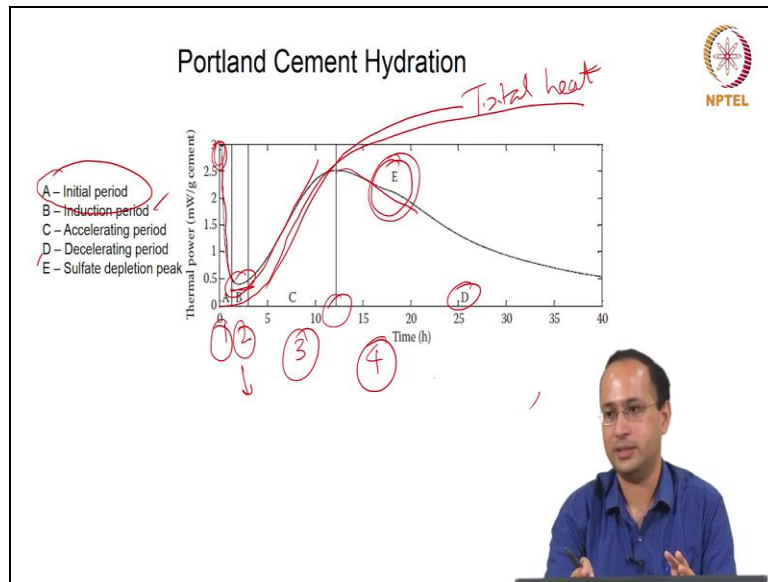


Characterization of Construction Materials
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Lecture 8
Calorimetry: Introduction and types of Calorimeters – Part2

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If we want to study Portland cement hydration, we want to first look into the stages of the hydration. Many of you must have seen this, but anyway we will discuss it here. So this is the typical rate of hydration plot for Portland cement. So what do you see? You see there are four different stages. At one here, is the 'Initial period' - A. It is called heat of dissolution.

So you have this cement and you are dissolving it in water. So basically, it is nothing but heat of wetting, and maybe some formation of products. Notice, you have very high rate of heat. It does not mean that the amount of heat is also high. It is a rate. Any powder for an example, even if it is non reactive, you will have this heat of wetting. But in this case you have heat of wetting and some reactions, some dissolution, some formation of calcium silicate hydrate, for an example.

So, you have a rapid release, a significant heat production rate, rate of heat hydration, and then it slows down. Then you come to this part - 2. 2 is nothing but 'Induction period'. Now you see that the reaction has slowed down, does not mean that it has stopped, still you have a positive

rate of heat of hydration. Can anyone tell what the importance of this induction time, induction period is?

So it is valuable to us because it gives us some time. It is also called 'dormant period'. Why is it happening, what is the cause for this? Right, I mean those reactions will take place, but primarily, you have a cement particle, it is reacting and something is forming on its surface. So imagine, you have these cement particles. Now, after some time something is formed on the surface that acts as a barrier.

You have water, then, it acts as a barrier for some time, but after some time, this barrier breaks down. But it gives you some time to finish your concrete for an example or maybe transport it. So it's very important, that's induction period. Then the reaction accelerates. It is called 'Accelerating period' - very important. Lot of hydration products are formed during this period.

And the peak is achieved around 12 to 14 hours. Then you see a slowdown, now this is a deceleration why because you have formed so many products. Now, imagine, you have so many products, now you are making it difficult. It's the diffusion control. If you want to make this remaining cement particle react you have to go, you have to cross this barrier.

So it becomes diffusion control. So that is why you see this decelerating period. So this is again the rate, note that it does not mean that you have a positive rate. Your total heat is increasing. So if we have to plot, for an example, cumulative heat. The plot will be something like this, this is total heat. So, the total heat plot you can see, after this main peak, the slope changes.

