Characterization of construction materials
Dr. Piyush Chaunsali
Department of Civil Engineering
Indian Institute of Technology, Madras

Lecture No - 25
Application of thermal analysis to study construction materials - Part 2

Hello everyone. So today we will look at the application of thermal analysis to study construction materials. How can we use these techniques to understand the construction materials better. That will be the goal of today's lecture.

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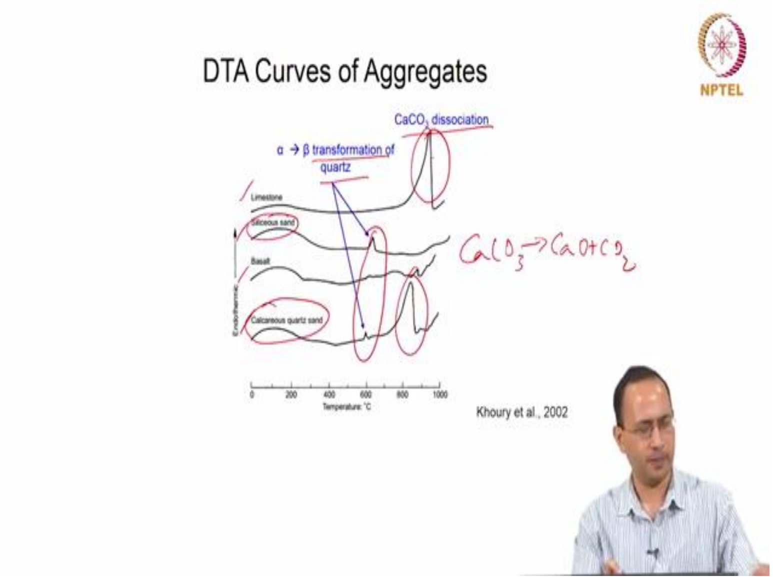

DTA Curves of Aggregates

$CaCO_3 \rightarrow CaO + CO_2$

Khoury et al., 2002

So if you look at DTA of aggregates, so we can use this differential thermal analysis to probe the aggregates we use to make concrete, for an example. What you see here is the DTA curves for different types of aggregates, starting from limestone, siliceous sand, basalt, calcareous quartz sand - these are the common aggregates used in concrete. How these respond to DTA?

So basically you see this quartz transformation, i.e., quartz transforms from alpha (α) to beta (β) form. That transformation occurs at around 575 °C. So these are the peaks which can be attributed to this transformation of quartz, and it makes sense because you are talking about siliceous sand and quartz sand, so it has lot of quartz, so that will transform, so DTA can be used to study that.

Also you see peaks, in limestone, and even calcareous quartz sand, this is because of $CaCO_3$ dissociation. You have calcite (calcium carbonate). So calcium carbonate will decompose like ($CaCO_3 \rightarrow CaO + H_2O$). So this is the decomposition. So you see these endothermic peaks - endothermic means you need heat. So, basically we can use DTA to understand the aggregates, which is the idea. You'll have to make a small powder, basically a few milligrams.

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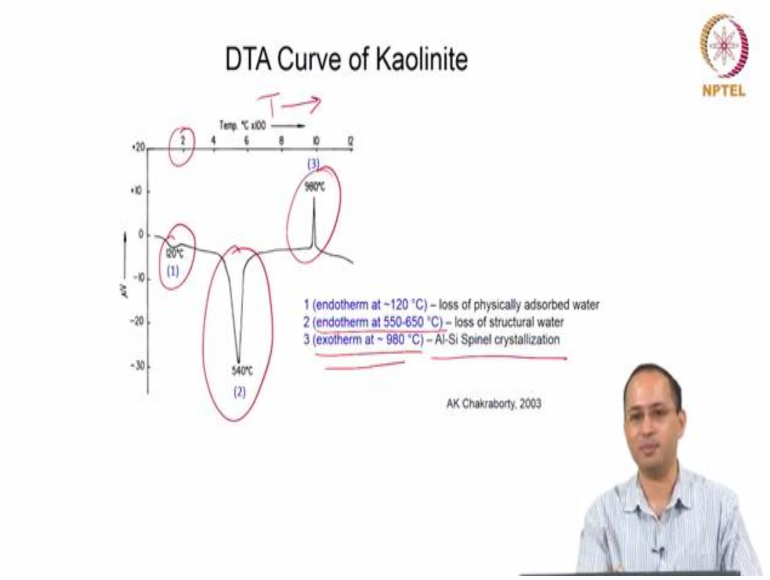

