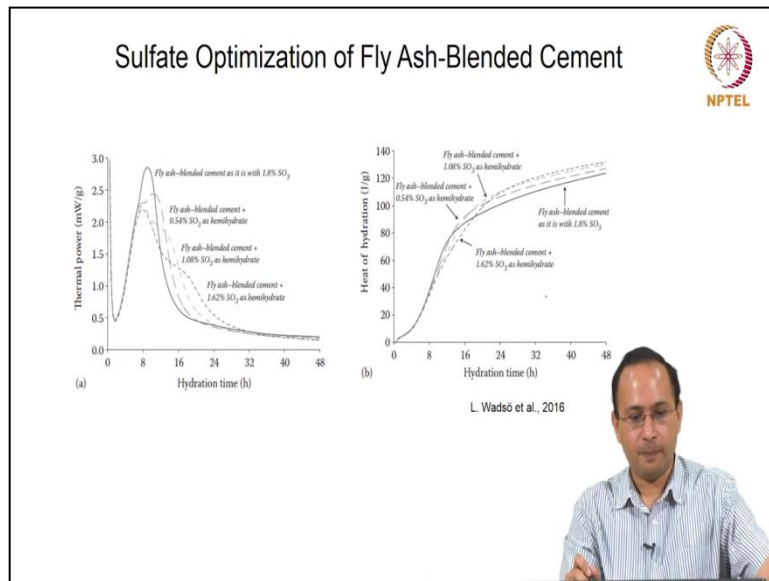
So, this is sulphate optimisation of fly ash blended cements. Lot of times, we use fly ash. Sometimes we use Class F, Class C. So in this case what we are seeing is this fly ash blended cement, with different dosages of hemihydrate. Hemihydrate is also a form of calcium sulphate. So this curve is for 0.54% SO_3, and as you're increasing, now this is 1.08%
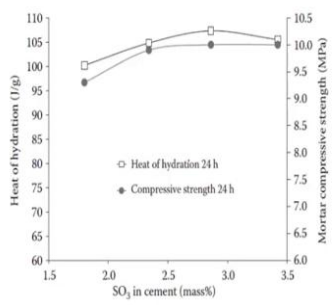
So, you see this peak. Now for 1.08%, this peak is shifting towards right. For 1.62%, the peak is here. And when you have 1.8%, you don't see that. So you can use this to get the optimum sulphate you need for your blend. Here (on the figure on right in slide) you are seeing the total heat of hydration as a function of time. So, it is nothing but the integration of this curve on the left. So we can also look into the total heat of hydration.

(Refer Slide Time: 21:17)

Sulfate Optimization Based on Strength and Calorimetry

Sulfate optimization based on strength and heat of hydration yield similar results.

L. Wadsö et al., 2016

Basically this compares what we get from heat of hydration test versus what we get from strength test. So here, on the X-axis we have sulphate doses, and we see that the trend is very similar; also the value of optimum sulphate we get is very similar. So that tells us that sulphate optimization based on strength and heat of hydration yields similar results.
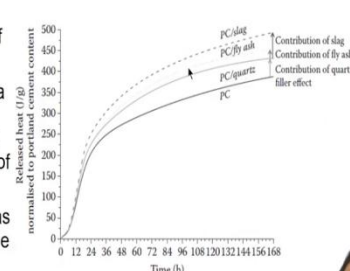
Rather than doing strength test, which is destructive, you can use this non-destructive measurement.

(Refer Slide Time: 22:05)

Reactivity of Supplementary Cementitious Materials

- Used for assessing reactivity of SCMs.
- Measurements are made with a constant mass of cement plus SCM or with the same mass of cement and different amounts of SCM.
- Inert reference material, such as quartz, is used to distinguish the filler effect.

L. Wadsö et al., 2016

Okay, we can also look into the reactivity of supplementary cementitious materials. We are using lot of new materials these days. And it is important to assess their reactivity, how reactive they are. So this technique can be used to assess the reactivity of SCMs. So, in this case, what

you see is the measurement from isothermal calorimetry. Whenever there is a measurement from the isothermal calorimetry, you will see the heat release rate or total heat being plotted.

So, in this case, total heat, joule per gram (J/g) is plotted against time. Now we want to examine the reactivity of materials. Now suppose you replace your cement with 15% fly ash. You want to see how reactive it is. So, before we discuss that, it is important to look into the filler effect. See, instead of fly ash or something which is reactive, if I add a material which is not reactive, like quartz for an example and use in the same amount, that is, 15% quartz.

