Characterization of construction materials
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Lecture No - 23
Thermal Analysis- Part 1

In this lecture, we will look at another technique which is commonly used to understand the construction materials, it is thermal analysis. So in the next few lectures we will talk about the principles and various applications of thermal analysis. The first question comes to the mind, what is thermal analysis.

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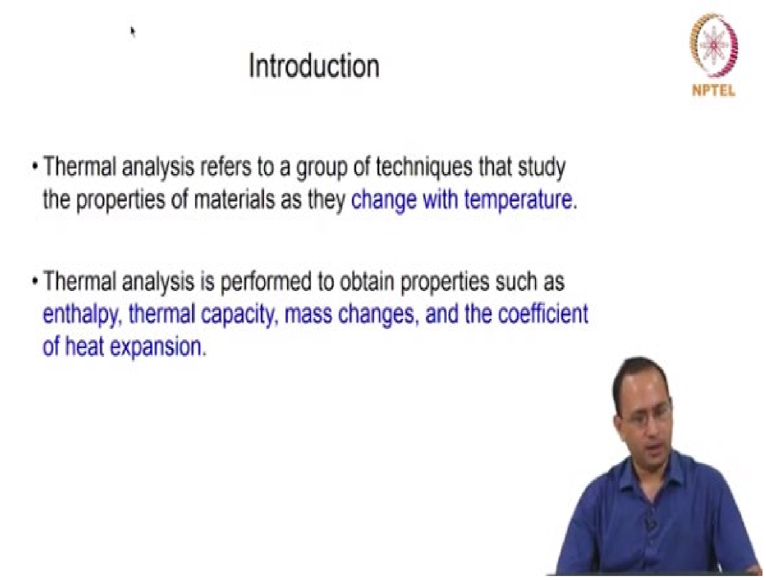

Thermal analysis refers to a group of techniques which, study the properties of materials as they change with the temperature. So, the focus is on the temperature, as you are changing the temperature and look how the properties are changing. For an example, if you heat up any material; the temperature goes up beyond a point then there might be change in phase, simple example is ice.

Ice will turn into water at 0 degree Celsius and then that water will evaporate at 100 degree Celsius. Another example could be burning of coal, if you burn coal to the gases coming out of coal are inflammable gases. So depending on the material you will see a particular response, and that is very unique to a particular material and the way it responds to a change in temperature.

This is the focus of the technique. So, thermal analysis is performed to obtain properties such as internal enthalpy, thermal capacity, mass changes and the coefficient of heat expansion.

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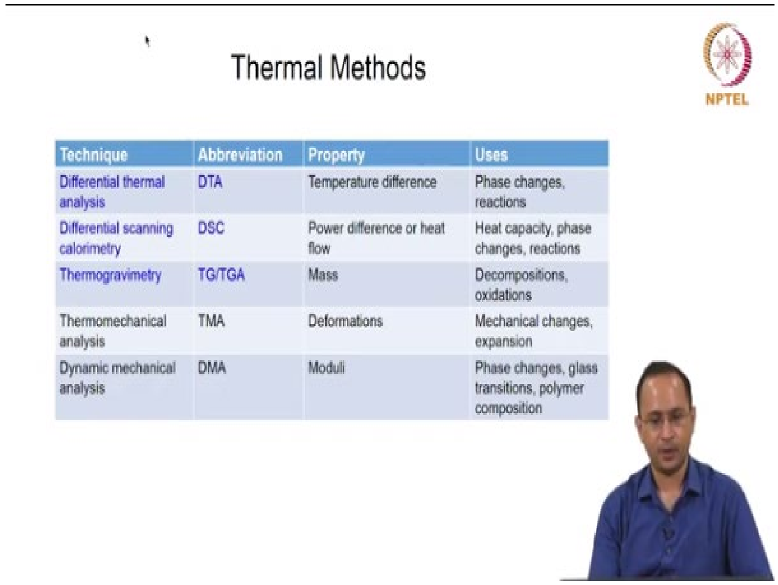

So lot of techniques come under the types of thermal analysis. We call these as thermal methods and they are used for different purposes. It is good to know why we are using a particular technique, for an example differential thermal analysis abbreviated as DTA is used for understanding phase changes, reactions, lot of reactions and in this technique we measure the temperature difference.

