Characterization of construction materials

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Lecture No - 24

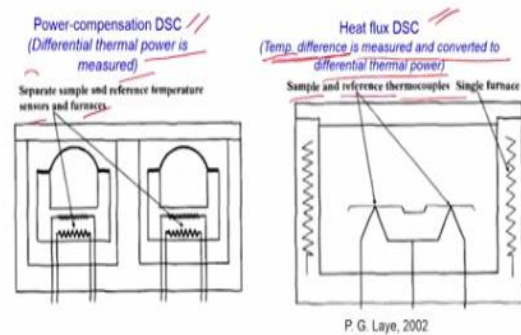**Thermal Analysis- Part 2**

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So, in DTA, we know that we are measuring the difference in temperature. First I will go over the techniques, and then we will look at the applications. Differential Scanning Calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured, as a function of temperature.

So here what we are measuring is the difference in the amount of heat, to increase the temperature of sample and reference are measured as a function of temperature. As you heat it up, your temperature will change, then you want to minimize that. So you are measuring the heat supplied. Suppose you need heat suppose it is endothermic reaction, it is taking heat, you supply heat.

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Types of DSC

Power-compensation DSC
(Differential thermal power is measured)

Separate sample and reference temperature sensors and furnaces

Heat flux DSC
(Temp. difference is measured and converted to differential thermal power)

Sample and reference thermocouples   Single furnace

P. G. Laye, 2002

So let us look at what are the common types of Differential Scanning Calorimeters. So, one is Power-compensation DSC. Idea is here we have a separate sample and reference temperature sensors and furnaces. So you will see two separate sample and reference temperature sensors and furnaces, they are separate. And, in this case Differential thermal power is measured.

In the Heat flux DSC, the sample and reference are put together, that is, they are not separate. And we are measuring the temperature difference. And then we are converting into thermal power. See eventually in DSC you are interested in measuring the thermal power. So in this case we are measuring differential temperature or temperature difference, and then converting it to differential thermal power. In Power compensated DSC, we are directly measuring the thermal power.

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DSC vs. DTA
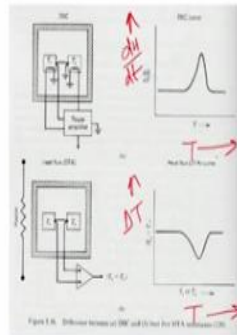
Wesley WM. Wendlandt, 1986

Now you must be wondering, what the difference between DSC and DTA is. As I explained in DTA, you have a temperature difference ΔT, plotted against the temperature.

$$\Delta T = T_S - T_R$$

Where T_S is the sample temperature and T_R is the reference temperature.

Here (upper graph in slide), we have power, $\frac{dH}{dt}$ vs. T, so here we are directly measuring the power. That is the difference between DSC and the DTA.
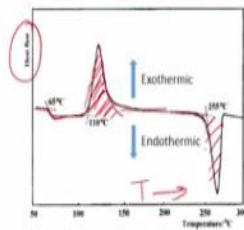
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DSC: Example

- 60-70°C: glass transition
- 110°C: crystallization
- 255°C: melting

P. G. Laye, 2002

So, let's see a few examples of DSC. So, here is a typical DSC curve for polyethylene terephthalate. So, what happens when you increase the temperature to the heat flow? This is the

temperature increase. So you see some drop (65°C). Then, the curve stays like this (till 110°C). Then you see the peak, this is exothermic peak. Then you see endothermic peak (starting from 255°C). Exothermic means you are releasing heat, endothermic means you are using heat.

So it can tell you what is happening, that is the point with this DSC curve. So, basically this small drop here tells you that it's the glass transition temperature range between 60 to 70°C. That is the glass transition happening. At 110°C, this is because of the crystallization, and we know crystallization is exothermic. So, it tells you what kind of reactions is taking place here.

At 255°C, then you have melting, melting will need heat. So you see endothermic peak. So, it can give you a lot of information about the reactions.