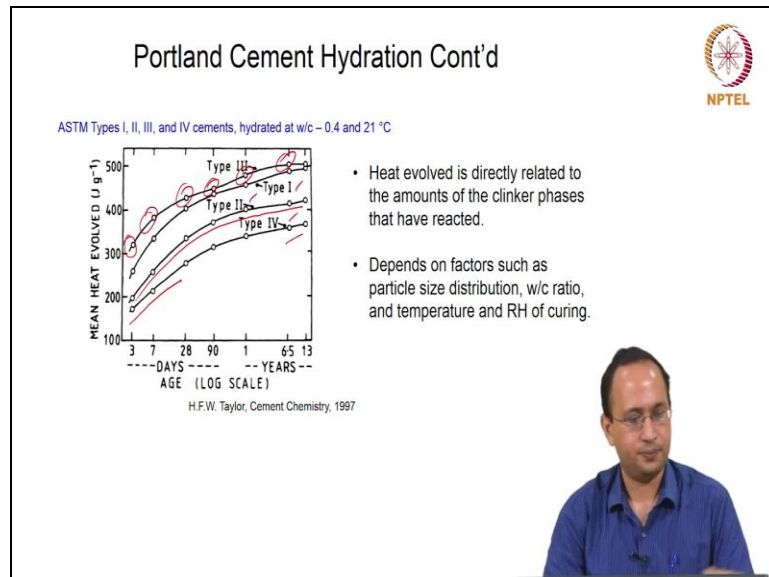
So you have this acceleration period, then your slope is changing. But still you are seeing in this increase. It will go on. So that was this deceleration thing period was 'D'. One more interesting observation here is, you see something in this decelerating period here. It is shown as E. For example, sulphate depletion peak. So you use some gypsum in your cement. Why is gypsum used? Yes, to prevent flash set.

But when the gypsum gets consumed fully, you form mono sulphate. Your Ettringite converts to mono sulphate. So this tells you about this sulphate depletion. It tells you that whatever gypsum you have added is finally consumed. So it is very important, because lot of times, this optimization of sulphate is done through strength test.

You optimize the strength - you add 1% gypsum, 2% gypsum, 3%, 4%, 5% and see which one is giving you the maximum strength. But Calorimetry can also tell you how much gypsum should be added; you do not have to do a destructive test. So, Calorimetry is a non-destructive technique. See the power of this measurement - tells you about lot of things, the rate, which are the critical stages because it is very important to know.

Suppose, you want to extend this dormant period, suppose you decide that you have to transport your concrete to 30 kilometres away, which needs at least one hour, for an example, may be included in traffic if it is one and a half hours, so you want to use some admixtures to delay this setting or prolong this dormant period. So what can you do? You can study; you can carry out these experiments and see what happens, when you have these additives.

So, we will come back to it, but I am trying to draw your attention that you can get a lot of information. So, this is the typical Portland cement hydration. Our focus will be to study this. How can we use Isothermal Calorimetry or Adiabatic Calorimetry to understand it better. **(Refer Slide Time: 08:10)**



Continuing this Portland cement hydration, suppose you have measured the heat evolved. So, here what you see on the y axis, you have a mean heat evolved at different days right 3 days, 7 days, 28 days, 90 days, one year, 6.5 years, 13 years, and you have compared different types of cements. So here ASTM Type I, Type II, Type III, Type IV cements are there. All of you must be familiar with this ASTM classification, right?


So you see that the Type III cement has the highest heat at all ages. Now, it is getting very similar to Type I at later age, but at least at earlier age it has more heat. Type II is low heat cement - moderate sulphate resistance. So, it has a little bit more C₂S, less C₃A. So you see that this is the trend. Type IV is low heat cement. So it has more C₂S. So, the heat is less because the reaction is slow, because you have more C₂S in the system.

So, heat evolved is directly related to the amounts of clinker phases that have reacted. You see here, you see the difference right? That difference is because you have different phases. The phase compositions of cements are different. Type I cement has maybe less C₂S compared to Type IV. Type IV has more C₂S. And the heat evolved will depend on the amount of each phase, how much C₃S you have, how much C₂S you have, because reaction is different.