DTA Curve of Kaolinite

1 (endotherm at ~120 °C) – loss of physically adsorbed water
2 (endotherm at 550-650 °C) – loss of structural water
3 (exotherm at ~ 980 °C) – Al-Si Spinel crystallization

AK Chakraborty, 2003

This is a DTA curve of kaolinite. Kaolinite is a type of clay, commonly found. So what happens when you increase the temperature? So you see, X-axis is temperature: 200, 400, 600, 800, 1000°C temperature. So you basically, if you look at the DTA curve up to 1000 °C, we are talking about, see 1100, 1200 °C, you see small peak here, labelled as (1) in the graph in slide, endothermic peak, which is because of loss of physically adsorbed water. It will always have some water, when you lose that water you see this peak.

The second peak - major peak (2), because of loss of structural water, the water present in the structure gives you this peak, endotherm, that is the endothermic peak at around 550-650 °C. So, you are losing structurally bound water.

And then you have this peak (3) at around 980 °C, it's an exothermic peak. See the difference endothermic and exothermic, here you are releasing heat. It is because of some crystallization, we are not going in detail, it is like, because your clay is made of aluminum and silicon. So there is this spinal crystallization which occurs at around this temperature. So, basically we can use differential thermal analysis to understand the clay. It can give us what kind of transformations can occur when you heat the clay to really high temperatures.

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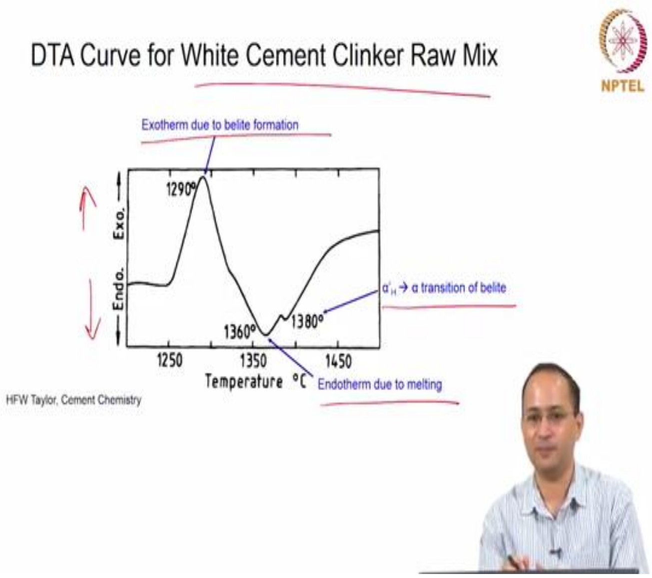

DTA Curve for White Cement Clinker Raw Mix

HFW Taylor, Cement Chemistry

Here is an example of DTA curve for white cement clinker raw mix. We are not talking about cement paste; it's white cement. So, here is the DTA curve, so you see endotherm is in this direction and the exotherm in the other direction. Usually when you plot DTA you will have to decide which direction is exotherm. Usually, it is drawn this way, as shown in figure.

So, this first peak around 1290 °C is the exothermic peak due to belite formation. Belite forms at around that temperature. So you can see that is given as exothermic peak. Then you see an endotherm due to melting, i.e., if you further heat it, melting will start. So you see this endothermic peak (1360 °C). These are the major things. Then the small peak (at 1380 °C) is because of the transition. Now your β has different polymorphic forms. So α'_H when it transforms to α gives you this. So these are some signatures we can get, through DTA.