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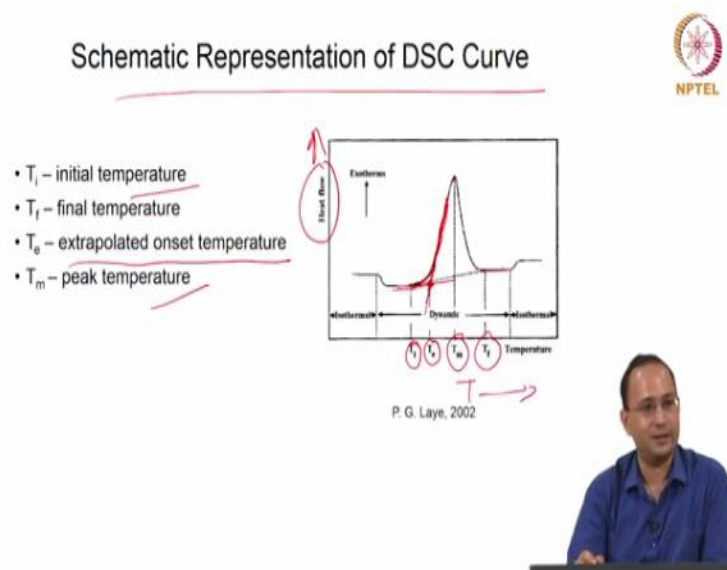
Now we will go towards the quantitative; how we can use it to measure things. So, before we do that, let us look at a schematic representation of DSC curve. So again, you always see when you talk about DSC, heat flow is plotted against temperature. Heat flow is plotted on Y-axis and temperature on X-axis. Now, you see this exothermic peak. So now the question comes what temperature should we use?

You see, T_i is initial temperature, you see that (in Graph in slide) beyond T_i you see that things are changing. It is not flat anymore and the slope is changing.

Then you have this linear portion. Now, if you draw a line tangential to the linear portion, and tangential to your initial portion. The point where it intersects is called T_e, which is extrapolated onset temperature.

See, T_i is initial temperature or you can say it as onset temperature. Things are changing now, now T_e is extrapolated onset temperature I will come back to it, why it is important? But for now you can see that we are extrapolating, as we are drawing a tangent here (initial), and then we are drawing a tangent on this curve. And where it is intersecting, that is T_e. T_m is the peak temperature, at the peak. T final (T_f) is this one, where it has now become flat. These are some of the characteristics.

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Now if you look at the effect of heating rate, for an example. Whatever we discussed earlier, like sample size, heating rate, all that will affect the DSC curve also, because it is basically same, and the response is going to be very similar.

In this case, we are measuring the heat. So, if you look at the effect of heating rate on the DSC curve you see, as we saw earlier, as you increase the heating rate, the peaks become broader and deeper.

That is what you are seeing here. So 1°C, 3°C per minute; what is happening? Peaks are becoming broader and deeper. What you notice is that your peak temperature is changing, but extrapolated onset temperature does not change. So that is the usefulness. So efficacy of extrapolated onset temperature, compared to peak temperature, because it does not change with heating rate.

See here, I mean, extrapolated onset temperature will be somewhere here, extrapolated means you extrapolate, and you take tangent at this initial regime. And then you draw a tangent. So, there is not much change. If you see the peak temperature has changed significantly. So there is some usefulness in using extrapolated onset temperature, because it is unaffected or is not as much affected as your peak temperature, when you are using different heating rates.