Each chemical reaction is different. If it is different, then the associated heat release is also different. So it depends on many factors such as particle size distribution. You all know that if you make your cement finer, you make it react more. You have higher heat which is evolved, water-cement ratio, temperature and relative humidity of curing. These all will affect your heat.

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Calculation of Heat of Hydration




$$H_t = a(C_3S) + b(C_2S) + c(C_3A) + d(C_4AF)$$

Compound	Co-efficient	Value of the coefficient (kJ kg ⁻¹) for age given below						Enthalpy of the complete hydration (kJ kg ⁻¹)	
		3 d	7 d	28 d	90 d	1 yr	6.5 yr		13 yr
C ₃ S	a	243	222	126	435	490	490	510	-517±13
C ₂ S	b	50	42	105	176	226	222	247	-262
C ₃ A	c	887	1556	1377	1301	1167	1372	1356	-1144 ¹ ; -1672 ²
C ₄ AF	d	289	494	494	410	377	464	427	-418 ³

¹ Reaction with gypsum to give monosulfate
² Reaction with gypsum to give ettringite
³ Reaction in presence of excess CH to give a hydrogarnet

H.F.W. Taylor, Cement Chemistry, 1997



So how can we calculate heat of hydration? We know that this is our hydration curve. How can we calculate? This is a simple calculation. The total heat of hydration can be written as summation of the contribution of individual phases. So through Bogue formulations, you can find out how much C₃S, C₂S, C₃A C₄AF you have in your cement.

And now in this table you see that the value of coefficients is given. So for an example, if you want to calculate the heat of hydration at 3 day what do you do? You take the coefficient as 243 for C_3S . If you know the C_3S , suppose you have 55%, then, if you know, how much C_3S you have C_2S , C_3A , C_4AF . So, you know this now and you just use the coefficients to calculate the total heat of hydration. Is it clear?

Obviously, these coefficients will not be same. So, you see that coefficient changing, 7-day is different from 28-day, 90 day, 1 year. In this study, they looked up to 13 years. So, basically, this simple relationship can be used to calculate the heat of hydration. It is nothing but the contribution from individual phases; also you see here enthalpy of the complete hydration. That is very important.

So, for an example, there is a pure C_3S phase that will release roughly around 517 kilo Joule per kg (kJ kg^{-1}). So, that is a number for pure C_3S . And similarly, obviously C_2S is slow in reacting. So, you have around 262 kJ kg^{-1} , which means 1 kg of pure C_2S will give you 262 kilo Joule of heat. These are pure phases. So you use these to finally calculate. Now, your Portland cement is nothing but a mixture of C_3S , C_2S , C_3A , C_4AF .

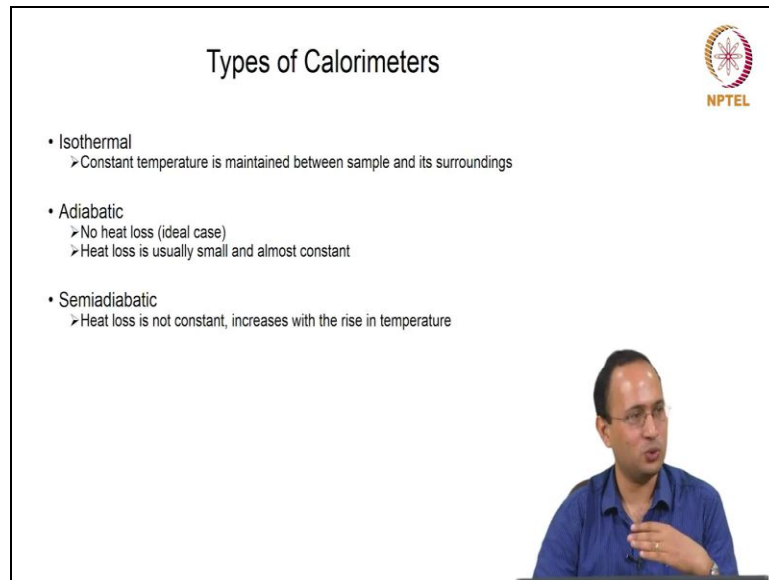
Now you know the values for the pure phases and you know how much of these phases you have. You can calculate the total heat of hydration. And also see here for C_3A . So, this value 1144 is for the reaction with gypsum to give mono sulphate, and 1672 is for the reaction with gypsum to give Ettringite. You have these different reactions. We are not going in detail, but in cement chemistry or any other class, you must have learnt the reactions.