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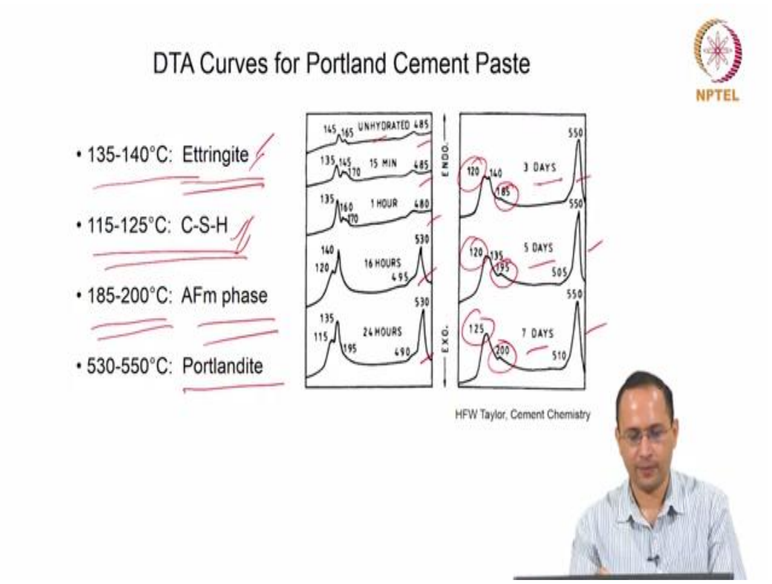

DTA Curves for Portland Cement Paste

- 135-140°C: Ettringite
- 115-125°C: C-S-H
- 185-200°C: AFm phase
- 530-550°C: Portlandite

HFW Taylor, Cement Chemistry

Now, let's look at the DTA curves of Portland cement paste. You mix cement with water and then make paste and also starting with the unhydrated part. You see how the DTA curves change with time - 15 minutes, 1 hour, 16 hours, 24 hours, 3 day, 5 day, and 7 day. What is the difference? You see some changes in the DTA curve, some things are forming. That tells you the reaction is taking place, new phases are being formed. So from here, you can identify what kind of phase is precipitating.

Starting with, you see first of all at 485 °C, around 500°C, you see major peaks. Now at 7 days you have a very prominent peak, it's because of portlandite. We all know when cement hydrates you form C-S-H and calcium hydroxide. So prominently, you see this peak, tells you and it is around 500 °C for an example. So this tells you that new phase has formed which is not present here or in very low amount in unhydrated, and at later age, significant amount of this phase is there.

Now you see a lot of things are happening at early age, from 100 to 140 °C, there a lot of phases. So first of all, Ettringite is formed in this range of 135 to 140 °C. That range is because of Ettringite.You can see that it overlaps with C-S-H, because calcium silicate hydrate will also lose water at that range. So you see at the later age, let's say 3 day, 5 day, 7 day, you see this peak around 120-125°C, it can be primarily due loss of water from C-S-H.

And then you also have AFm phase; your AFt phase (ettringite) gets transformed to monosulfate. For this, just refer to any standard book on cement hydration, we are not going in detail, but AFm phases are formed. So you see at around 185 to 200 °C; this is because of AFm phases. So see, from DTA curve we get lot of information, what kind of phases are formed.

So it also poses a challenge, sometimes there might be overlap. Like you can see here ettringite, C-S-H, there is a quite a bit of overlap between them. So if you really want to identify what kind of phase you have, you'll have to try other techniques. But idea is the DTA curve can be used to get some insight, like the kind of changes the material undergoes when it is undergoing temperature change.