Filler effect is nothing but, when you add any filler in your cement, which is non-reactive, it provides additional nucleation sites. Also, you will have more water-cement ratio, suppose you have cement plus quartz. So, initially you have 100%, cement. Now, you have 85% cement, 15% quartz. Now your water-binder ratio is same, so that means you have more water available for cement.

So, this first curve, it is for Portland cement. When you now replace Portland cement with quartz, you see this increase. Quartz is not reactive, we know that, this is the effect of filler; this is the contribution of quartz that is called filler effect. This happens because, firstly, you are providing additional nucleation sites, and also you are increasing the water-cement ratio. So, if you use like 15%, fly ash, for an example, you have to isolate the effect, because anything which is reactive, you will have filler effect, and also you an effect of the reaction.

But in case of fly ash, what you see here, this is the contribution of fly ash, so you see this dotted line, that is because of the chemical reaction, because we know that fly ash reacts with calcium hydroxide and it is called pozzolanic reaction and forms additional C-S-H. So, you can differentiate, so this overall contribution is because of the filler effect, and contribution from its chemical reactivity. So it's a useful tool.

So usually inert materials are used like in this case, most of the time you use quartz, if you want to understand the filler effect. In the case of slag, we know that slag reacts even more, you see contribution of slag is even higher than fly ash. So that's the usefulness of this technique in assessing the reactivity of these various materials.

(Refer Slide Time: 25:33)

Reactivity of SCMs Cont'd
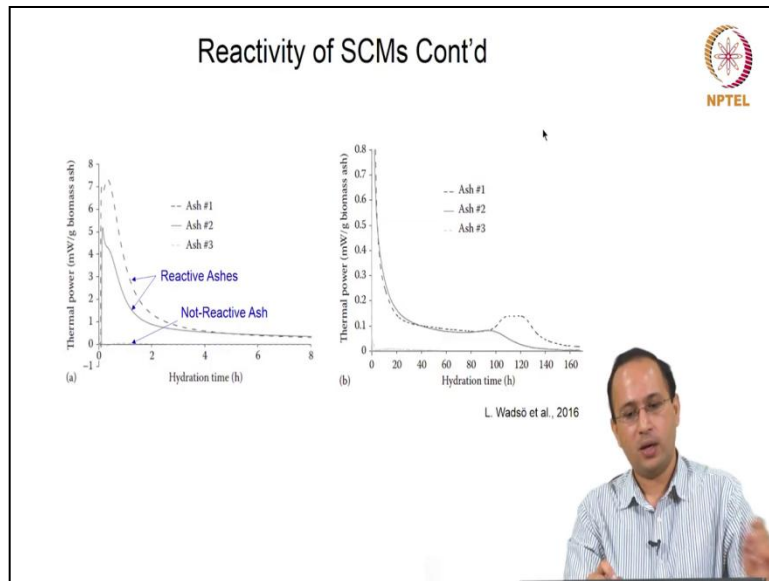
Also, we can look into individual SCMs, in this case here, they looked into biomass ash. You can see the difference between a reactive ash and non-reactive ash. You have few different materials, for an example. Just to begin with, you want to look into the reactivity, whether a particular ash is reactive or not. So, if you look at this plot, for non-reactive ash, your signal is so weak, so you are not even getting anything. For the reactive ashes you are getting some signals. So this technique can be used quickly to assess or see if the material is reactive or not.

(Refer Slide Time: 26:22)

Cement-Admixture Interaction
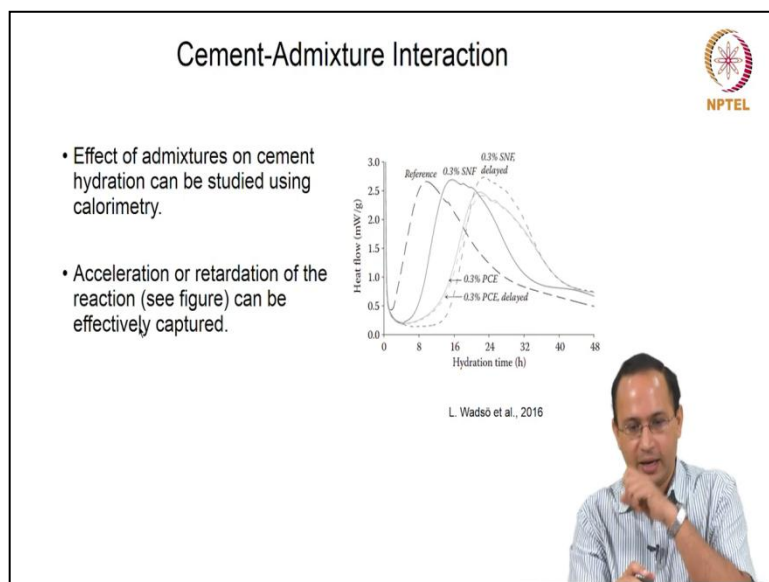
- Effect of admixtures on cement hydration can be studied using calorimetry.