C_3S reacts with water to give C-S-H (calcium silicate hydrate), same with C_2S . Whereas, C_3A reacts with calcium sulphate or gypsum to give AFt or Ettringite. Then AFt converts to AFm – monosulphate.


It is good to know these enthalpy values for pure phases, because then if you know how much of it is there, you will be able to calculate. Is it clear? Simply, you are basically breaking down your system.

You are assuming that your cement is made of four phases. And if you know the amount of these phases and you know what the enthalpy of the complete reaction is, complete hydration of pure phases you will be able to calculate total heat of hydration.


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Types of Calorimeters


NPTEL

- Isothermal
 - Constant temperature is maintained between sample and its surroundings
- Adiabatic
 - No heat loss (ideal case)
 - Heat loss is usually small and almost constant
- Semiadiabatic
 - Heat loss is not constant, increases with the rise in temperature



Moving on, now we know about the Portland cement hydration and what are the phases which are of importance. Now we will focus on measuring. How do we measure? So we will focus on primarily three types of calorimeters. Isothermal - as you can guess - Isothermal calorimeter is used when you are interested in measuring heat at constant temperature. So, in isothermal, you maintain the temperature.

Constant temperature is maintained between the samples and surrounding. So how do you do it? You have cement hydration going on and you know that the cement hydration will release some heat and that heat you can remove, to maintain the temperature. Obviously, when the cement hydrates, the temperature will increase, because there is a heat.


If you can remove that heat, then you will be able to maintain. Now, you are measuring that heat. The heat that you are removing from the system, you are measuring it. So that way you are monitoring this process.

Adiabatic - In adiabatic, what do we do? No heat loss should occur between the sample and surrounding. That is the ideal case, but usually, the heat loss is small and almost constant. We will go over these techniques but right now just to understand these are different techniques.

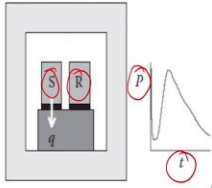
Semi-adiabatic is similar to adiabatic, but only difference is heat loss is not constant, increases with the rise in the temperature. The adiabatic your heat loss is small and almost constant. In semi adiabatic, heat loss is not constant, it increases with the rise in temperature.

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Isothermal Calorimeter



- Heat flow or heat production rate (P) is measured.
- A reference sample (R) without any heat production is also present.
- Heat capacity of the reference sample (R) should be same as that of the sample (S).
- The output is the difference between the sample signal and the reference signal.
- Usually, small (1-100 g) samples of paste or mortar are used.



L. Wadsó et al., 2016



Coming back to isothermal calorimeter, we are maintaining the temperature and then measure the heat. So, heat flow or heat production rate is measured here. How do you do it? You have a reference sample also. So you have a sample, your sample (S) and you have a reference sample (R). We will come back to it. So, reference sample without any heat production is also present. We will pick a sample which does not release any heat and we are measuring the difference basically.

So, the output is the difference between the sample signal and the reference signal. This is all done to reduce the noise. Important point to keep in mind is, the heat capacity of the reference sample (R) should be same as that of sample (S). That is very important. Heat capacity of the reference should be same as should be same as that of your sample, but it should not release any heat. So for an example, you can take quartz or water for an example, as a reference.