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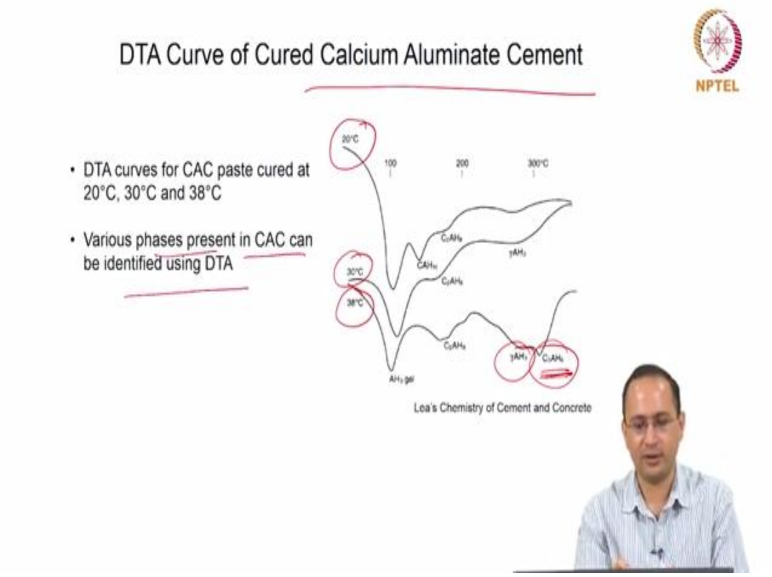

DTA Curve of Cured Calcium Aluminate Cement

- DTA curves for CAC paste cured at 20°C, 30°C and 38°C
- Various phases present in CAC can be identified using DTA

Lea's Chemistry of Cement and Concrete

Let's see the DTA curve for cured calcium aluminate cement, CAC. Calcium aluminate cement is different from Portland cement. It has calcium aluminate, if it hydrates, forms calcium aluminum hydrate (CA). We talked about the conversion, that's what happens at high temperatures. So you can see here, these are the DTA curves of cured calcium aluminate cement, cured at different temperatures 20 °C, 30 °C, 38 °C. So we talked about the conversions, so you can see here in 38 °C cured sample, you see C_3AH_6. This is the conversion that happens. Usually it may take time, but using DTA we can identify what kinds of phases are formed? So when you cure CAC at 38 °C, you see presence of C_3AH_6. And also you see γAH3, which is the crystalline form of AH3 or gibbsite. Initially you have amorphous gel. So, various phases in calcium aluminate cement can be identified.

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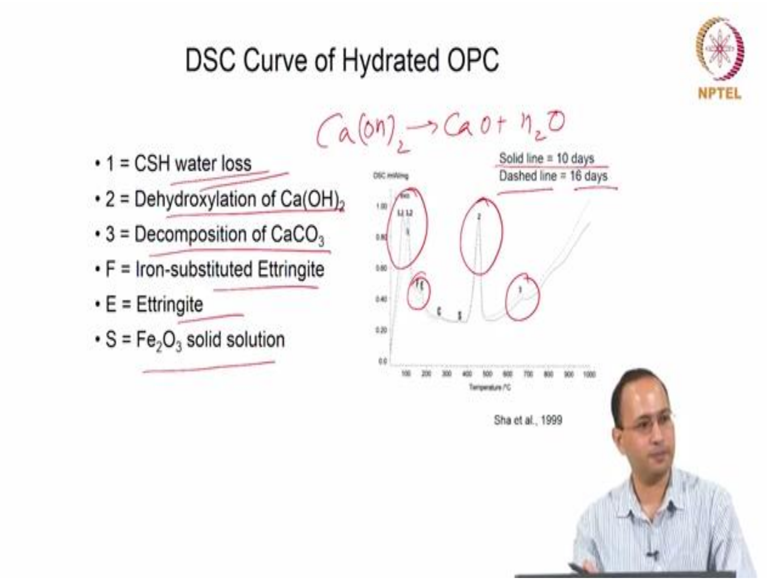

DSC Curve of Hydrated OPC

$Ca(OH)_2 \rightarrow CaO + H_2O$

- 1 = CSH water loss
- 2 = Dehydroxylation of $Ca(OH)_2$
- 3 = Decomposition of $CaCO_3$
- F = Iron-substituted Ettringite
- E = Ettringite
- S = Fe_2O_3 solid solution

Solid line = 10 days
Dashed line = 16 days

Sha et al., 1999

Coming back to DSC, now we are talking about heat. So DSC curve of hydrated OPC. So DTA, DSC curves will look similar, only thing is Y-axis will be different. In DTA, you will have temperature as Y-axis, and in DSC you’ll have heat flow. So again, you get the similar information.

