Characterization of construction materials
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Lecture No - 26
Application of thermal analysis to study construction materials - Part 2

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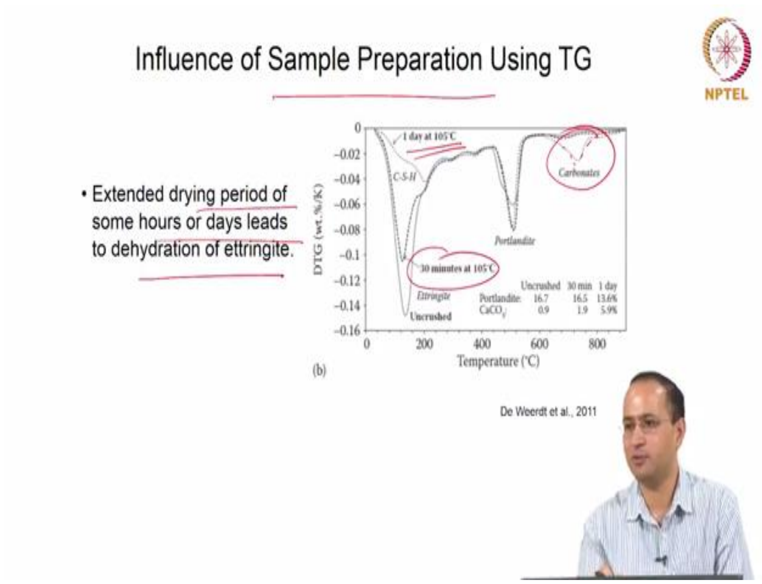

Also we can use this thermogravimetry to find out the influence of sample preparation. It depends on the material, right? So in this case, if you want to evaluate the effect of drying, for an example, what happens when you dry the sample? So (Refer Figure in slide), this is 1 day drying at 105 °C this is 30 minutes at 105 °C, this is no drying. So these effects can be evaluated.

Here you have an example of the sample preparation, so you see, that when you heat your sample for one day at 105°C, peak is drastically reduced, compared to uncrushed. So it tells you that the drying process is affecting the amount of C-S-H and ettringite in this case. So you have to pay close attention for how long you are drying; even this 30 minutes of drying at 105 °C will affect your initial peak.

Also you notice that when you dry it for 1 day at 105°C, you see it could be because of the carbonation, you might have carbonated your sample, so you have additional carbonation so that tells you about the possible reason why you are seeing this carbonation. So basically different sample preparation methods can be evaluated, that is, this could be a tool where you can evaluate your sample preparation method.

Here is you say extended drying period of some hours or days leads to dehydration of ettringite, primarily it affects ettringite, also you will start losing water from C-S-H, but primarily the difference you see because of the dehydration of ettringite.

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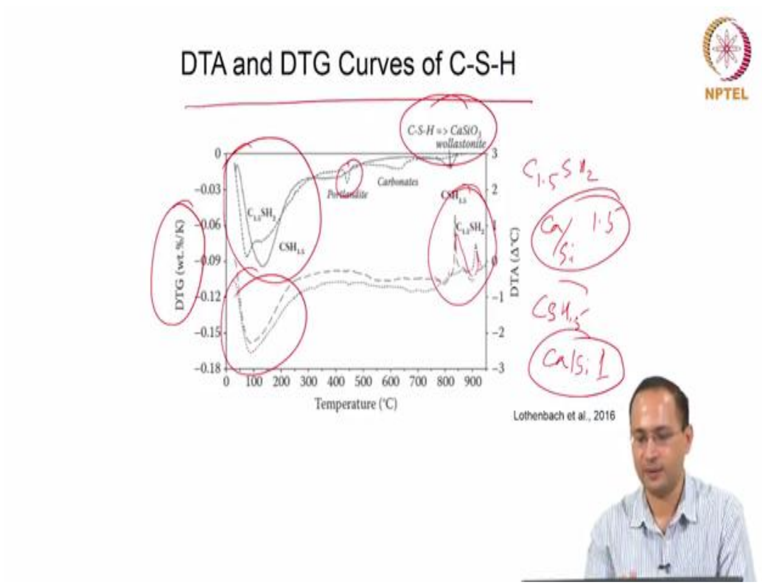

Okay, so here now it is a DTA and DTG curves of C-S-H, if you look at pure C-S-H, calcium silicate hydrate phase. There is no TG, but it is DTG, which is the first order derivative of TG curve, so you see this primary region again because of the loss of water from C-S-H here they have used two different types of C-S-H; one is $C_{1.5}SH_2$ which corresponds to calcium to silica (Ca/Si) ratio of 1.5 and the other is $CSH_{1.5}$ which corresponds to Ca/Si ratio of 1.