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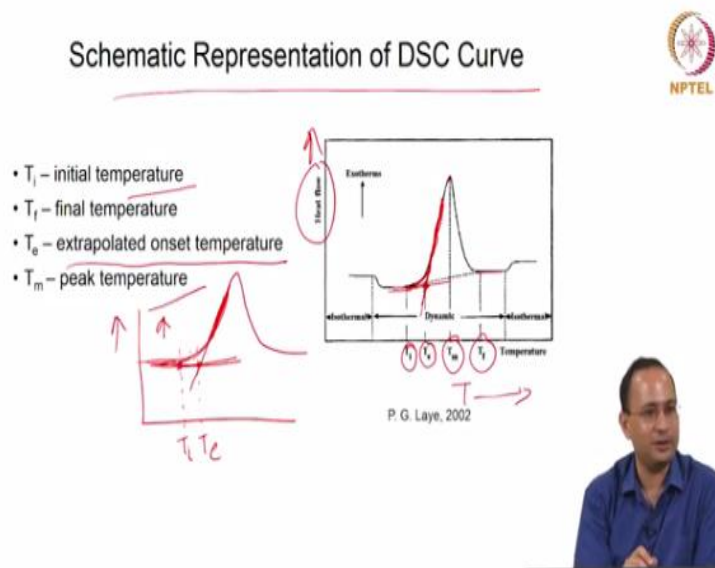
Question is how do we get this extrapolated onset temperature. So, so let us look at this plot (drawing in slide – Refer Figure 1), so you have this exothermic peak. So, you have the flat region where nothing is happening.
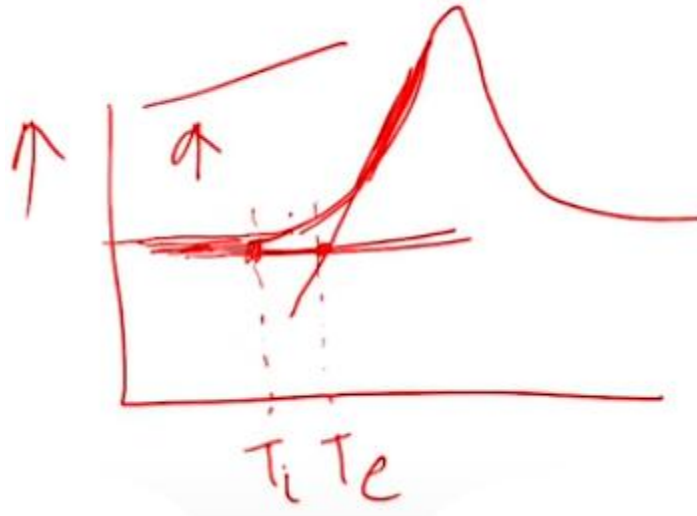
Figure 1 Extrapolated onset temperature

Things are changing, suppose this is the point T_i when the slope starts changing. Now you are in this linear regime, assume this is a linear part, and now you can draw a tangent here. Now you can initially you have, you draw a tangent here (flat region), so it will intersect at some point that can be taken as extrapolated. So it is an extrapolated onset temperature. So your onset temperature is T_i, but this is extrapolated.

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So, heat capacity can be calculated. Basically we are calculating the power. And if you integrate, that is, if you calculate the peak area, you will be able to calculate the heat capacity. Enthalpies

of transitions and transformations - any transformation, or transition which happens, we can calculate associated enthalpies, because basically we can measure the heat - that is the idea.

Purity - if you are talking about the impurity in something, we can see we can measure the purity, degree of purity. And also, chemical kinetics, thermal conductivity.

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Let us look at how do you calculate heat of transition? Something is happening, when something is transforming or transitioning. We want to know what the heat of transition is. So basically, this is a simple equation:

$$\Delta H\, m = KA$$

Where ΔH is the heat of transition reaction

m is the mass of reactive sample

K is the calibration coefficient

A is the curve peak area.

Here you can calculate the area under the peak, for this particular transition. The calibration coefficient, you can get for particular instrument, if you know heat of reaction of a material. So you use standards, where you know what the heat of reaction is. Then you can get the calibration coefficient, you know 'K'. Now you do your experiments, you can calculate A, A is the peak area, and then based on the mass, you can calculate ΔH. So this equation gives you heat of transition.
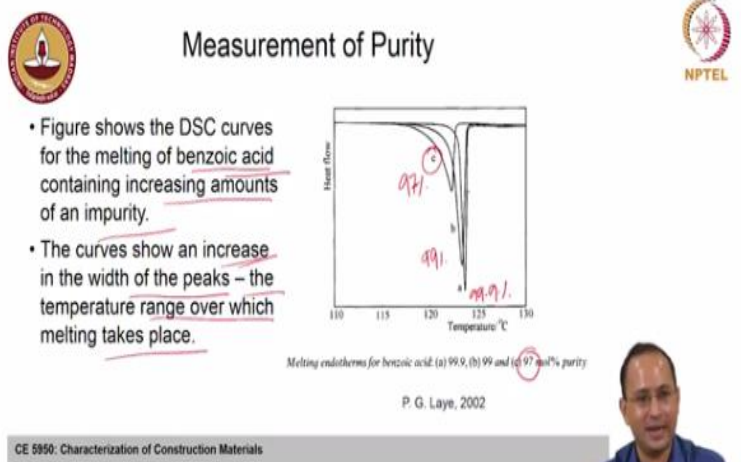
Measurement of purity - here is an example; the figure shows the DSC curves for the melting of benzoic acid containing increasing amounts of an impurity. So, you have benzoic acid and as we increase the amount of impurity, how it affects your DSC. So is what do you see here? 'c' is 97% purity, 'b' curve is for 99% purity and 'a' is for 99.9% purity.