So here we have two different samples. One is the solid line which refers to 10 days-old sample. The dashed line refers to 16 days-old sample. But you see similar peaks. So what you see, Peak 1 primarily is because of water loss from C-S-H, which occurs at around 100°C regime. Then comes Peak 2, major peak, which is at around 450, 500 °C. This is because of loss of water from Portlandite; dehydroxylation of calcium hydroxide. What does that mean? $Ca(OH)_2 \rightarrow CaO + H_2O$

This is very powerful. So we can see that change. And also third peak, obviously it is small. It depends on the amount of calcium carbonate you have in system. If you have a significant amount of calcium carbonate then you will see a significant peak here, but here you see small peak but that tells you about the decomposition of calcium carbonate, .

We have some other smaller peaks you see here, because of iron-substituted ettringite (F), ettringite (E) and also some solid solution. So but the idea is you are able to identify easily the major peaks.

That is a good question, how do we understand? You'll have to look at, so you'll have to do test on, like, pure phases. So calcium hydroxide for an example, when you just take calcium hydroxide and do test, you will get a signature. So then, it is like a matching, when you do peak matching for your X-Ray diffraction, there is a database where we know the information. So Calcium hydroxide, when you heat it up, it will start decomposing at only at around 450 °C. There is a slide on that. So, it will be more clear. So more or less. So in Portland cement system, peak around 450 °C tells you that it is portlandite, because that is where the portlandite (calcium hydroxide) dehydroxylates.

Similarly calcium carbonate, that occurs at later stage, at around 600-700 °C, you will start seeing that. What happens is the decomposition of calcium carbonate into calcium oxide and carbon dioxide.

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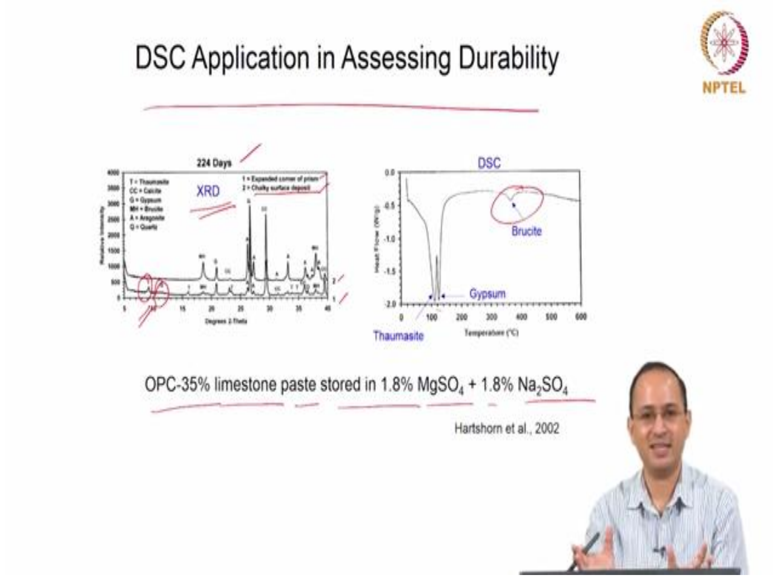

DSC Application in Assessing Durability

OPC-35% limestone paste stored in 1.8% $MgSO_4$ + 1.8% Na_2SO_4

Hartshorn et al., 2002

Again the point is to look at multiple techniques to get better ideas. So here let us look at the application of DSC in assessing durability. So, on the left side you have XRD plot. XRD tells you what kind of phases you have. So here you see Pattern 1 and 2, where 1 is OPC with 35% limestone paste stored in 1.8 % $MgSO_4$ and 1.8 percent Na_2SO_4 for 224 days.

So we are talking about a kind of sulfate attack. So in this case what we are talking about is, thaumasite type of sulfate attack. So you see the formation of T - thaumasite here, denoted as T. It’s very close to ettringite. We discussed that in XRD. So you have this X-ray diffraction pattern from two different places. So Pattern 1 is expanded corner of prism, so apparently what they did is, they exposed these prisms to this solution for a long time (224 days), then they took sample from expanded portion, the corner of prism and did XRD, and found this. Chalky surface deposit, there must be some surface deposit and they did XRD on that. So you have a different X-ray diffraction pattern.

