

Characterization of Construction Materials
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Lecture 9

Calorimetry: Sample preparation, Practical note and Heat of hydration Part 1

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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	377	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

Hi everyone today we will continue our lecture on calorimetry. So what we learnt in the last class was about the calorimetry. Calorimetry is basically about measuring heat. We measure heat production rate and total heat which gives us information about all kinds of processes whether it is physical, chemical or biological. We looked at the different processes and saw the usefulness of calorimetry in giving us some insight about the changes which occur during the process.

Let me clarify few things; I think few of you may have some doubts about it. So yesterday we discussed about calculating the heat of hydration on the slide but we said that the total heat of hydration can be calculated as per this equation and you see, that in table we have this compounds C₃S, C₂S, C₃A, C₄AF and also you have coefficient associated with this a, b, c, d and for different times like 3 days, 7 days, 28 days, 90 days, 1 year, 6.5 years and 13 years.

So, if you have to calculate heat of hydration after 3 days, you will use the coefficient for the 3 days and also, you notice that the coefficients are changing with time, So the coefficient used for 28 days is different than the one which is used for 3 days. So, these coefficients were

developed through experiments done long back in 1950 by Copeland and his co-workers. They measured heat of hydration at different time intervals. You basically plot heat versus time, and you have these data points for an example.

This could be 3 days, 7 days, and 28 days so, you measure the heat of hydration. In this particular study, they measured the heat of hydration at later ages like 28 days, 90 days and 1 year they used the method of heat of solution. The problem with conventional calorimetry is the signal becomes really low after few days for example after 7 days, you would not get strong signal. So, the reaction slows down.

So it is very hard to measure that intensity of signal, in this case we use the heat of solution. It is nothing but you are dissolving your sample in hydrochloric acid for an example. It could be a mixture of nitric acid and hydrofluoric acid as well, so you know the heat of solution for your raw powder cement and when 50% of it has hydrated.

You use that sample to get the heat of solution for that. Now you calculate the difference because we know, the heat of solution for 100% cement hydration and the heat of solution coming from 50% hydrated cement and by this you can calculate the heat of hydration for that particular time. So, that they could measure the heat because we cannot continue doing the experiment for longer time durations like 90 days, 1 year and 6.5 years.

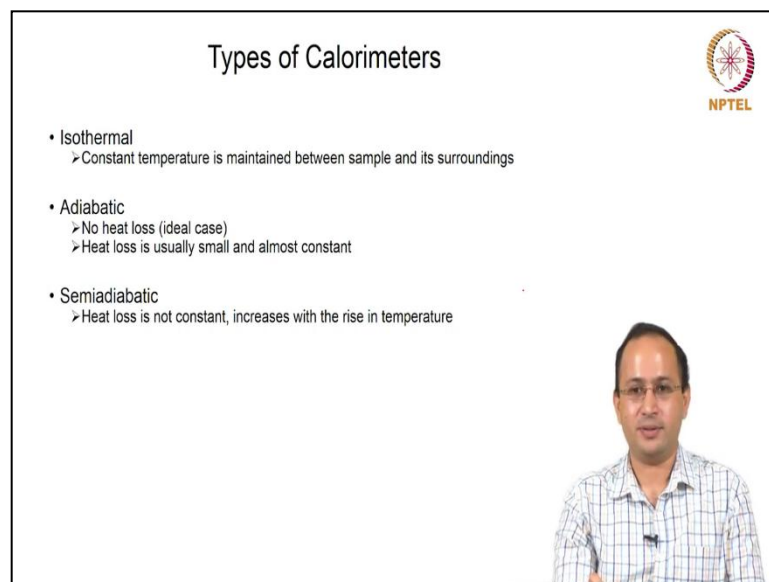
If you are wondering like how we calculated the heat of hydration after 13 years, for this if we prepared samples today and then we collected the data sample for whole 13 years. We calculate the heat of solution in this case by subtracting it from the heat of solution of 100% hydrated cement. So, now you have this data for plotting H which is heat of hydration versus time.

Now you want to get a simplistic relationship between this heat and the phase composition. Any particular cement will have a particular phase composition. Phase composition means for a particular cement will have some amount of C_2S , C_3S , C_3A and C_4AF . You know that to begin with how much C_3S and other phases you have in the particular system under study. So now you can adopt the optimisation method or you can use the least square method to calculate for this particular period of 3 days as for I know my total heat and amount of different phases present in the cement so what will be the combination of these Coefficient a, b, c, and d it simply is least square of which you can use to get that.


Same process can be applied for 7 days. So, you know the heat at 7 days now, you know the composition. You can again optimise that and observe the changes basically increase in total heat. So you will have difference in the coefficients for 7 days.