You know that commonly, we have Ca/Si ratio of 1.6 or 1.7 in C-S-H, present in Portland cement paste. So in this study they looked at C-S-H of different Ca/Si ratio. So you see these regions in C-S-H with higher Ca/Si ratio you see some portlandite also because the Ca/Si ratio is higher.

Also at around 800, 900 °C, you see this transformation; C-S-H transforms to crystalline form of wollastonite ($CaSiO_3$). So that also you can capture here clearly. So, this is the DTA curve now. So, top one was TGA and here you have the DTA plot. So you can basically see the difference.

So the bottom one is DTA, so you see those changes at early temperatures like 100, 150 °C in DTA also, then you see primarily this transformation. So when you talk about the transformation DTA is very good technique to capture them.

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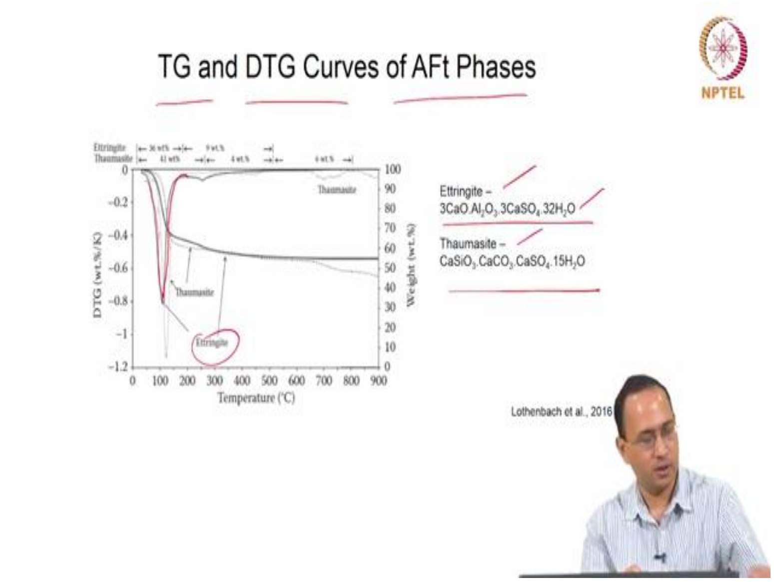

Now, if you look at the TG and DTG comes for AFt phases, AFt phase means in this case, we are looking at ettringite, thaumasite, right? The formula is:

Ettringite – $3CaO.Al_2O_3.3CaSO_4.32H_2O$

Thaumasite - $CaSiO_3.CaCO_3.CaSO_4.15H_2O$

So you can see clearly, you have a lot of water in ettringite, where you have 32 moles of water. So you will lose this water, that is the point. You can also see the primary region where you lose water is in this range 100 - 150 °C.

And you can also identify the difference between thaumasite and ettringite. So ettringite peaks occurs at early temperature and the later one is because of the thaumasite. And here the weight loss is given.

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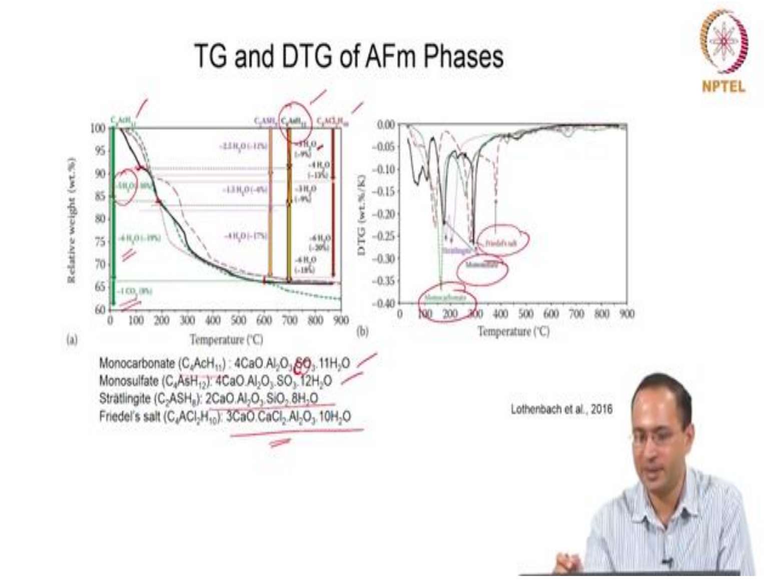

Similarly if you look at the AFm phases, we are talking about monocarbonate, monosulphate phases. And additionally you have this Friedel's salt is also there, which is a chloride form. So you are losing water at different temperatures, so let us look at the left plot (on slide).