But let us look at this, so you are seeing the formation of thaumasite. That can also be confirmed here. Look at the DSC curve. Here you see two major peaks, one is because of thaumasite and one is because of gypsum. If you look at the XRD, you see formation of both, thaumasite and gypsum. And there is another signature here, which is because of Brucite (magnesium hydroxide). So when you combine techniques, that gives you more insight, but one technique can also be used to identify the changes or phase formation.

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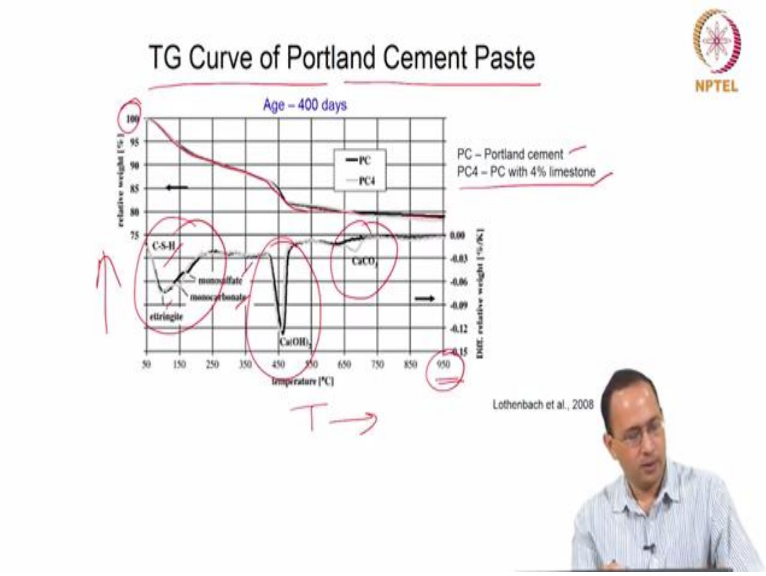

TG Curve of Portland Cement Paste

PC – Portland cement
PC4 – PC with 4% limestone

Lothenbach et al., 2008

Now we will look at thermogravimetry, it is commonly used because we can quantify it. Basically we can and find out the phases, phase amount like calcium hydroxide, calcium carbonate easily. So it is commonly used, you will see lot of papers on this.

So how does a TGA curve of Portland cement paste look like? So TG is basically measuring the mass-loss, mass change with temperature. So you always see on X-axis, you have temperature, Y-axis you have relative weight. When you start your experiments nothing is lost. So it's 100%. That is how you will see lot of times. So 100% means nothing has been lost. So when you start heating the sample, you see mass loss. So this your mass-loss curve. So you see when you reach 950 °C, in this case, you will have almost lost 20% of weight. Now, your relative weight is around 80%.

Earlier we also talked about the importance of DTG. So by looking at this curve, we see there is something happening here, but visually we can get more information when you take the derivative. So derivative means you are using the same data, no new information, but you are plotting the slope. So from the derivative plot, easily you can identify that there are three regions of significance.

One is this early region at around 100 to 150 °C. Second is somewhere here ($Ca(OH)_2$) Third is somewhere here ($CaCO_3$). Lot of things are happening, so around 100 °C you start losing water; you are losing water from C-S-H, the ettringite also starts decomposing, you have other phases, monosulfate, monocarbonate in this case, because we are talking about two samples here. The dark one is PC, Portland cement, and the bright one is, PC4 means Portland cement with 4% limestone. So notice in limestone case, first of all, you see this extra peak. Since you have more limestone, you are going to see more mass-loss because of limestone, calcium carbonate. So this is evident.

Here again, whenever you see peak at around 450°C, it is because of portlandite, because OPC will hydrate and form C-S-H and calcium hydroxide. But this region at around 100 to 150 °C, you have an overlap of lot of peaks - ettringite, C-S-H, which is why it is very hard to quantify these phases because it could be anything, it could be C-S-H, it could be ettringite. But monocarbonate or monosulfate are a little away, they are different, but at least there is a big overlap between C-S-H and ettringite. So we can clearly use this TGA to quantify calcium hydroxide where there is no overlap and calcium carbonate without an issue.