So, you have a coefficient a with value 510, b of value 247, c having value as 1356 and d with value of 427. These values of coefficients are very close to enthalpy of the complete hydration of these pure phases. In last lecture, we discussed that if you hydrate pure C3S for example, it tells you that it will release 517 kilo joule of heat per kg. So, we see 510 is very close to 517 that make complete sense because by this time reaction is almost complete.


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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



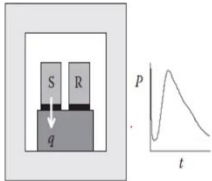
Primarily looking at different types of calorimeter, we have three different type namely isothermal, adiabatic and, semiadiabatic. In isothermal calorimeter, we try to maintain constant temperature and in adiabatic we want to prevent heat loss and if there is heat loss, we want to minimise that and keep it almost constant. In semiadiabatic the heat loss is not constant, it increases with 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.



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It is important to note that isothermal calorimetry is used only for small samples primarily samples weighing about 1 to 200 gram. So it is usually used for paste or mortar. In this type, we have reference sample which has similar heat capacity to that of the sample under consideration.

We measure the difference between actual sample and reference sample which gives thermal output (Thermal Power versus temperature).

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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



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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.

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In semiadiabatic, we are completely insulating the sample to prevent the heat loss. We are completely insulating the sample and measuring the temperature. So the output of this technique is temperature versus time and it is converted back to calculate the heat of hydration by considering into heat capacity of sample. The advantage of this technique is that it can be used for concrete or mortars samples weighing up to 10 kg.

But as we know that as the temperature increases, it influences the hydration. As you are insulating and as a consequence of cement hydration, the temperature will increase which will further influence the cement hydration which needs to be kept in mind.

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Adiabatic Calorimeter

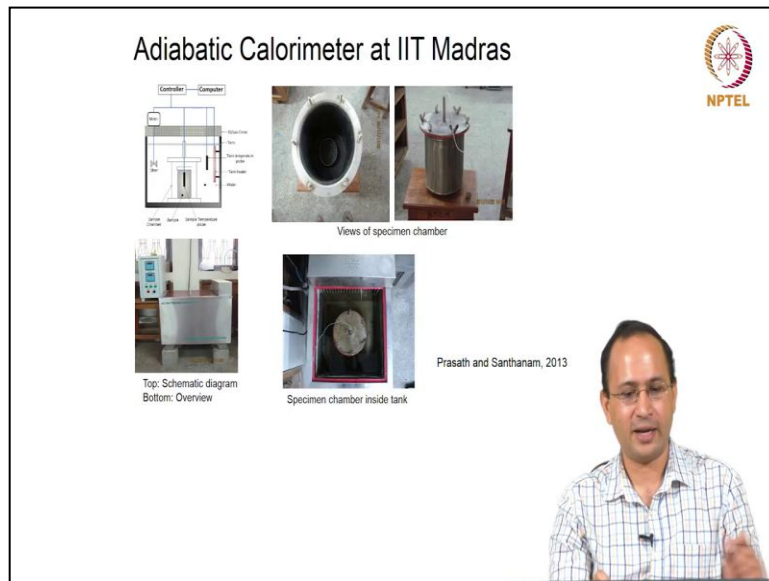
- Temperature of the sample surroundings is maintained at the same level as that of sample to prevent heat loss from the sample.
- Additional heat is supplied as the sample temperature increases during the hydration.
- Commonly used for mortar and concrete.

RILEM TC 119-TCE, 1997

In adiabatic we are trying to minimise the heat loss by maintaining the temperature of surrounding as close to the sample temperature. So, here you have the sample surrounded with

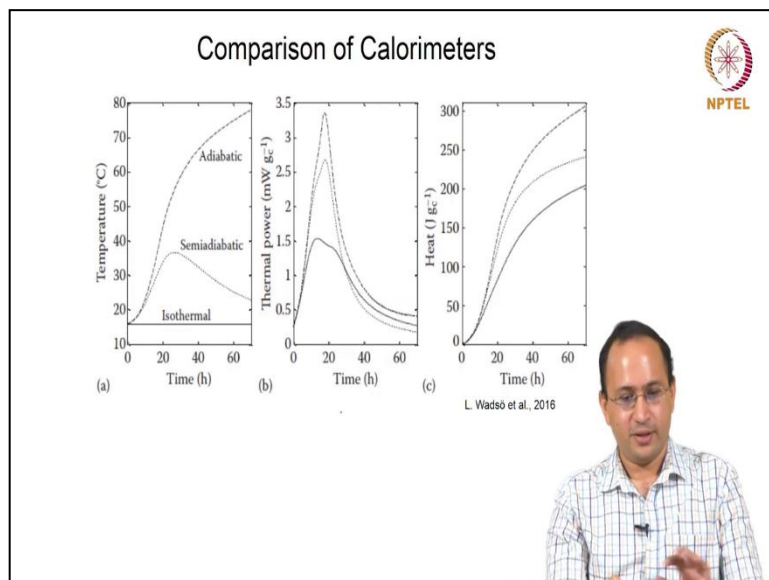
water bath, suppose the temperature of sample increases by 1°C we also increase the temperature of water bath by 1°C by this heat loss is minimised.