See how the purity affects your DSC curve. So, the point is, this DSC measurement can be used to assess the purity. So the curve shows an increase in the width of peaks – basically, the temperature range over which the melting takes place. If it is purer, the peaks will become narrower. So, idea is you can use the DSC curves and get an idea about the purity, if you are thinking about assessing the purity in your sample.

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Thermogravimetry

- In thermogravimetry, change in sample mass (mass-loss or gain) is determined as a function of temperature and /or time.

- The measured mass-loss curve provides information on:
  - Changes in sample composition
  - Thermal stability
  - Kinetic parameters for chemical reactions in the sample

The third technique which we will talk in this thermal analysis will be Thermogravimetry. It is very commonly used. So what does thermogravimetry mean? In thermogravimetry, we measure the change in mass. In DTA, we are measuring change in temperature between sample and reference. In DSC, we are measuring the heat between sample and reference. Here we are measuring the mass change as you increase the temperature.

So basically we are determining the mass loss or gain, depending on the reaction as a function of temperature and/or time. And this measured mass-loss curve can provide information on:

- Changes in sample composition - what kind of changes is happening?

- Thermal stability, how stable the sample is.

- The kinetic parameters for chemical reactions in the sample.

Again, these are the physical and chemical processes, which can be studied using thermogravimetry, because there is some mass change. If you are interested in mass change, then you can use thermogravimetry. So gas adsorption, desorption, phase transition, decomposition, when something is decomposing with some mass loss, chemisorption. So, these are the phenomena causing mass changes. As long as there is mass change, we can use thermogravimetry to capture them.
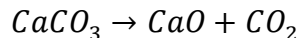
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So weight loss can happen when you have decomposition, when something is decomposing. Simple example one can think of is, this also decomposition right?

$$CaCO_3 \rightarrow CaO + CO_2$$

$CaCO_3$ is converting into calcium oxide and carbon dioxide.

Evaporation - you are losing moisture, loss of volatiles.

Reduction, Desorption. These are the typical processes, where we have weight loss.

Similarly you can have weight gain also. If there's oxidation, suppose you have a material which can oxidize, then you will see weight gain. Absorption also. So these are all processes where you can have either, weight loss, or weight gain, and as long as there is a weight loss, like change in the mass, thermogravimetry can be used. And obviously these processes are kinetic, that is, there is a rate at which they occur.

They won't happen immediately, so kinetics plays a role, so how fast a reaction takes place. So that also has to be kept in mind.

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So typical, TG instrument, Thermogravimetry, either use TG or TGA, when you refer to papers, often times, you will see people using TG or TGA for this technique. So this is a TGA or TG instrument. So basically, you have a sample pan here. Next to sample pan here, you have a thermocouple, because we are interested in measuring temperature, because we are heating the sample, and then we are measuring the weight.

So you see you have a big component here, it is called thermobalance. You want to make sure that you are able to measure the small weight change. So, thermobalance is here. You have also a furnace. Now you are heating the sample in a controlled environment, and so there is a furnace.

And you can purge it, depending on the use. You can use nitrogen you can use other gases. For cement, we use nitrogen because we do not want it to react with the atmosphere. So there is a way to change the purge gas.