Next is differential scanning calorimetry DSC where we measure the power difference or heat flow. The differential thermal power can be used to calculate the heat capacity and to understand the phase changes and various reactions.

The next one is thermogravimetry (TG or TGA) where we look at various reactions like decomposition, dehydration, dehydroxilation, oxidation etc. In this technique, we measure the change in mass. There are a couple of others like thermo mechanical analysis and dynamic mechanical analysis where we measure deformations which is used to understand mechanical changes.

Dynamic mechanical analysis or DMA is used for measuring moduli or it can be used to determine the polymer composition, glass transitions, phase changes. But in this course we will focus on DTA, DSC and TGA, which are commonly used in construction materials.

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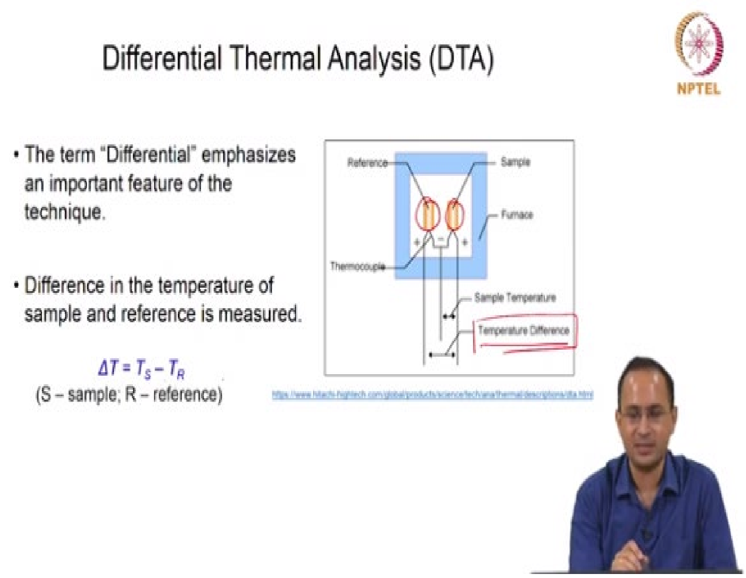

For differential thermal analysis, the term differential emphasizes an important feature of the technique. In this we measure the difference in the temperature of sample and reference. You have a reference along with your sample and as you are heating your sample and reference together; you measure the difference temperature difference that is the key concept.

So you can see sample and reference are in the same cell in the diagram. You have thermocouples to measure the temperatures and finally we measure the temperature difference as given by equation below:

$$\Delta T = Ts - Tr \quad \text{(s-sample; r- reference)}$$

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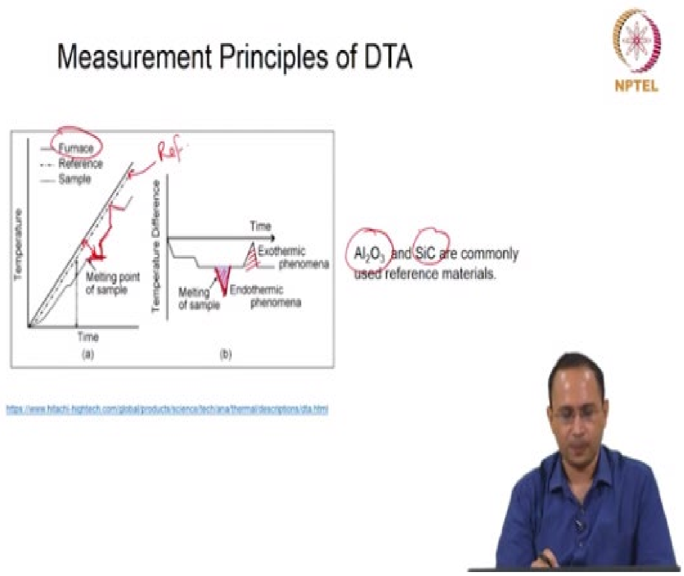