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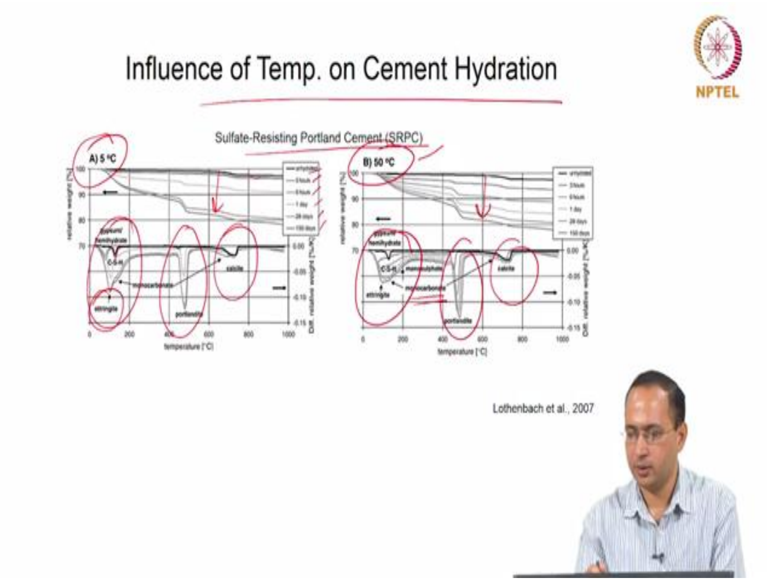

Influence of Temp. on Cement Hydration

Sulfate-Resisting Portland Cement (SRPC)

Lothenbach et al., 2007

Also, we can use this TG to understand the influence of temperature, like, what happens when you increase the temperature from 5 °C to 50 °C?

So again, here is an example of Sulfate-Resisting Portland Cement - SRPC. You see lot of lines, lot of curves. Here you have unhydrated, means without water, then you add water so what happens after 3 hours, 6 hours, 1 day, 28 days, 150 days, so we are monitoring the progress of hydration. How the hydration affects the TG curve is what we are looking at.

So at 5°C, you see that initially there is not much mass-loss. But slowly you are seeing increase in mass-loss. Look at the legends, it is clear. Because you are forming products, you are forming new phases, so that is because of the dissociation, decomposition of the new phases. So again, you see three big regimes. In Portland cement, you will see these, at around 100-150 °C that will be one region, then you have around 450 °C - portlandite, then you have calcite, 600-700 °C.

See also you can notice, portlandite peak initially it is here then it is increasing, because it is directly related with the amount. We are measuring the mass change. So more mass-change means more amount, and so you see change in the peak, so it can tell you how the hydration is progressing? What is increasing? What is decreasing? So in this case, you see increase in portlandite with time. See here also, initially you see some gypsum/hemihydrate. Then it disappears, because gypsum will react with C3A and form ettringite. So initially you see that, but later on you see all ettringite, and C-S-H.

Same thing, if you do at 50 °C, one thing you will notice, if you cure your sample at high temperature you change things. See here, if you look at the weight-loss curve on the left side, there is a slow change (compare at 3 hours, 6 hours, etc.). But here at 50 °C, you have a rapid change, which is the effect of increase in temperature. So you are accelerating the reaction, which gets reflected in DTG also. DTG is nothing but first order derivative of your TG curve. So again, similar regions can be identified. And depending on the composition, in this case, you have monocarbonate, because they used little bit of limestone in this case. But we have to be careful, when you want to quantify ettringite using TG, because the peak is overlapped with C-S-H, because C-S-H also starts losing water at about that temperature. So for quantifying ettringite, X-Ray Diffraction is a better technique. But for quantifying Portlandite, Calcite, you can easily use thermogravimetry, because there is no overlap.