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We saw the kind of calorimeter we have at IIT Madras in last lecture. In detail, we have a sample in the sample chamber inside the water bath, and we have a controller to control the temperature of the water bath. We also have a sensor which goes in the sample and measures the temperature of the sample and then triggers the controller to control the temperature of water bath.

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Let us compare the three different types of calorimeter primarily Isothermal, adiabatic and semi adiabatic. Looking at the first plot where we are plotting temperature and time, for isothermal obviously we are trying to maintain the temperature. So, for isothermal it will give you a

constant temperature which for this case is around 15 degree Celsius. Now for semi adiabatic case, you have the same temperature sensor in the sample. But we see the increase in temperature as the heat loss is prevented. The heat generated due to cement hydration is trapped inside which leads to rise in temperature.


In adiabatic further you see higher temperature. In semiadiabatic you have higher heat losses because at higher temperatures we will have higher losses.

In adiabatic you do not have that much high losses so we see increase in the temperature. Similarly we can correlate it to the thermal power. Similar trends are seen for thermal power. Then we can integrate this thermal power to calculate the heat because we know that power is Joule per second and if it is integrated over time will give total heat.

So similarly the trends are seen for isothermal, semiadiabatic, adiabatic. It is important to mark the difference in values we get using a particular technique.


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Operational Issues: Isothermal Calorimetry


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- High precision thermostat is required to maintain constant-temperature environment.
- Stable laboratory temperature will improve the precision of calorimetric measurements.
- Measurement of calibration coefficients, baselines, and the time constants.
 - Calibration coefficient (ϵ): transforms the voltage from the heat flow sensor to thermal power
 - Baseline (U_0): signal (unit: volts) from the calorimeter when no heat is produced
 - Thermal power (P): $\epsilon (U-U_0)$; Specific thermal power = $\epsilon (U-U_0) / \text{mass of binder}$
 - Time constant: needed for rapidly changing processes; measure of thermal inertia of the sample that 'blurs' details in rapid events

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Now we look in to operational issues related to Isothermal calorimetry. In isothermal calorimetry, we are trying to maintain the temperature. So, it is very important to have a high precision thermostat.

High Precision thermostat is required to maintain constant temperature environment. So, stable laboratory temperature will improve the precision of calorimetric measurement. For example,

you have a calorimeter in a room and you want to do experiment at 22 degree Celsius and your room temperature is 40 degree Celsius so that is not good.

So, you need to have a stable laboratory temperature. Also the temperature should be stable, it should not fluctuate. It should not have a huge difference also the variation should be very low. Firstly, we have to calibrate the calorimeter which is very important. In isothermal calorimetry the basic thing is measuring the voltage.

So you have reaction suppose an exothermic where the heat is released. The heat flow sensor pick up when there is heat release or increase in temperature and this temperature increase can be related to the voltage. Now you want to convert that voltage to power.

So, the calibration coefficient simply transforms the voltage obtained from the heat flow sensor to thermal power. So, you have to get an appropriate calibration coefficient. For obtaining the calibration coefficient, firstly we should obtain the baseline signal U_0 when there is no reaction occurring or when there is no heat.

So, you have this reference baseline U_0 . Now, you know the U when there is a reaction you have some voltage. The difference between U and U_0 will give you the contribution from the reaction. This $U - U_0$ has to be related to P or thermal power through this calibration coefficient which you should know for the calorimeter used. This is the reason why it is always important to calibrate your calorimeter when you had to change temperature.

For different conditions, you cannot use same calibration coefficient which is among some of the issues which people face while working with calorimeters. Another thing is time constant. Time constant is nothing but thermal inertia. Simple way of understanding it is suppose you want to give some power, but if you measure actually you would not get the same.

Like for example you have there is certain amount of input and you want to raise the power for that but actually you see some lag of that power. This lag is attributed to thermal inertia. So, it is needed for rapidly changing processes. When the process is very rapid suppose when we are looking at early age hydration or hydration which takes place within hours, it is very important to pay attention to time constant.