So the next query is what the measurement principle behind DTA is. Now we said that we are measuring the temperature difference. So basically if you look at the left plot of temperature versus time. So you have a furnace for an example, you have a sample in reference now you are heating both together. So first look at the furnace temperature and we have programmed our heating rate in such a way that it increases linearly, so we notice the solid line which clearly shows how the furnace is heating up.

Now, you have to make sure you use the reference which is not reactive. Alumina and silicon carbide are commonly used reference materials, because they do not change with in the temperature range we are interested in. So, you see some lag here but more or less the reference temperature also is increasing at the same rate.

You have this dotted line for reference. So when sample melts, the sample temperature is increasing but when the melting starts, then the temperature does not increase.

So you see there is a flat line here, which means temperature is constant. It is because once melting starts there is no increase in the temperature. But once the melting is over then you see there is an increase in temperature then it comes to raising part. If we plot the temperature difference in differential thermal analysis; we are plotting temperature difference with time.

So there is a time axis, so what you see in melting is difference. This is the difference between reference and sample. So when something is melting you see the difference is increasing. Once melting is completed, you see the difference has decreased which tells that it is an endothermic phenomenon.

Endothermic as melting requires heat. So, endothermic peak tells you that something is melting. It depends on the temperature where you are in the plot, exothermic means then you will release heat when you release heat then the temperature difference will reduce. It depends on the reaction the material; what happens as you heat it up so in this case you see this exothermic peak and the thermic reaction will lead to increase in temperature of sample hence your difference with reference will reduce.

So these are some signatures like in a DTA curve you see this kind of things. You will see endothermic peaks and exothermic peaks which tells about the kind of reaction that takes place. So it is also important to keep in mind the reference material which is used in DTA analysis. Alumina is commonly used reference material to analyze cements for an example and silicon carbide is too used for the same purpose.

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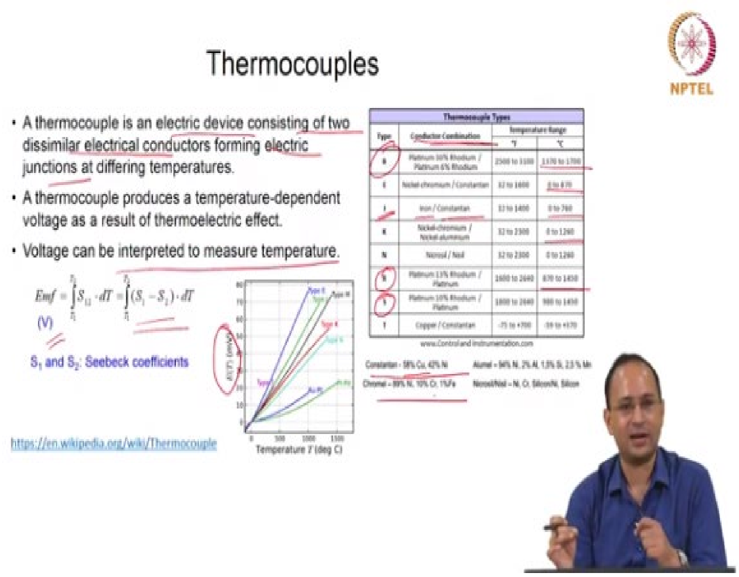

Thermocouples are used to measure the temperature. The principle involved in thermocouples is when you join two dissimilar metals and if there is a temperature difference that will lead to thermoelectric current and by measuring that voltage, we are able to measure the temperature.