Also isothermal calorimeter can be used for the paste or mortars, because the amount is limited. You can use typically 1-100 gram of sample, it is small. You are not talking about kgs, so that is the also limitation of this technique. You can only use it for paste and mortar. And the amount is up to 100 gram. So you finally get this power, thermal power (P), changing with T . Thermal power tells you about the heat production rate.

This is a typical signal you get. We will convert it later. Come back to it. But idea is, you have a reference and sample, you are measuring the difference between reference and sample. Basically, how are you doing is, whatever heat is generated is sent to the heat sink, that heat will cause some temperature difference.

You have a heat flow sensor. That temperature difference will lead to the voltage. So, you are measuring the voltage. And now you have this sensor where you have voltage, you are also measuring the current. Once you know the current and voltage, you can calculate the power, or you can do it through current and resistance also, you know that.

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Isothermal Calorimeter Cont'd




- Thermal mass of the reference sample should always be similar to the thermal mass of the target sample.
- The thermal mass of a given material is calculated by multiplying the mass by its specific heat capacities.

Material	Specific Heat Capacity J/g.K
Cement, portland unhydrated	0.75
Fly ash	0.80
Gypsum	1.08
Limestone	0.91
Quartz	0.71
Sand	0.80
Slag	0.80
Water	4.18

ASTM C1702, 2009

Handwritten calculations:

$$R = \frac{8.52}{4.18} = 2.036 \text{ kcal} \quad \text{or} \quad 3 \times 0.75 + 1.5 \times 4.18 = 8.52 \text{ J/K}$$



So, thermal mass of the reference sample should always be similar to the thermal mass of target - very important. Okay, so I will show you how to do it. Suppose, you want to make a paste, you decide to add cement and water. That is how you make paste, right? And the heat capacity of cement is, in this table, you can see 0.75 Joule per gram, per Kelvin (J/gm.K) and water is 4.18.

Suppose, you decide that you are using 3 gram of cement and 1.5 gram of water, so you can calculate the thermal mass of this system - cement and water. How will you do it?

$$3 * 0.75 + 1.5 * 4.18 = 8.52 \text{ J/K}$$


That is the thermal mass. Obviously, this will change right if you want to try different water - cement ratio and other things, or if you want to add sand. But you can calculate what the approximate thermal mass is.

So in this case, it comes out around 8.52 Joule per Kelvin (J/K). Now you want to keep this same. So you want to calculate how much reference you have to use. So, suppose you decide to use water, so what do you do? (suppose R is reference weight) so you know this is the thermal mass here to get, and you know the capacity, so it gives you 2.04 grams of water. Simple calculation to show you how to balance, because now you are sure that your reference and sample have similar thermal mass.

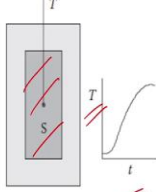
Basically, heat capacities are similar, same. Now you are measuring the difference, whatever is happening because of the reaction you are measuring the difference, because water is not going to release any heat. You can use quartz also, a lot of times commonly used reference is quartz. You can see here right. So, the thermal mass of a given material is calculated by multiplying the mass of its specific heat capacities.

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Semiadiabatic Calorimeter



- The sample (S) is insulated and the temperature (T) increase is measured.
- Corrections must be applied for the heat losses to the surroundings.
- Large samples (around 0.5-1 kg cement mortar to 10 kg of concrete) are used.