But if you are looking at the main peak of Portland cement hydration for an example, which occurs at around 10 to 14 hours, you may not need this time constant but it is important because the measure of thermal inertia of the sample influences your rapid events.

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Time Constant

$$P_c = P + \tau \frac{dP}{dt} \quad \text{Tian Equation}$$

P_c is the corrected thermal power and τ is the time constant.

- Tian equation is used to correct rapid processes for the time lag of an instrument.
- Time constant describes the thermal inertia of the sample.
- Time constant can be calculated using the eq., $\tau = \frac{\sum C}{k}$
 - ← Heat capacity on sample side of heat flow sensor
 - ← Apparent thermal conductance of the heat flow sensor
- Tian eq. is not needed in the study of slow processes, like the main hydration of cement, but is very useful in the study of early hydration and other rapid processes.

L. Wadso, 2010



The time constant can be related to Tian equation as written below

$$P_c = P + \mathcal{T} \frac{dP}{dt}$$

Where P_c is the corrected thermal power and, \mathcal{T} is the time constant. So, again this equation can be used to correct the rapid processes for the time lag of an instrument. Especially it is important when you are looking at any rapid process like earlier hydration of cement.

Time constant can be calculated using this equation


$$\mathcal{T} = \frac{\sum C}{k}$$

Where, $\sum C$ is heat capacity on the sample side of heat flow sensor. We are talking about you have a sample in container, we call it ampoule and you have a ampoule holder also, so it is the summation of heat capacities of sample, ampoule, and ampoule holder. k is apparent thermal conductance of the heat prosensor.

You have a heat prosensor, you know the conductance so that you can calculate time constant. So again just to keep in mind, Tian equation is not needed in the study of slow processes like the main hydration of cement but is very useful in the study of early hydration and other rapid processes.


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Practical Notes



- Important to use proper references which have similar heat capacity as the sample, but no heat generation.
- For the same sample sizes and the same w/c ratio, the references don't need to be changed.
- Change references for different sample sizes.
- If baseline stabilization takes long time (more than half a day), this could be due to a bad reference.
- External mixing influences initial values of heat of hydration, hence the first 30 min of hydration contribution is generally ignored.

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Till now we have learnt about what we get from isothermal calorimetry, limitation in terms of kind of samples which be analysed. Also it is important to pay attention to a few practical notes. It is important to use proper references which have similar heat capacity as the sample but no heat generation for isothermal calorimeter. In last lecture, we saw that how do we do that.

Here we have to calculate the thermal mass by taking into account specific heat capacities of the material which we are using. For example, if you want to study cement paste you have cement and water as constituents, you know the heat capacities of cement and water. You can calculate the total heat capacity or you can calculate the thermal mass. Then you want to have equal thermal mass so, you know the heat capacity of your reference material.

In last lecture, we looked into the water but you can also use quartz then you can basically have similar heat capacity. Reference sample also has similar heat capacity but does not generate heat as there is no reaction. For the same sample size and same water cement ratio the references need not be changed. If you are using the same water cement ratio for example and same size so you may not need to change references.

As for different sample sizes, the thermal mass will changes that means we need to change references as well before conducting the experiment. If baseline stabilization takes long time or more than half a day this could be due to bad reference. So these are some signals you can get, you have to first get the baseline stabilization. If it is taking long time that means there is an


issue mostly you have not chosen your reference correctly or maybe the amount of reference is not correct. Usually, we mix sample outside the isothermal calorimeter.

Suppose you decide to study the cement paste hydration or cement hydration and you mix cement paste outside for few minutes, then you keep it in the calorimeter but that can create some disturbance. Early external mixing influences initial value of heat of hydration because you are not mixing it inside a controlled environment. So, usually when you mix it outside, it is good to ignore the initial 30 minutes of data because there is some influence of the external mixing.

But these days you can also get isothermal calorimeter where you can mix samples inside. So, you condition your samples. In this case you put cement and water at particular temperature and it will mix in a controlled environment. For this you do not have to ignore the data because you are getting in reliability in that.


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Operational Issues: Semiadiabatic Calorimetry



- Temperature stability and accuracy
 - Crucial when heat of hydration should be quantified.
 - Better control of temperature fluctuation and air flow around calorimeter is required.
- Calibration
 - Complicated and time consuming.
 - Requires measurement of electrical energy for maintaining a constantly increasing temperature of a calibration cylinder.
 - The heat loss coefficient and the heat capacity of the calorimeter are determined.