So you have two different materials that is very important and if there is a temperature difference that will lead to this electro-motive force EMF or voltage. Once you measure that voltage, you can get an idea about the temperature. So thermocouple produces temperature dependent voltage as a result of thermoelectric effect and based on the temperature difference; we get different voltage that can be calibrated.

So depending on the type of materials in particular thermocouple; you can calibrate it using the plot of voltage versus temperature shown for different types of thermocouples. So if you know the voltage, you can easily calculate the temperature using the characteristic function.

This voltage basically depends on the temperature difference and the Seebeck coefficients. Seebeck was the scientist which proposed this theory named as Seebeck effect. This shows there is a dependence between voltage and temperature depending on the material. So you see there is a table showing different types of thermocouples like type B, E, J, K, N, R, S, and T and their corresponding conductor combination with respective temperature ranges.

Type B, R, S are commonly used for high temperature measurement, which is 1370 to 1700 degree Celsius. So it depends on the requirement for the kind of temperatures to be measured. If you want to measure load temperatures then you can use type E, J thermocouples.

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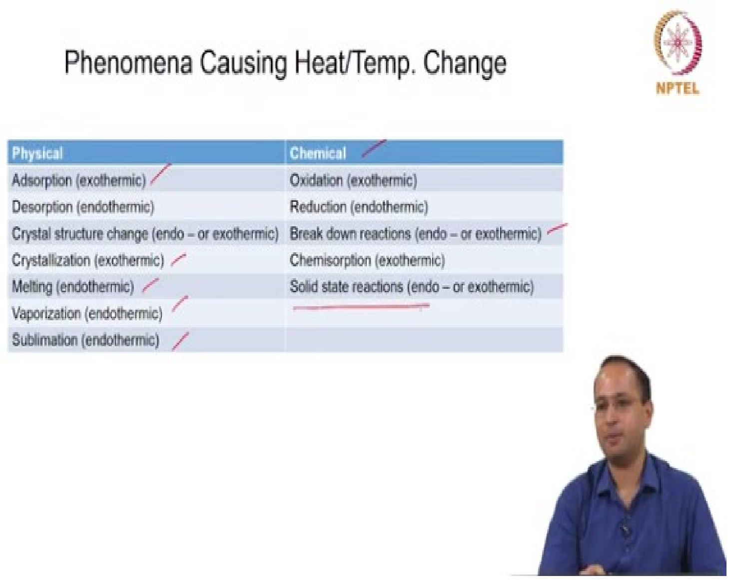

So now let us look at the kind of processes or phenomena which can cause this temperature change. We want to study a process, so we want to know about the kind of processes that can be studied using this technique as long as there is a heat release or heat absorption. For example adsorption, looking at the physical properties something is getting adsorbed so it is typically exothermic reaction, and you know release of heat so we can measure this.

Desorption it is an endothermic process. Crystal structure changes, crystallization, melting, vaporization and, sublimation are the examples of physical processes. Similarly you may have oxidation what we typically see when you expose materials to oxygen.

Chemisorption, it is different than adsorption in a sense that you do not have chemical bonds in adsorption but you have some chemical bonds and solid state reactions in the former case. These are some physical and chemical processes where you have some temperature heat temperature change.