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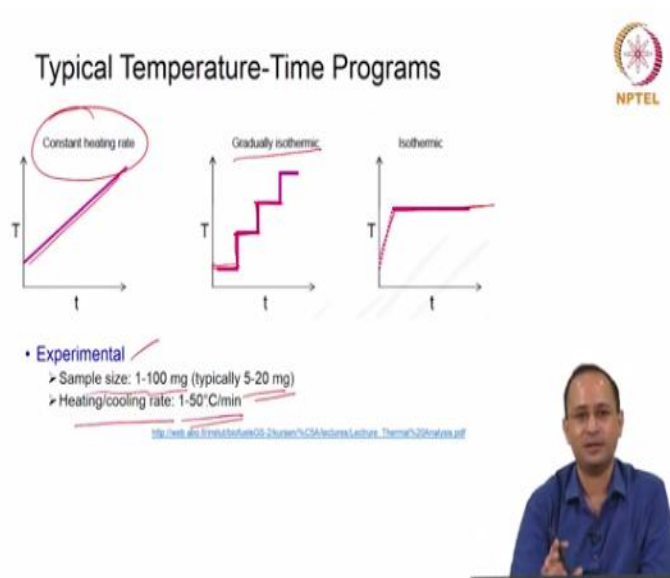
So what kind of temperature-time programs are we talking about? So you can either linearly increase the temperature, so it is like a constant heating rate, temperature is increasing linearly with time. Or you could have gradually isothermic, keeping temperature constant, and then you are ramping it up, keeping it constant, ramping it up. Another could be, just go to a particular temperature and keep it there. It is isothermic.

You understand the difference. These are the ways you can change the temperature of the furnace. So experimentally, we are talking about sample size of about milligrams. 1-100 milligrams can be used easily, and usually for cement, we use 20-30 milligrams, that is the amount we use. And heating to cooling rate, depending on the application, but you can vary it from 1 to 50 °C/ minute. In one minute you can change temperature up to 50 °C easily.
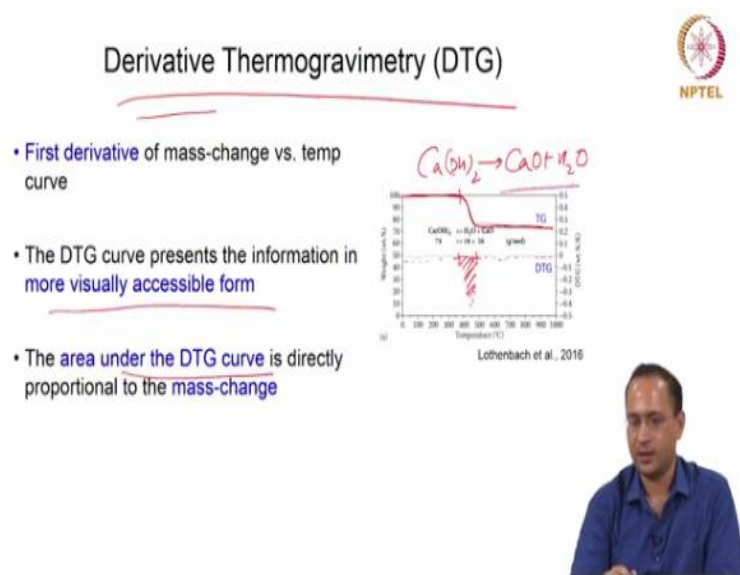
Typically we go 1100 °C. So when we talk about the mass loss, so here we have a mass-loss curve. So this is the calcium hydroxide, what happens when you heat $Ca(OH)_2$?

$$Ca(OH)_2 \rightarrow CaO + H_2O$$
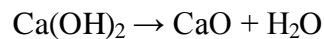
At some point of time it will lose water. You see here (Figure in slide – TG curve), up to around 400°C you do not see any change, and beyond 400°C, you see change, and then nothing happens. So that tells you there is a dehydration, it is losing water or dehydroxylation.

We are talking about now Derivative thermogravimetry. Derivative thermogravimetry is nothing but first derivative of your mass-change vs. temperature curve. So you have this mass-change vs. temperature curve. Now if I take the derivative of this, it will give me the second plot, which is here (DTG curve).