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Now we look in to the operational issues related to semiadiabatic calorimetry. Temperature stability and accuracy is very important. It is very crucial when the heat of hydration needs to be quantified and better control of temperature fluctuation and air flow around calorimeter is required. It is very important to know the temperature of surrounding where your calorimeter is placed and that is why you need to have a stable rooms where you can control the temperature.

You cannot just keep in a room where the temperature is not controlled as that influences both measurements of isothermal calorimeter and semiadaibatic calorimeter. Calibration in this case


of semiadiabatic calorimeter is complicated and time consuming. It requires the measurement of the heat loss. In semiadiabatic you are insulating your sample and measuring the heat loss.

The main thing is that is the heat loss. Even if you have insulated the sample, there is going to be heat loss and that heat loss will change with temperature. For example if the temperature is 100 degree Celsius the heat loss will be higher as compared to temperature of 60 degree Celsius. You have to understand the heat loss and for that you have to calibrate it. So it requires measurement of electrical energy for maintaining a constantly increasing temperature of calibration cylinder.

You give some electrical energy to this calibration cylinder to maintain the increase in temperature. Now you turn it off and then you measure the heat loss or temperature loss that is how you will be able to calculate the heat loss. And also can use that to calculate the heat capacity. So heat loss coefficient and heat capacity of the calorimeter need to be determined. So these are the steps for calibration.


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Sample Preparation: Isothermal Calorimeter


NPTEL

- Sample a homogenous specimen (paste or mortar) out of the mix
- Weigh the constituents in the vial and mix inside the vial with a plastic spatula
- Internal mixing in the calorimeter preferred for better studying the initial hydration (within 30 mins)
- Important to keep in mind that mixing energy influences the hydration rate (see the next slide)

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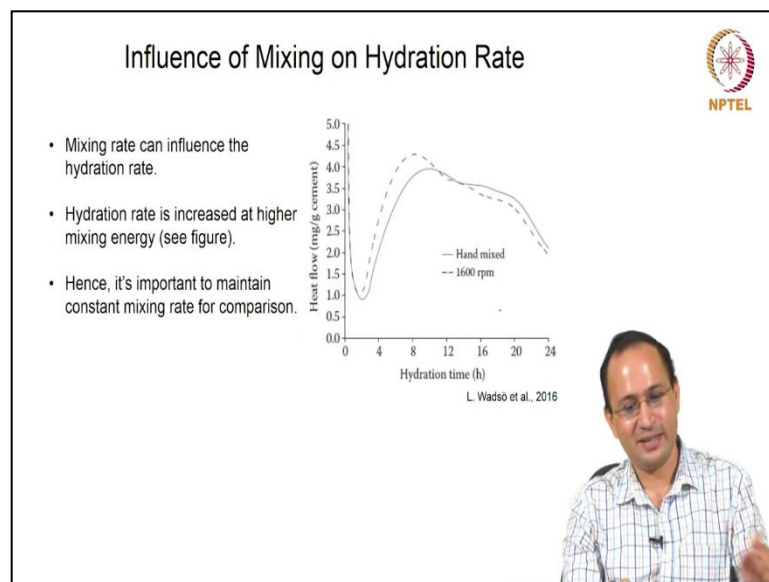


Now, looking for the sample preparation for isothermal calorimeter, so we need to always make a homogeneous specimen. So if you are talking about cement paste, you want to make sure that the sample is representative. Similar thing applies to mortar also. It is very important for these kinds of studies. So it is important to have multiple samples and making sure that the samples are homogeneous.

We have to weigh the constituents in vial and mix outside inside the vial with plastic spatula. In this process we weigh the vials and put the constituents in the small vials and weigh it. Then you know, how much of cement you want to use. You are weighing the cement and then you are adding water for an example and then you are mixing it. Internal mixing in the calorimeter is preferred for better studying initialised.

As I said because if you want to look into the hydration occurring within one hour, then you have to go for internal mixing rather than external mixing. It is also important to pay attention to the mixing energy which influences hydration. So suppose you decide to mix it outside and you mix it for 2 minutes and someone else mixes for 3 minutes, this will have different mixing energy.

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Here we see the influence of the mixing energy on a plot of heat flow versus time. One is hand mixed sample and other is mixed at 1600 RPM. So, when you have 1600 RPM, you accelerate hydration and see that the curve also moves towards left. So the mixing rate can influence hydration rate. It is very important to have a similar protocol all the time.

If you do not follow similar protocol, a small change will influence significantly because this technique is very sensitive as we are talking about milli-watts or nano-watts of signal. Hydration rate is increased at higher mixing energy. That is why it is important to maintain constant mixing for comparison.

You should not mix one sample for 2 minutes, another for two and half minutes and next one for 3 minutes for the same study that will significantly influence the data.