L. Wadso et al., 2016



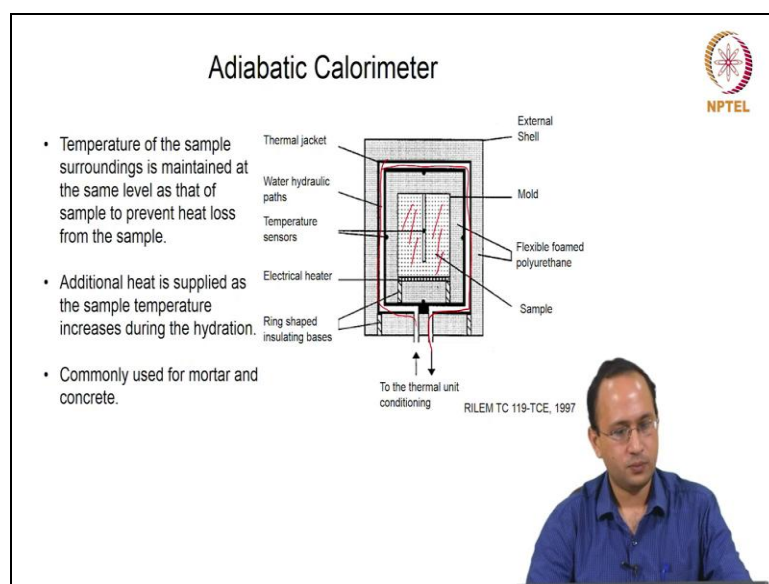
Now you know the about the isothermal calorimeter. Now, we will come back to semi-adiabatic calorimeter. Semi-adiabatic calorimeter, what we said about semi adiabatic calorimeter is that, you want to have the constant heat loss. It will be small, but constant. Ideally, you want to have zero heat loss. So, simply put, your sample is insulated and the temperature increase is measured. So, imagine you have the sample insulated, and because you want to prevent this heat loss and you have embedded a sensor where you can measure the temperature (T). Now the question is how do you do it? So, you measure the temperature, but the corrections must be applied for the heat losses. You know that even though we have tried to make it completely insulated, but there will be heat losses. So, those corrections you will have to apply and you measure the temperature.

So, the typical output is this temperature versus time. But the advantage of this technique is that you can use the large samples. Large samples like you can use mortar, concrete up to 10 kg. But what is disadvantage? Anyway we will come back to it. See what happens you have made this very insulated. Now what happens due to the reaction there will be heat release.

That heat release will increase the temperature and that increase in temperature will influence your cement hydration, you understand. In the isothermal case, we are trying to maintain the temperature; whatever heat is being released, we are removing it and measuring that heat. In this case, we are measuring the temperature, this is the insulated system. So there will be temperature rise that will affect your cement hydration.

Although you started at 20 °C but then, as soon as it goes to 30, 40, 50 °C, it will start affecting your cement hydration. So, see the advantages and disadvantages. But the advantage is you can look into the concrete, close to reality. If you are using concrete in any building structure, you want to study how the concrete performs, like what is the interaction between cement and aggregates, other things.

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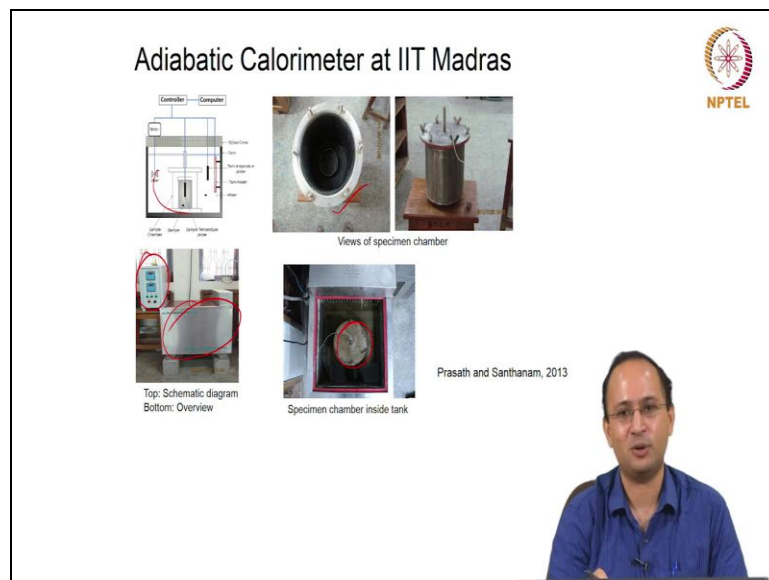


This is the final one, adiabatic calorimeter - similar to what we have seen. In this case also the, we want to reduce the heat loss but how are we doing it? We are not insulating it completely, but temperature of the sample surroundings is maintained at the same level. So, how we are doing it? We know that your sample temperature due to the hydration will rise, but we are also rising the temperature of the surrounding. So that there is no heat loss.