Basically DTG curve presents the information in more visually accessible form; it is easier to see peaks. Basically, there is no new data, you are re-plotting the same data, but you are just taking the first derivative. Now I can see, up to here it is flat, so I can just measure this, I can find out what is the temperature range where it is losing water.

So it just gives you information in a more visually accessible form, so whenever you see data in literature (in papers), you often see TG with DTG. And area under the DTG curve is directly

proportional to the mass-change. If you can calculate the area under the curve, it will give you the mass-change. Here is an example of calcium hydroxide dehydration.

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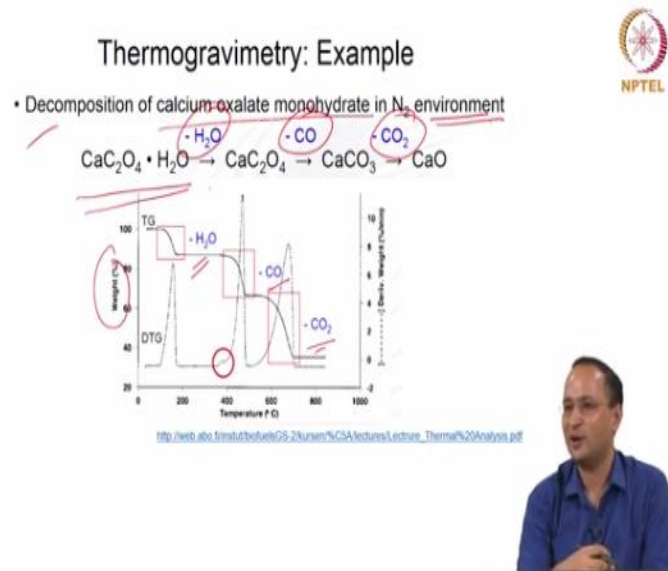
One example – let us look at the decomposition of calcium oxalate monohydrate ($CaC_2O_4.H_2O$).

$$CaC_2O_4.H_2O \xrightarrow{-H_2O} CaC_2O_4 \xrightarrow{-CO} CaCO_3 \xrightarrow{-CO_2} CaO$$
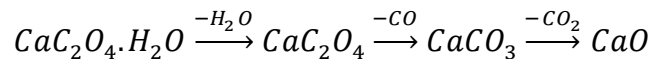
So, it has three stages. First, it loses water. Secondly, it loses carbon monoxide (CO). Thirdly, it uses CO_2. So, we will be able to capture that using TGA, that is what it shows. When you look at the curve, you see the first stage where you have a loss of water; second stage corresponds to loss of CO. Third stage corresponds to loss of CO_2. And this is the decomposition of calcium oxalate monohydrate in nitrogen (N_2) environment. So, that's the significance or power of this TG. Depending on the reactions when they occur, you will be able to capture it as long as there is a mass change. If there is no mass change, you won't be able to use this technique. If you have phase transition, where there is no mass change, then thermogravimetry will not be useful, and then you will have to use DTA or DSC.

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Factors Affecting TG Curve

Heating rate: Higher rates lead to better-defined, narrower peaks but also to higher observed dehydration and dehydroxylation temperatures

• Sample mass: Higher quantities of a phase lead to a seemingly higher dehydration temperature and to a broader peaks

• Furnace atmosphere: the type of reaction may get affected by the atmosphere

Factors affecting TG curve, it is very important to pay attention to these factors.

- **Heating rate** affects your TG curve - higher rates lead to better-defined, narrower peaks, but also higher observed dehydration and dehydroxylation temperatures.

- **Sample mass** - higher quantities of a phase lead to a seemingly higher dehydration temperature and to a broader peaks.

- **Furnace atmosphere** - that will depend on the type of reactions, suppose you are using TG for cement paste, and you have a CO_2, then you will have carbonation forming $CaCO_3$.

So these are the things which affect your TG curve.

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Application of Thermal Analysis to Study
Construction Materials

Okay, we will stop here, in the next class; we will go over the application of thermal analysis to study construction materials. Thank you.