- Acceleration or retardation of the reaction (see figure) can be effectively captured.

Also, we can look into the cement-admixture interaction. We use lot of chemical admixtures, for an example, these days, be it a retarder, be it an accelerator, any concrete will have some chemical admixture. How do you assess its impact? So, here you see that reference is the cement without any admixtures, and you see the effect of different types of admixtures, such as SNF, PCE. These are two commonly used admixtures in concrete industry.

So, we can see, when you have 0.3% SNF, sulpho-naphthalene based, it delays your hydration. See the difference, the main peak is delaying. So this is basically delaying your hydration. . Also you see the effect of delayed addition; here they have looked into delayed addition of admixtures. Sometimes you add your admixture in water and then mix with the concrete, sometimes you add it later. So in this study, how SNF admixture influences the hydration (even in delayed addition) was studied.

In this case they found that delayed addition also delayed the onset of main hydration peak. In case of PCE, polycarboxylate based admixture, you don't see much difference between delayed and the one where you mix it immediately. So, these kinds of things, like how a particular admixture influences your hydration can be studied using this isothermal calorimetry. Acceleration and retardation both can be captured.

In this case we are seeing the retardation. Sometimes, in accelerator, you might even see something like this (Refer Figure 2), you're cutting down on your dormant period. So this measurement can tell you a lot. That is the point.
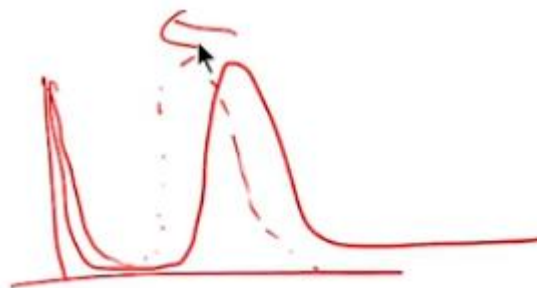
Figure 2 Effect of addition of accelerator

(Refer Slide Time: 29:01)

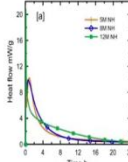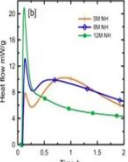So far we were looking at the Portland cement based systems. We can also study new cements. These days we are talking about low CO_2 cements, like for an example, alkali-activated binders, calcium aluminate cement, calcium sulfoaluminate-belite cements. So this tool can also be used to understand the hydration characteristics of these binders. In this case, we can call them Rapid setting binders.
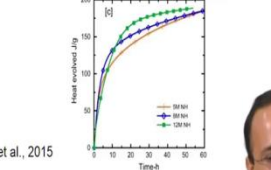
(Refer Slide Time: 29:30)

So, we'll see how we can use this tool. So alkali-activated slag, all of you may know that slag, for an example, we are talking about the system, where we are not using Portland cement. We are activating these alumino-silicate materials by using alkalis, could be sodium hydroxide, could be a combination of sodium hydroxide and sodium silicate, but you have a high pH solution which is used to activate these alumino-silicate materials.

So here we see the effect of molarity. So, in this case, the researchers looked into the effect of molarity on the hydration of slag. So 5M, 8M, 12M NH (NH is sodium hydroxide). How does that influence your hydration? So we are looking in this plot, the hydration occurring within 24 hours. If you see, a lot of things are going on in this region, because we do not see much difference here.

But, now we can also capture, because if you do internal mixing, we discussed that earlier, in isothermal calorimeter, if you mix sample internally, then you can also capture what is going on within 1 hour, 2 hours. So, here in this, you can now see what is going on within 2 hours (Fig (b) in slide), now you see the difference. How your concentration is affecting the appearance of this peak. As you're increasing the concentration, your reaction rate is also going up. So that's the power of this technique. In Fig (c) in slide, is the total heat evolved, and you see that, 12 M NH is at the highest, because you are accelerating the reaction.

Obviously, eventually may be 5 M NH will be able to catch up. But at least within this time frame, you see the difference between different concentrations. So that is the insight, if you have different concentrations, you can't just say that, you are increasing the concentration to 6 M NH and that the effect will be similar. It's influence on the hydration can be studied using calorimetry.