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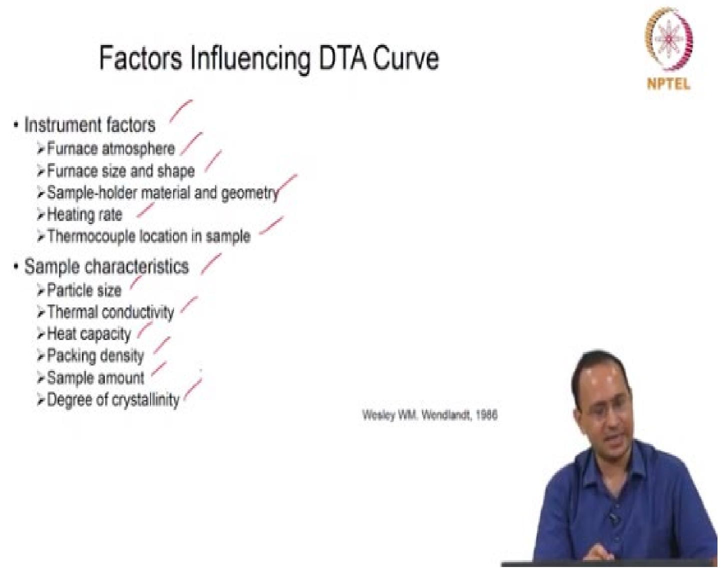

Now let us look at the factors which influence DTA. So, we know how to measure the temperature using thermocouples. If you carry out an experiment it is important to look at the instrument factors like furnace atmosphere, furnace size and shape, sample-holder material and geometry, heating rate and thermocouple location in sample.

Suppose you have oxygen then you may trigger oxidation; if you have a carbon dioxide you may have carbonation. Also, there are sample characteristics such as particle size, thermal conductivity, heat capacity, packing density, sample amount and degree of crystallinity.

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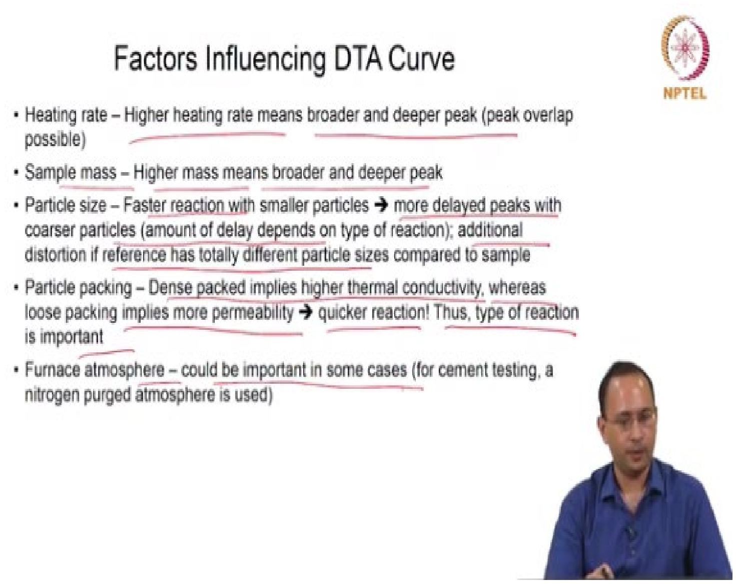

Heating rate means higher heating rate means broader and deeper peaks, peak overlap is possible for this case. You may get endothermic peak and exothermic peak depending on the temperature change. So when you have increase in the heating rate it means your peak will be broader and deeper. One of the factors influencing is sample mass; higher mass means broader and deeper peak.

Particle size is another crucial factor which affects the DTA curve. So everyone is familiar with the fact, you have smaller particles that tends to react faster as you have higher surface area. So it leads to more delayed peaks with the use of coarser particles. Also there is an additional distortion if the reference has a totally different particle size because we are talking about the reference material.

If there is a very much difference between the particle size of a sample and reference you will see some distortion in the peak. Particle packing affects the DTA curve as dense packing implies higher thermal conductivity whereas loose packing implies more permeability that leads to quick reaction.

So higher thermal conductivity leads to quicker reaction that is the type of reaction is important. Furnace atmosphere could be important in some cases for an example in cement testing, we usually use nitrogen purged atmosphere because it does not react with cement. We do not want cement to react with carbon dioxide which leads to carbonation.