Let us look at the monocarbonate, the formula is C_4AcH_{11} which is $4CaO.Al_2O_3.CO_3.11H_2O$. It is formed when you have either limestone in your system or maybe because of carbonation, you may have formation of monocarbonate. So you see how much water is lost in this region. Firstly 5 moles H_2O you lose from the total of 11 moles, so you lose 5 mole H_2O up to here, roughly 16%. Then beyond 200°C to around 600°C, you lose the remaining 6 moles. Then you have a loss of carbon dioxide (CO_2).

Monosulphate is $4CaO.Al_2O_3.SO_3.12H_2O$, and from this plot you can also see monosulphate now C_4AsH_{12}. Black line in figure is for monosulfate. 3 moles of water is lost initially, then you have further 3 moles of water lost, so it can give you idea when you are losing the water from the phase.

Friedel's salt - when you have a chloride you see the formation of Friedel's salt and also strätlingite phase is plotted just for comparison.

And this is the DTG (Figure in slide on right), when you take derivative of TG curve, you will see appearance of these peaks, because the slope is changing and so you will see peaks. So monocarbonate, monosulphate, Friedel's salt, sometimes you have multiple peaks. These are the things you have to pay attention to; depends on what kind of phase composition you have.

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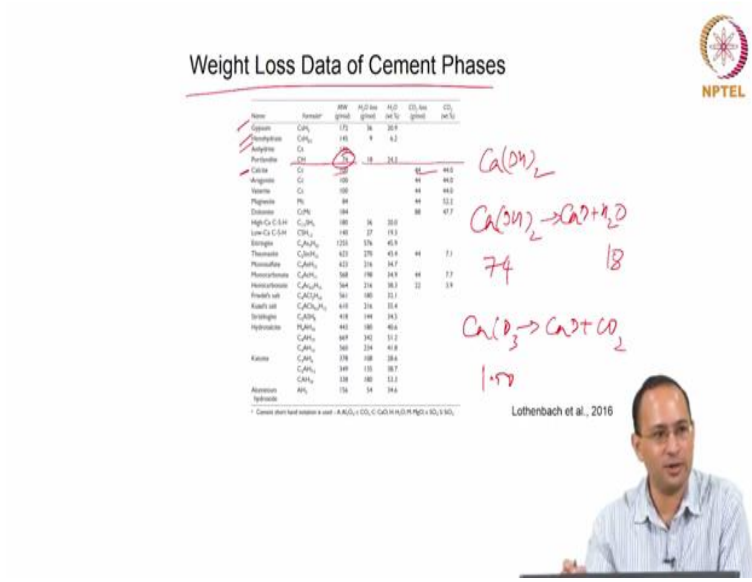

So here is a table you can use for the weight loss. This is the weight loss data of cement phases, starting with gypsum, hemihydrate, anhydrite, let us look at the portlandite. So, in portlandite, molecular weight is 74, add respective molecular weights of calcium, oxygen, hydrogen. And then how much water will you lose? 18 grams. So what is basically happening is:

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

So, molecular weight of $Ca(OH)_2$ is 74, and that of water (H_2O) is 80.

Similarly, you can get it for calcite, for an example.

$$CaCO_3 \rightarrow CaO + CO_2$$

So you have the information here. Molecular weight of calcium carbonate is 100 (calcium is 40, carbon is 12, oxygen is 16), you can calculate the molecular weight and that of CO_2 is 44. We will use this information to quantify the amount, so here's the table and you can look at it.