(Refer Slide Time: 31:49)
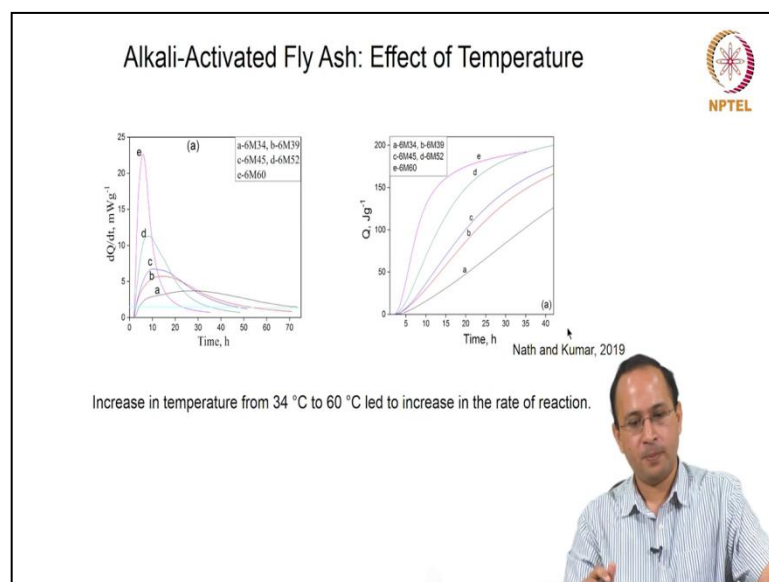
This is an example of alkali-activated fly ash. We are looking at the effect of temperature. How does temperature affect the hydration? So here you see basically, A is the test done at 34 °C, B is 39 °C. So, the temperature went to 60 °C, and you see that increase in temperature also

accelerated the hydration. Similar thing, if you plot the total heat, you see the higher temperature lead to higher heat of hydration.

This data is for 40 hours, may be it might catch up, we do not know, but at least up to 40 hours, there is a difference. So these kinds of things like the effect of temperature on the hydration of even new binders, rapid setting binders can be studied. And especially if we have to look at the early age, then you have to make sure that you mix your sample internally and not externally.

(Refer Slide Time: 33:02)
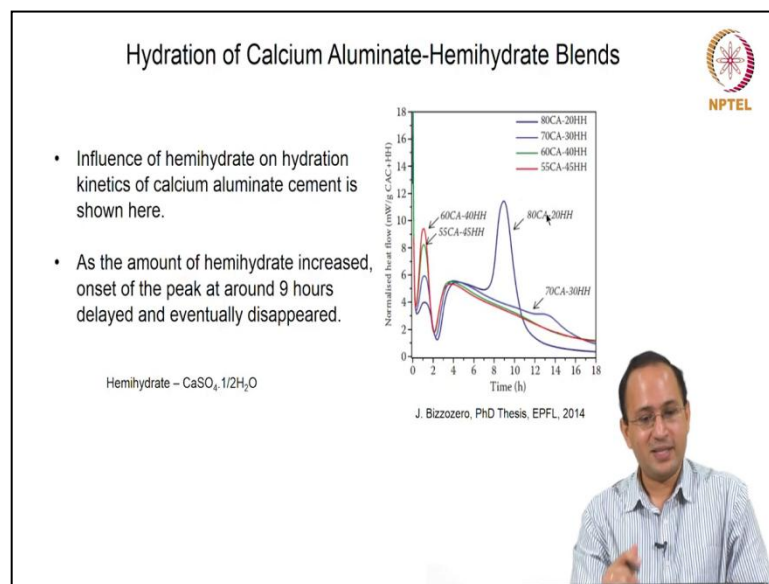
This is the example of hydration of calcium aluminate cement, also low CO_2 cement. Here we can see the effect of hemihydrates. The calcium aluminate cement with hemihydrates, you can think of it as adding gypsum to cement. Here also we are doing some sort of optimization. So in this case, if you increase from 20HH (HH is hemihydrates) to 30HH, what happens to this peak? This peak is shifting. So you can see the changes in the hydration kinetics, hydration characteristics through this technique.
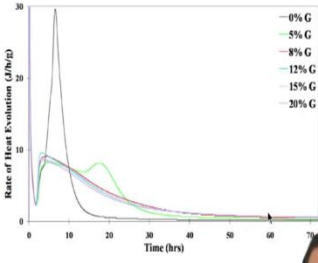
From 20HH to 30HH, you shifted this peak and the intensity also decreased. Now further, for 40HH, the peak disappeared. So these kinds of changes can be captured using calorimetry.