So the sample surrounding is maintained at the same level as that of sample, to prevent this heat loss. So for that you may have to provide some additional heat. Suppose, cement is hydrating and the temperature is going up to 40 or 50 °C, then you have to raise the temperature. So here is the schematic of this. You see your sample, and you are measuring the temperature and what else you have?

You have this thermal unit conditioning, this is your thermal jacket basically, surrounding it. That is how you are maintaining the temperature right. And also you want to insulate the sample so that there is no loss. But the idea is, you are maintaining the temperature of sample and surrounding. It is also commonly used for mortar and concrete.

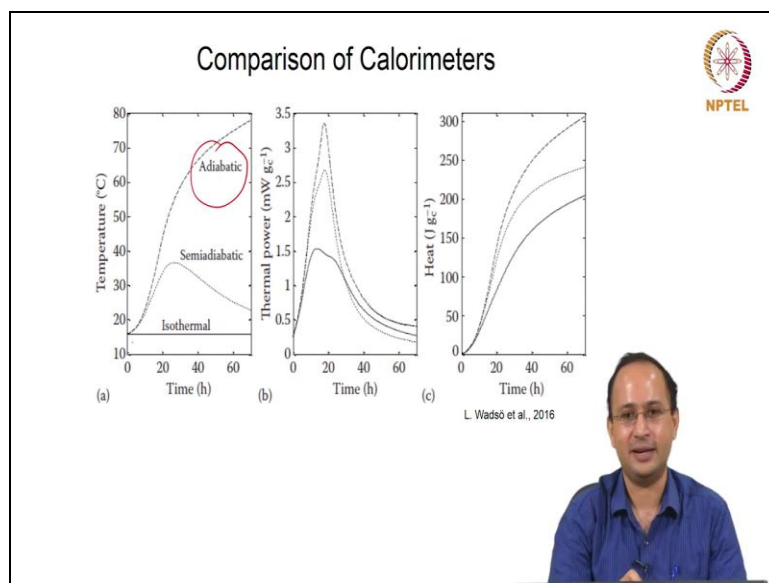
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So this is the adiabatic calorimeter we have at IIT Madras. Now, you know the principle of adiabatic calorimeter. You can see - this is the big water tank. Inside it, we have this sample holder. This is a top view, sample holder looks like this. So, you put your concrete in this sample holder and it is in the water bath. So, here you see it is in the water bath. So basically you are sensing the temperature of your sample.

And also, then you have sensor in your water bath. And as you want to make sure that there is not much difference between the sample temperature and your sample surrounding temperature, you have a program controller. Controller minimizes the temperature difference between the sample and the ambient.

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Finally this is the last slide. We will start from here in the next lecture, but I just want to show you. Here I am plotting temperature we are seeing temperature versus time, for three different types of calorimeters isothermal, semi adiabatic, adiabatic. Isothermal - no brainer, why is it same? Because we have made it same, so you see constant temperature. Semi-adiabatic you see increase in temperature because you have this insulated system so there is no heat loss.

You have adiabatic, so you see the difference in adiabatic. Your Delta H (ΔH) is very small. ΔH is very small, even at high temperature. So what happens with the semi adiabatic as you raise the temperature, even if you go like 70 °C, your losses will also be higher. So that is why you do not see and the question is why the adiabatic calorimeter gives you higher temperature than semi, semi adiabatic. So we will start from this slide in the next lecture. Thank you.