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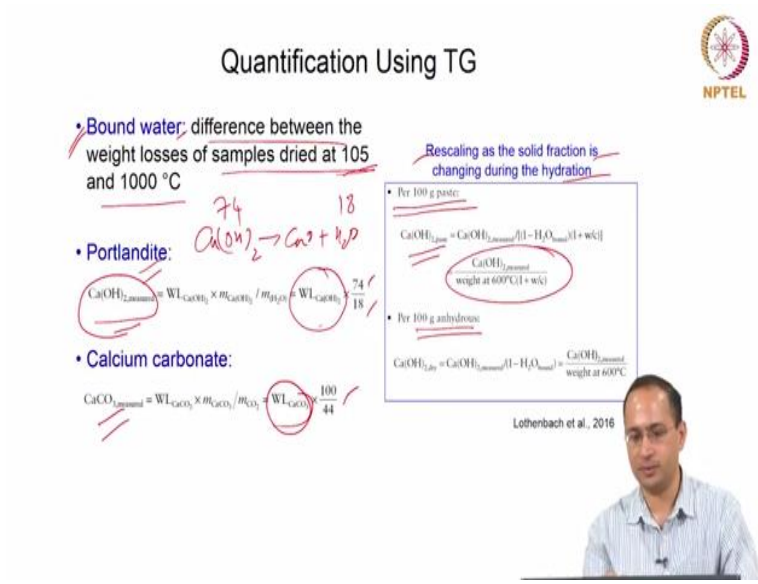

Now the question comes how do we quantify the portlandite? That's very important as that can tell you about the progress of hydration, it can tell you about the reactivity of fly ash. So first of all, we can calculate the bound water also. The bound water is not free water; bound water as the name signifies, it is water that is structurally bound. Anyway we are heating our sample, this is the difference in the weight (Formulae given in slide).

When you heat your sample from 105 °C to 1000 °C, but why 105°C, you want to make sure there is no free water, so you heat your sample to 105 °C (around 100 °C), so that you remove free water then you heat it up to 1000 °C. You can use that to get information on bound water.

Now how do you calculate the portlandite? So calcium hydroxide can be calculated.

$$\mathrm{Ca(OH)_{2,measured}} = \mathrm{WL_{Ca(OH)_2}} * \frac{\mathrm{m_{Ca(OH)_2}}}{\mathrm{m_{H_2O}}} = \mathrm{WL_{Ca(OH)_2}} * \frac{74}{18}$$

Where $WL_{Ca(OH)_2}$ is the weight loss in TG. So you have done thermogravimetry, and so you know weight loss. In that regime, 400 to wherever you see that peak. And then you can calculate it, because that weight loss is because of the loss of water. How did we calculate this?

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

So $m_{Ca(OH)_2}$ is 74 and m_{H_2O} is 18 and the weight loss you are seeing is because of the loss of water.

So if you know the loss of water, how do you calculate calcium hydroxide? so calcium hydroxide can be calculated by measuring the weight loss from TG, that is because of loss of water, times 74 by 18, gives you measured calcium hydroxide (given in the equation below again).

$$Ca(OH)_{2,measured} = WL_{Ca(OH)_2} * \frac{m_{Ca(OH)_2}}{m_{H_2O}} = WL_{Ca(OH)_2} * \frac{74}{18}$$

Similarly you can use TG curve to calculate calcium carbonate amount, so calcium carbonate is as given in the equation below:

$$CaCO_{3,measured} = WL_{CaCO_3} * \frac{m_{CaCO_3}}{m_{co_2}} = WL_{CaCO_3} * \frac{100}{44}$$

Where WL_{CaCO_3} is the weight loss in the TG curve.

Again, very important after you have done this now, you have to rescale it. Lot of times people do not do rescaling. Rescaling is done because your solid fraction is changing during the hydration. Cement is hydrating, as we discussed in X-Ray diffraction, your solid fraction is changing with the time. Cement is reacting; you're forming more C-S-H, calcium hydroxide. So the solid fraction is changing, that we know.

So you have to rescale it, which means once you know the measured quantity from previous equations, then based on this formula you can calculate, you can normalize it by 100 grams of paste in this case, or you can do it per 100 gram of anhydrous, so that you compare. If you have a time-series data, you want to compare your data at 3 day, 7 days, 28 days, then it will be useful. Same thing what we have discussed in X-Ray diffraction.