(Refer Slide Time: 34:07)

Hydration of Calcium Sulfoaluminate-Belite Cement

- Influence of gypsum on the hydration of CSAB cement was studied using isothermal calorimetry.

- There was no significant effect on hydration beyond 8% gypsum.

I. Chen and M. Juenger, 2011

Here is an example of hydration of calcium sulfoaluminate-belite cement. Again for this cement you have to add gypsum. You want to find out what is the optimum gypsum. In this case, we can see that, this is a 0% gypsum case. You have this peak, because of sulphate depletion, as you are increasing the gypsum, 5%, 8%, you see first peak is moving. You are delaying that peak, because you have more gypsum in the system.

And further at 8%, do not even see that peak. So 8%, 12%, 15%, 20%, there is no difference. So, in this case, we see that there is no significant effect on hydration, beyond 8% gypsum, so it could be optimum gypsum for this type of binder.

(Refer Slide Time: 34:59)

Comparison of Different Calorimetric Methods

Method	Advantages	Disadvantages
Isothermal calorimetry	Very repeatable at early age	Low signal after several days requires costly instrumentation
	Easy to test at different temperatures	Small samples extracted from larger sample preparation may result in nonuniform binder content
	Easy to measure the effect of SCM and admixtures	Small paste samples may give erroneous kinetic effects of admixtures when compared to concrete
Semiadiabatic calorimetry	Simple and cheap equipment for testing in industrial lab	Indirectly calculated heat from temperature rise and estimated heat loss
	Well established for providing concrete data for prediction of temperature and risk of thermal cracking in field structures	Extensive calibration procedure
	Historically well-established standards	Temperature rise alters cement hydration
		Rather poor repeatability

We looked at various applications of these techniques. So you see that, it can range from determining heat of hydration, estimation of activation energy, influence of water-cement ratio,

influence of curing conditions, assessing the reactivity of different materials and looking into hydration of new cements, . So it is very versatile. Now it is also good to remember the differences, primarily we'll focus on isothermal and adiabatic calorimetry, because heat of solution is not much used these days.

So what is the advantage of using isothermal calorimetry? Very repeatable at early age. Easy to test at different temperatures, because it is isothermal, you can change the temperature. Easy to measure the effect of SCM and admixture.

What are the disadvantages? The low signal after several days requires costly instrumentation. See if you want to monitor your hydration for long time, beyond days or for weeks, then you should be able to measure the low signal, because your cement hydration slows down with time.

So, that is one challenge. Small sample extracted from large sample preparation may result in non-uniform binder content. Since we are using only small sample, so you have to make sure that you have a representative sample. Small paste samples may give erroneous kinetic effects of admixture when compared to concrete. See eventually, we want to predict performance in concrete. So, how can you predict the performance in concrete just based on paste? That is another challenge here.

In the adiabatic calorimetry is simple and cheap equipment. It's very simple, relatively cheap equipment for testing in industrial labs. We can use large samples.

And what are the disadvantages? If you want to calculate the heat, you have to calculate indirectly. You are not measuring it directly, you are measuring temperature. Now, you have to make some assumptions to calculate the heat of hydration. So it is an indirect calculation. Also there is an estimated heat loss.

The calibration procedure is extensive. Also, temperature rise will alter cement hydration. In adiabatic, you are basically insulating your sample. So, as the temperature rises, that will also affect your hydration and the repeatability is not as good as isothermal calorimeter.

(Refer Slide Time: 37:44)

Finally, we'll conclude this lecture, that calorimetry provides an effective way to monitor hydration of cementitious materials. And many applications of calorimetry we have seen which is listed here; it can range from determination of heat of hydration, activation energy to understanding the effect of various materials on cement hydration. And also, hydration of paste/mortar/concrete can all be studied using calorimeter. If you want to study the hydration of concrete, for example, then you can choose adiabatic calorimeter.

If you want to just study the hydration of paste, mortar, then isothermal calorimetry is useful. Depends on what the goal is. If you want to study the effect of temperature, then go for isothermal calorimetry.

(Refer Slide Time: 38:33)

So, that concludes our lecture, and here are the references which I used for this lecture, I would like to point out that this (reference no. 2) is a very good reference. There is a chapter on calorimetry in this book, which is very useful, lot of things have been taken from this, and cement chemistry, as usual is very good resource, and we can see we referred to lot of other things which are listed here. So that concludes this lecture.