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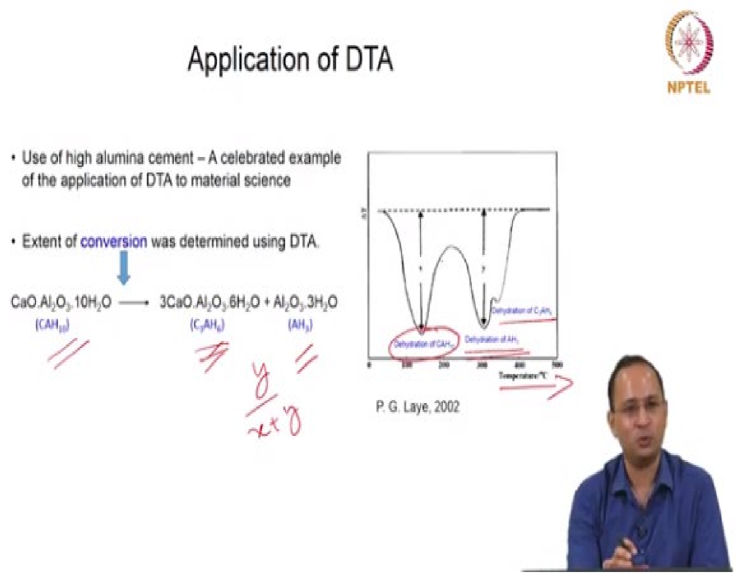

So, I will give you an example, so one of the most celebrated example of the application of DTA to material science is the use of high alumina cement which in some circumstances led to the weakening and in extreme cases to the collapse of concrete structures. So high alumina cement was used 30 to 40 years ago so at the time, these issues were observed.

The problem actually arose because of the conversion. When we add water to calcium aluminate cement, we form the calcium aluminum hydrate and this gets converted to C_3AH_6 and AH_3. So this conversion leads to loss of strength.

Now in this typical DTA curve, for calcium aluminate cement. The first peak in the plot shows dehydration of CAH_{10}, and you are forming the two phases C_3AH_6 and AH_3.

So now the second peak is due to dehydration of AH_3 and this peak is bigger, third one is because of the dehydration of C_3AH_6.

This is obviously a not the exact extent of conversion because we are now looking at the peak height which does not take in to account the overlap of peak. Then it gives you some approximate reasonable value but you can just quantify the extent of conversion.

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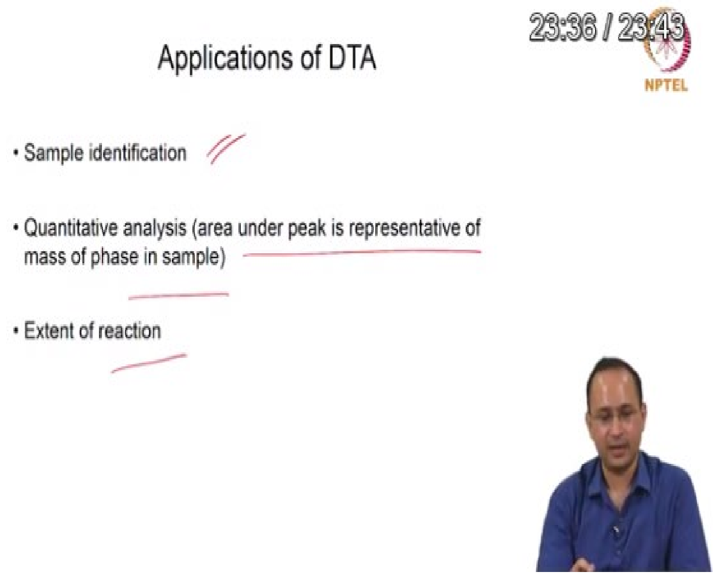

Applications of DTA are sample identification, because you can identify samples as they will have a particular signature. Dehydration is an example as it is dependent on the phase as it has particular signature. Quantitative analysis, where area under the peak is the representative of mass of phase in sample. Also extent of reaction or the degree of reaction can be calculated, this is among the application of DTA.