Per 100 g paste:

$$Ca(OH)_{\ 2,paste} = \frac{Ca(OH)_{2,measured}}{\left[(1 - H_2O_{bound})\left(1 + \frac{w}{c}\right)\right]} = \frac{Ca(OH)_{2,measured}}{\text{weight at } 600°C(1 + \frac{w}{c})}$$

Per 100 g anhydrous:

$$Ca(OH)_{\ 2,dry} = \frac{Ca(OH)_{2,measured}}{(1 - H_2O_{bound})} = \frac{Ca(OH)_{2,measured}}{\text{weight at } 600°C}$$

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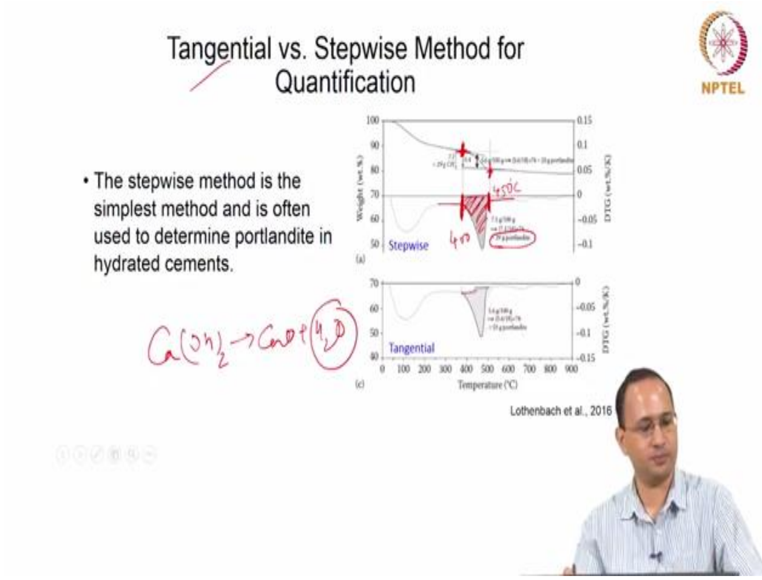

So how do you quantify? So there are few methods - the tangential and stepwise method. So you have this TG curve. And when you plot DTG when you take derivative, you know when the slope is changing. So up to here it is flat then it is changing (Refer Figure (a.) in slide). And beyond this point, it is again flat. So, you know that this is the temperature range first of all. Now, how do you calculate the area, because the area under the DTG curve will give you whatever loss has occurred, like in case of calcium hydroxide it's because of water.

we want to quantify how much water is lost. Then we will use that information to calculate the amount of calcium hydroxide. Because what is happening? $Ca(OH)_2 \rightarrow CaO + H_2O$. This is happening. What you are measuring is H_2O. You have to measure this first. Once you know this then you can calculate calcium hydroxide.

So one way is this is the stepwise method. Stepwise means you plot DTG and you just take this area (whole area). Tangential is when you plot the tangent here (from initial flat portion) you plot tangent here (from later flat portion). So then you take the area (Refer (c) in figure in slide).

Stepwise means you directly measure the weight loss. So, you know that where the slope changes in this case, from DTG and beyond this the slope does not change (Refer figure (a.) in slide). So you know, this is the weight loss curve. So you can identify what is the weight loss.

This is the stepwise directly from here to here. That will give you the area of this. Since it is easy people often use stepwise method. So basically once you know, what is the temperature range, you just measure the weight loss. So, you know, from DTG, you know, it starts here suppose, let's say 400°C and it stops here let's say 450°C. Now you go to your TG, you check the weight, you see the difference 400 to 450°C, that is the stepwise, and it is easier then tangential. So, if you are following a particular method, you have to be consistent, you cannot just follow methods according to samples. There will be some difference in this case; you see stepwise gives you roughly around 29 grams of portlandite and the tangential method will give you 23 grams of portlandite.

Similarly you can do that for calcium carbonate also. So plot DTG, you will know the temperature regimes then calculate the area or just measure the mass loss in that.

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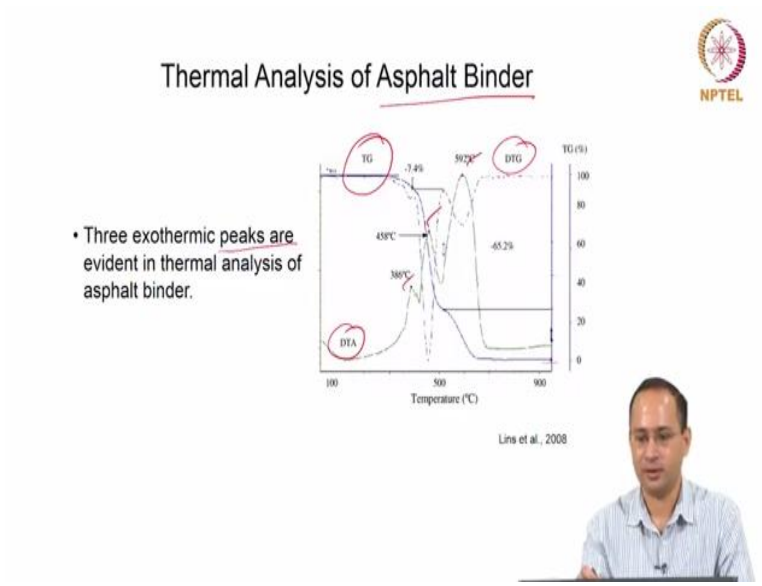