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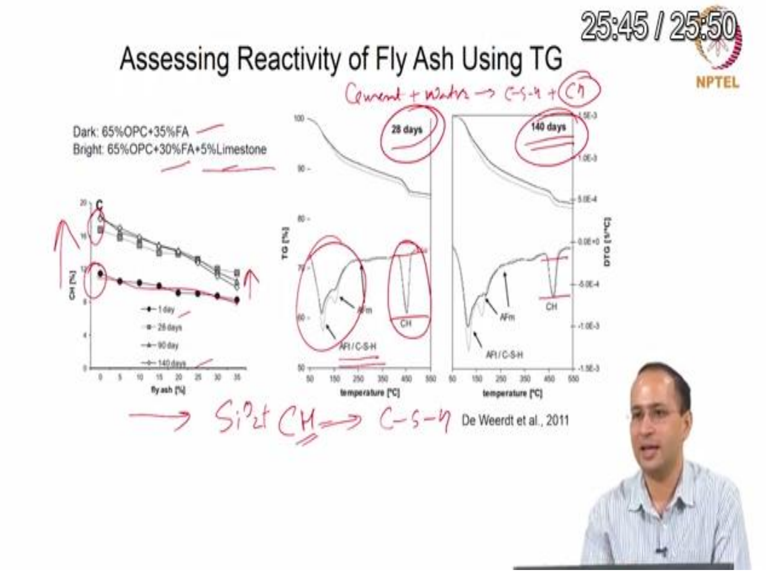

Assessing Reactivity of Fly Ash Using TG

Cement + water → C-S-H + CH

Dark: 65%OPC+35%FA
Bright: 65%OPC+30%FA+5%Limestone

→ SiO2 + CH → C-S-H

De Weerdt et al., 2011

Also, we can use it to assess the reactivity of fly ash. We use fly ash, and why do we use fly ash in concrete? Because fly ash is pozzolanic, which means it reacts with calcium hydroxide and forms calcium-silicate-hydrate. See when cement is hydrating it gives you C-S-H and calcium hydroxide. Cement + Water → C-S-H + CH. Now somehow if you could get some amorphous silica, and make it react with CH, you will form additional C-S-H. So, how do you assess reactivity of fly ash? If it could measure calcium hydroxide - that will tell you how reactive the fly ash is, because if it is reactive, it will react with calcium hydroxide and decrease the amount. It will react at a faster rate and then there will be a reduction in the amount of calcium hydroxide.

So, that is what you see. So, first of all, let us look at the TG curves. So dark lines are for 65 % OPC, 35 % fly ash and the bright ones are for 65 % OPC, 30 % fly ash, and some limestone 5 %. So you see this typical response of TG. Now if you plot DTG, it becomes clearer. What you see is a region here, we are looking at the region up to 550°C, in this case, because of calcium hydroxide and this initial region where you have C-S-H, Aft, ettringite, and then you have a subsequent peak AFm. .

What difference do you see? When you do thermogravimetry at 28 days and at 140 days, you would expect your fly ash will react with calcium hydroxide and the amount of calcium hydroxide will reduce. That is what you would expect because of the pozzolanic reaction. So the two graphs (28 days and 140 days) are on the same scale here. So you can just compare the peaks. So you see a reduction in the amount of CH. So, it tells you about the pozzolanic reaction.

Now same thing has been plotted here. CH (%) means percentage of calcium hydroxide, plotted against the fly ash amount (%). So when you have a 0% fly ash, you see that cement is hydrating and then with time it increases. Your cement is hydrating and you have more and more calcium hydroxide formation. What is happening, when you are adding fly ash? Your amount of calcium hydroxide is decreasing. And at 1 day, this could be because of dilution also. But with time what you see at 140 days, you see that CH amount is lesser as compared to the mix with no fly ash. So you are consuming calcium hydroxide.

So it is a very good way to assess the reactivity of pozzolans using thermogravimetry, by quantifying the amount of calcium hydroxide, because that is what directly it corresponds to. Pozzolanicity means reaction between amorphous phase of your pozzolan with calcium hydroxide. So by finding out how much calcium hydroxide is left, you can tell how much has been consumed.