Thermal analysis can be also used for asphalt binder; this is one example where you use the TGA. So you see here lot of things, first TG curve is there, so the blue one (in figure) is TG curve, you see the continuous mass loss by around 600-700°C it is almost zero, everything is lost nothing is left, you see almost 100% weight loss. This is the TG. Now this is the DTG - change in slope (blue line). Then this is the DTA (green curve).

So basically idea is you can also monitor the changes. Something is happening, a lot of complicated reactions, but idea is you can use this thermal analysis technique to understand the Asphalt binder, so here you see three exothermic peaks.

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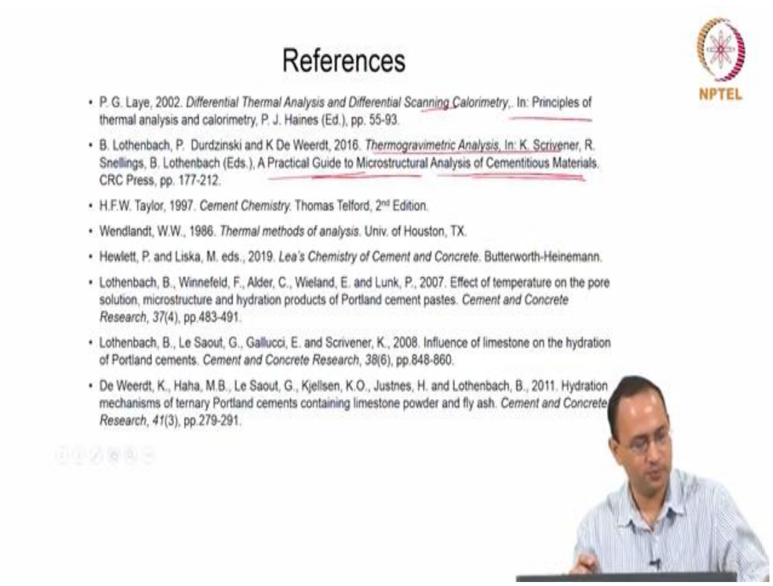

With that we conclude the module on thermal analysis, again references are here, as I said the most of it was taken from this book: "Practical Guide To Microstructure Analysis Of Cementitious Materials", also there are some other books which are very good if you are further interested to know more.

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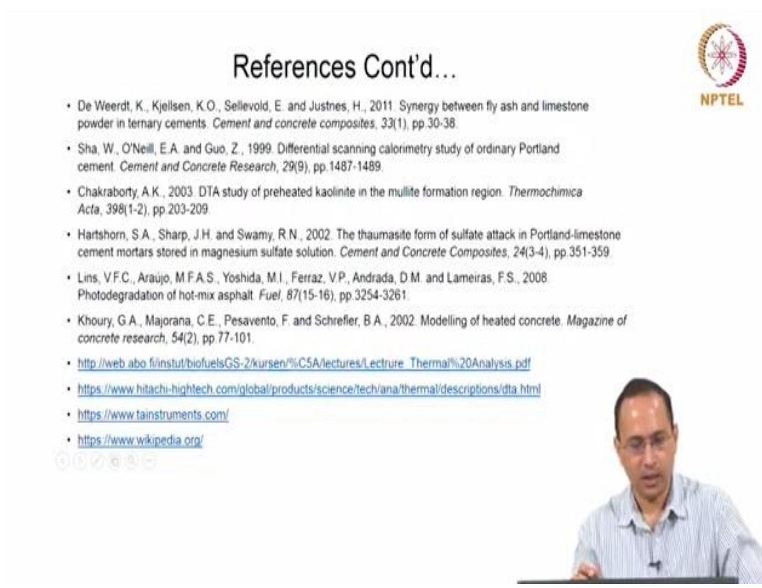

And some web links which were used and with that, I will conclude this lecture.